

HELLENIC REPUBLIC UNIVERSITY OF IOANNINA SCHOOL OF SCIENCES DEPARTMENT OF MATERIALS SCIENCE ENGINEERING

«PREPARATION AND CHARACTERIZATION OF ADVANCED NANOHYBRID MATERIALS WITH THE USE OF NANOPARTICLES AND TRIBLOCK TERPOLYMER MATRICES»

ZAPSAS GEORGIOS MATERIALS SCIENCE ENGINEER, MSc

PhD THESIS

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ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ ΣΧΟΛΗ ΘΕΤΙΚΩΝ ΕΠΙΣΤΗΜΩΝ ΤΜΗΜΑ ΜΗΧΑΝΙΚΩΝ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ

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Ο Πρόεδρος του Τμήματος

Η Γραμματέας του Τμήματος

Καρακασίδης Μιχαήλ Καθηγητής Ξανθή Τουτουνζόγλου

Dedicated to my parents Christos, Panagiw and my brother Vaggelis

Μαλαματένια λόγια στο μαντήλι Τα βρήκα στο σεργιάνι μου προχθές, Τ' αλφαβητάρι πάνω στο τριφύλλι σου μάθαινε το αύριο και το χθες, μα εγώ περνούσα την στερνή την πύλη με του καιρού δεμένος στις κλωστές

Manos Eleftheriou, 1974

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Table of Contents

Abbreviations	5
Chapter 1: Motivation and Objectives	7
Chapter 2: Background	11
2.1 BCP-Based Nanocomposite Materials	11
2.2.1 Microphase Separation and Self-Organization of Block Copolymers	11
2.2.2 Equilibrium Morphologies and Phase Diagram for Diblock Copolymers	15
2.2.3 Microphase Separation and Self-Organization of Triblock Terpolymers	17
2.3 Block Copolymers for Patterns and Templated Self-Assembly Applications	
2.3.1 Strategies for Fabricating Patterned Nanostructures	21
2.3.2 Block Copolymers in Templated Self-Assembly (TSA)	22
2.4 Nanoparticles Arrays in Block Copolymer Domains	23
2.4.1 Strategies to Control Nanoparticle Locations within BCPs Matrix	23
2.4.2 In situ Approach toward Polymer Based Nanocomposites	24
2.4.3 Ex-situ Approach and Chemical Affinity	27
2.5 Guiding the Microphase Separation in BCP Thin Films	
2.5.1 Surfaces and Interphases Effects	
2.5.2 Solvent Vapor Annealing	
Chapter 3: Instrumentation-Synthesis-Functionalization	46
3. 1 Characterization Techniques	46
3.1.1 Atomic Force Microscopy (AFM)	46
3.1.2 Transmission Electron Microscopy (TEM)	
3.2 Supplementary Analytical Techniques	
3.2.1 Size Exclusion Chromatography (SEC)	
3.2.2 Proton Nuclear magnetic Resonance Spectroscopy (¹ H-NMR)	54
3.2.4 X-Ray Diffraction (XRD)	
3.2.5 Thermogravimetric Analysis (TGA)	55
3.2.6 Substrate Treatment	55
3.2.7 Annealing Process	56
3.2.8 Film Thickness Measurements	
3.3 Molecular Characterization of BCP hosts and Functionalized Nanoparticles	57
3.3.1 Overview	57
3.3.3 Introduction to Anionic Polymerization	59
3.3.4 Solvents and Materials	60

3.3.5 Purification of Solvents60
3.3.6 Purification of Monomers
3.3.7 Synthesis of Triblock Terpolymer BCP Systems
3.3.8 Synthesis of PS- <i>b</i> -PB- <i>b</i> -PI _{3,4}
3.3.9 Molecular Characterization of the Diblock Copolymer and Triblock Terpolymer Matrices
3.4 Functionalization of Nanoparticles
3.4.1 Nanoparticles Characterization
Chapter 4: Morphological Characterization74
4.1 Overview
4.2.2 Morphological Study of Diblock Copolymer Nanocomposites (diBCP/NCPs)83
4.2.3 Morphological Study of Magnetic Nanocomposites (BCP/ Iron NPs)
4.2.5 Morphological Study of Noble Metal Nanoparticle Nanocomposites (BCP/ Noble Metal NPs)
4.3.1 Morphological Study of Triblock Terpolymer Nanocomposites (tri/NCPs)104
4.3.2 Morphological Study of Iron Oxide NPs Nanocomposites (triBCP/IONPs) 111
4.3.3 Block Sequence Relation with the Particle Placement for Preferentially Grafted Particles
Chapter 5: Conclusions 122
Abstract125
Περίληψη126
References

Abbreviations

AFM	Atomic Force Microscopy
ATRP	Atomic Transport Radical Polymerization
BCC	Body Centered Cubic
BFP	Back Focal Plane
BCPs	Block Copolymers
CM-AFM	Contact Mode Atomic Force Microscopy
DD	Double Gyroid
diBCP	Diblock Copolymer
DSA	Directed Self-Assembly
IONPs	Iron Oxide Nanoparticles
IMDS	Intermaterial Dividing Surface
HPC	hexagonally packed cylinder
ISL	Intermediate Segregation Limit
¹ H-NMR	Proton Nuclear magnetic Resonance Spectroscopy
LSPR	Local Surface Plasmon Resonance
NPs	Nanoparticles
ODT	Order Disorder Transition
TOO	Order Order Transition
PNC	Polymer Based Nanocomposites
PS	Polystyrene
PB	Polybutadiene
PI	Polyisoprene
SAD	Selected Area Diffraction
SE	Spectroscopic Ellipsometry
SEC	Size Exclusion Chromatography
SCFT	Self-Consisting Field Theory
SSL	Strong Segregation Regime
TA	Thermal Annealing
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TP-AFM	Tapping Mode Atomic Force Microscopy
triBCP	Triblock Terpolymer
TSA	Templated Self-Assembly
WSL	Weak Segregation Limit
XRD	X-Ray Diffraction

Symbols

Latin

A_0	Drive Amplitude
A _{sp}	Amplitude Setpoint
Tg	Glass Transition Temperature

Greeks

γ	surface tension
Θ	crystallographic measurement angle (deg or ⁰)
λ	wave length (nm)
X	Flory Huggins interaction parameter

Chapter 1: Motivation and Objectives

The first announcement in which nanotechnology was not considered just a typical material invention but a very potential breakthrough in Science and technology was made by Richard Feynman in his talk at the American Physics Society meeting in Caltech on December 29, 1959 which was entitled: "*There is plenty of room at the bottom*". Only until 1974 the initial use of the term "nanotechnology" was defined by Japanese Professor Norio Taniguchi through a title on his work which was entitled: "*Nano-technology' mainly consists of: the processing, separation, consolidation, and deformation of materials by one atom or by one molecule*". Furthermore, in 1986 the first published book on the topic of nanotechnology with the title: "*Engines of Creation: The Coming Era of Nanotechnology*" and published by Dr. K. Eric Drexler. The importance of this book was so significant that was translated in many languages whereas an updated version was realized in 2007.

In the coming years, a great number of nanostructured systems aroused also from the development of two major disciplines: the rise of cluster science and as well as the invention of scanning tunneling microscopy (STM), the forerunner of atomic force microscopy (AFM), both of them being really important characterization tools. The above evolutions led to a modern technological environment, paving the way for discovery initially of fullerenes (1986) and carbon nanotubes (1991) and thereafter noble and oxide metal nanoparticles with basic trends being the reduced length scale between 1 and 100 nm and as final goal to achieve new physical and chemical properties. This "Next Industrial Revolution" as many scientists wish to call all these latest breakthroughs in nanotechnology opened new routes in several nanodisciplines including nanoelectronics, nanomechanics, nanomembranes, nanobiology, nanobioengineering and many others.

Following this vigorously growing nanotechnology era, polymer based nanocomposites (PNC) has gained a lot of interest in the scientific world due to their unique capability to combine two or more highly important features. Polymer nanocomposites (PNC) are prepared by incorporating nanofillers such as nanoparticles within a polymer host. Initially, the nature of a heterogeneous combination between the polymer matrix and one or more dispersants with critical dimension scale lower than 200 nm or even 100 nm exhibit combined properties of the individual constituents. From the host polymer matrices properties such as elasticity, processability and thermal stability are combined with those of the inorganic nanofillers (basically NPs) such as hardness, chemical resistance, optical and electrical properties. This inorganic nanofillers addition into polymer matrices affords the ability to perform remarkable changes on the aforementioned physical and mechanical properties which is possible due to the large surface area which increases the interactions between the nano-inclusions and the polymer.

Two general pathways are suitable for nanomaterials manufacturing, compatible to their following assembly method: "*top-down*" and "*bottom-up*". Both of them may contribute in either autonomous devices or integrated systems, leading to sophisticated concepts in nanoenginnering [Seg04]. All methods originating from the "*top-down*" approaches involve as a principal guideline the size reduction of large scale materials all the way down to the nanoscale (e.g. lithographic techniques). Although it is possible to produce periodic features, irregular characteristics are obtained relating to the shape and size in several nanometer structures by these fabrication methods [Xia99]. By operating "*top-down*" processes another important obstacle is the imperfections onto the surface structure caused mostly by milling impurities which together cannot be easily removed. This results into the fact that industry and scientists are seeking more cost effective procedures in order to produce low impurity level devices.

The opposite manufacturing method "*bottom-up*" has the ability to create materials consisting from atomic or molecular units in an easier manner by fabricating nanodevices with less defects and more homogeneous composition [Ham03]. In a solid, liquid or gas phase, precursors are available to produce an impressive variety of nano-building blocks via several chemical or physical deposition methods. According to the physical tendency of matter or by an externally applied driving force, these small components interconnect each other in order to form a self–assembled arrangement of well ordered sub-domains, such as polymer nanocomposites. Over the last two decades, block copolymers (BCPs) have received as well significant attention as a foresighted class of materials for the fabrication of such nanoscale composites either in bulk or in thin films [Par03].

The nanofillers incorporation of different size and shape into self-assembled BCP matrices has evolved into a leading "*bottom-up*" process, whilst the additional motivation of spatial filling on these nanoadditives (e.g. nanoparticles or NPs, quantum dots or QDs) into BCP domains was considered as a subject of significant ongoing investigation. Thus, directed self-assembly (DSA) of BCPs and surface chemically functionalized NPs constitute experimentally reliable tools for the formation of novel and promising polymer nanocomposites, generating hybrid materials far away from the corresponding properties of common plastics as homopolymers or blends.

Between several high impact contributions in soft matter technology, two of them have shown to support highly organized BCP structures of distinct microdomain spacing and long range order features. The former refers to the polymerization procedure followed in the BCP synthesis since it is of crucial importance to control the synthetic conditions and variables including molecular characteristics, block sequence and molecular architecture. To predict a BCP structure, as well as the corresponding domain periodicity, the implementation of anionically synthesized macromolecules in combination with high vacuum conditions is considered fundamental since this polymerization method has shown magnificent potential in nanotechnology applications since it ensures predictable molecular characteristics (total and for individual block molecular weight, polydispersity index) since undesirable impurities such as atmospheric oxygen and moisture are absent [Had00].

The second characteristic innovation is related with the ability of the BCP to selfassemble in a templated form in which the demonstrated length scale is too extensive as to be comparable with the characteristic periodicity of the BCP. Also, the orientation of the BCP domains can be directed by topographically or chemically patterned templates. The knowledge of physics, chemistry even thermodynamic parameters that govern this selforganizing process sets a solid foundation to successfully handle templates self-assembly method (TSA) [Che06].

Concerning the feature size, the fabrication of devices that are designed to focus on applications in opotoelectronics and magnetic storage media are set as fundamental for the particles size which is ranged within typical sizes (below 100 nm). The explanation is given by the fact that only in such dimension scales, the anticipation of magnetic, optical and electronic behavior different from macro and micro counterparts maybe successful. Precise localized control of the nanoparticles and sufficient space at such low dimensions renders anionically synthesized BCPs as very good templates in order to produce tunable nanostructured hybrid materials from the viewpoint of the aforementioned requirements. The manner upon which the BCP matrix is related with the deposited and well dispersed nanoparticles can be visualized in the following Figure 1.1.



Figure 1.1: Schematic illustration of the dependence of the BCP matrix and the incorporated nanoparticles (NPs) in the final nanocomposite material.

The incorporation of nanoparticles into a polymer matrix can provoke a significant impact on a wide range of nanocomposite properties. Improvement of mechanical strength, conductivity, permeability and catalytic activity, optical and magnetic properties has been significantly mentioned in the literature. These characteristic features of BCP/NPs are determined in part by the functionalities (electronic, optical and mechanical) of the nanoparticles and the polymer matrix. The self-organization ability of BCP behavior offers a time-effective and reproducible process to generate a periodic platform for particles hosting. Simultaneously, the additional selective localization of various shaped nanofillers within one of domains enables the development of polymer based nanocomposites of discrete target properties. The fabrication of these highly organized arrays has been considered as an attractive approach for potential applications in optoelectronic materials, magnetic storage media, sensor devices etc.

The perspective to use ABC type triblock terpolymers as structure directing platforms leads to a particular exciting class of hybrid materials. The utilization of a three chemically different component system demonstrates another important extension to the concept of nanoparticles direction throughout the BCP self-assembly. Beyond AB diblock and ABA triblock copolymers, the alternative platform of a three chemically different component scaffold can display more sophisticated multi-functional nanocomposites including air and space technologies with unique combination of strength and toughness.

The single component of nanoparticle arrays within AB copolymer matrix that exhibit a single LSP resonance (Local Surface Plasmon resonances) is well demonstrated in the literature. ABC terpolymers may be utilized as the nanoparticles host to incorporate two different types of nanoparticle arrays displaying therefore two characteristic LSP resonances. ABC terpolymers have the potential to be exploited as basic building blocks for plasmonic devices and sensors by incorporating metal particles of Ag and Au. At low diameter dimensions, they give rise to unusual optical properties with the most characteristic being the LSP excitations inspiring the fabrication of smaller and more sensitive photonic devices.

The selective occupation of two building blocks by two different particles whereas the third can be remained intact enables the ABC terpolymer as an attractive nanostructured pattern. The coexistence of both particles in a common system is directly related to binary surface plasmon resonance in order to operate at visible or near infrared frequencies. Long range order of a BCP template can ensure large arrays of gold/silver nanoparticles while the NPs successful deposition significantly changes the propagation properties of surface polaritons (SPPs).

Chapter 2: Background

2.1 BCP-Based Nanocomposite Materials

The ability to control not only the length scale but also the spatial organization of block copolymers (BCPs), microphase separation has led to the evolution of polymer-based nanocomposites with various types of nanofillers (such as carbon related materials and nanoparticles). The linear A-*b*-B type BCPs is the simplest system since it is comprised from two chemically different segments, covalently bound to each other and being in most cases immiscible. The number of segments or blocks can be increased leading to triblock copolymers (A-*b*-B-*b*-A), triblock terpolymers (A-*b*-B-*b*-C), tetrablock copolymers (A-*b*-B-*b*-A) and to multicomponent systems which have been prepared according to the potential application depending always on properties (physical, chemical, optical, stimuli-responsiveness) as well as on the self-assembly either in bulk or thin films.

A widely developed class of BCPs made from incompatible components is able to self-assemble into microphase separated domains with periodically fixed spacing and domain characteristics. Industrial synthesis of BCPs was initially demonstrated in the 1950s by scientists in BASF and ICI and involved the development of triblock systems of poly(ethylene oxide) and poly(propylene oxide), as a new class of synthetic surfactants. Among other applications the specific materials found widespread use not only as surfactants but also as anti-foaming agents, cosmetic materials and drug release materials [Oma13]. Accordingly, the example of thermoplastic elastomers, a hybrid BCP system which consists of a rubbery block (polyisoprene, polybutadiene) and a glassy block (e.g polystyrene), led to the preparation of industrially applicable products, yielding to improved impact strength of thermoplastics in automobile and domestic appliances market over the last four decades.

BCPs have demonstrated considerable attraction in nanotechnology, nanomanufacturing and nanopatterning especially in the semiconductor industries due to their ability to direct self-assemble. Based on the already acquired knowledge on direct self-assembled materials for nanotechnology applications the scale-up towards industrial scales and/or industrial pilot lines is of great importance. Taking into account the challenges for direct self-assembly (DSA) of nanostructures and the patterning requirements according to demand, the chemistry involved should be very straightforward in order to have very well organized nanopatterns in large dimensions with exclusion of defects and dislocations leading to enormous potential for the final composite and/or hybrid materials.

2.2.1 Microphase Separation and Self-Organization of Block Copolymers

A-*b*-B diblock copolymers serve as a great template for tailoring nanoparticles (NPs) organization due to the fact that regular periodic arrays and long-range alignment of such a

BCP template controls the NPs distribution throughout the polymer host. When polymers are mixed the result is often to undergo phase separation as the same tendency is followed from small molecule mixtures as long as nucleation and growth or spinodal decomposition mechanism is being obeyed.

In block copolymers, complete phase separation cannot be achieved since they are chemically linked with a covalent bond which is usually denoted as a junction point. Phase separation occurs due to the weakness to form large A and B phases. Instead the blocks minimize their connectivity and produce simple topologies up to astonishingly complex mesoscale structures.

In principle, phase separation in a BCP molecule is driven by two opposing forces among segments: the unfavorable enthalpic gain obtained by the local segregation and entropic elasticity resulting from the localization of the junction points on an interface [Bat02]. In order to avoid unfavorable block interactions between chemically different segments, phase separation occurs, while to maintain uniform density, polymer chain stretching is also encountered. Stretching reduces the interfacial area between the domains (known as IMDS: Intermaterial Dividing Surface) however, it also reduces the number of possible conformations [Boc02]. Thus, regarding this competition between enthalpy and entropy, thermal conditions and requirements indicate which tendency will prevail.

When temperature is increased, entropy dominates and the block copolymers are in a disordered state for a given BCP of same chemical composition. On the other hand, upon reducing the temperature, BCP domains are separated and well-ordered microstructures are formed. Microphase separation being a self-assembly driven phenomenon is given by the minimization of the free energy of mixing by the involved blocks. Gibbs free energy of a block copolymer system is expressed in terms of Flory Huggins theory for a A-b-B diblock system as stated in equation 2.1.

$$\frac{F}{(kBT)} = \frac{f}{NA} ln(f) + \frac{1-f}{NB} ln(1-f) + \chi f(1-f)$$
(2.1)

Consisting of three portions, the above equation (2.1) depends critically on entropic contributions (entropic losses from stretching the A and B blocks, first two terms) and on interfacial energy or the enthalpic penalty due to mixing (third term). Therefore, microphase separation is determined by three factors:

- Total degree of polymerization N, which is inversely proportional to entropy change
- Relative concentrations f_A and f_B of the units A and B, respectively (where $f_A = N_A/N$, $f_B = N_B/N$ and $f_A + f_B = 1$) in order to describe the A-b-B interactions and
- The Flory–Huggins interaction parameter, χ , which is temperature dependent and is calculated from equation 2.2:

$$\chi = \frac{a}{T} + \beta \tag{2.2}$$

In equation 2.2 the symbols α and β are specific parameters attributed to the different BCPs and are dependent from the entropic and enthalpic terms, respectively of the total free energy.

However, it is the segregation of the blocks that reduces the number of intramolecular interactions between chemically different blocks. The tendency of the blocks to segregate is determined by the product χN which represents the enthalpic-entropic balance and dictates the phase behavior of BCP as a function to volume fraction (f) [Bat91]. Changes in this product χN by increasing N (total polymerization degree) or reducing the temperature (increasing therefore the value of χ as is evident from equation 2.2) lead to the transition from disordered to order state concluding to microphase separation between the two different segments in the simplest case of a diblock copolymer. This transition is well known in the literature as order-disorder transition (ODT) and a schematic is shown in Figure 2.1 [Abe05]. Regarding the polymer chains conformation, ODT represents the transition from the homogeneous melt to well-ordered and microphase separated domains.



Figure 2.1: Schematic representation of the order-disorder transition (ODT) for a simple diblock copolymer.

The other critical transition dictating the segregation strength in a BCP melt is called order-order transition (OOT). This transition does not indicate whether the polymer blocks are immiscible, but only suggests the transition from an equilibrium morphology to another according to the preparation of the film, the thermodynamics involved and whether the blocks are strong or weakly segregated. Therefore, by altering the value of χ or N the OOT is possible in the weak segregation regime (as long as the volume fraction is kept constant) and not in the strong segregation limit (χ N>100) where an OOT from one morphology to another is possible only when the volume fraction changes [Lei01].

Three segregation regimes have been defined to explain the progress of microphase segregation and the thermodynamic stability in the equilibrium domains. For illustrative

purposes, consider the formation of alternating lamellae phases consisting of symmetric blocks in A-*b*-B diblock with $f_A = f_B = 0.5$ and $f_A + f_B = 1$. The lamellae morphology is recognized as the most common phase related to the microphase separation of BCPs, since it is formed by involving in such symmetric systems a 2nd degree transition from disorder directly to a well-ordered morphology expanding in large volume fraction regime (0.38-0.62) [Far09]. Depending on the value of the χN product the following four cases may be considered:

 $\chi N \ll 10$: The polymer melt is disordered, the average concentration is stable everywhere and equal to the volume fraction. The A/B interactions between the two chemically different blocks are very weak and the unperturbed dimensions for the chains are being adopted [Mat97].

 χ N~10: In this case an equilibrium between entropic and enthalpic factors is established leading to ODT but still the BCP is not well microphase separated especially in the case of asymmetric segments.

 χ N>10 (slightly): The system undergoes to the weak segregation limit (WSL) and still the A/B interactions are weak but the average concentration changes from area to area. The structure's periodicity is an analogue of N^{1/2} and microphase separation is a sinusoidal function of concentration. The interface thickness is large due to partial mixing of the A and B blocks within the interface and the junction points are mostly located on the center of the interface. Especially in this case and when the value is approximately equal to 10.5 or slightly higher a symmetric diblock copolymer undergoes from disorder to order alternating lamellae morphology as mentioned above. In this case the WSL expands in the area of $10.5 < \chi < 38$ in which the smaller value corresponds to a symmetric diblock copolymer whereas the highest value corresponds an asymmetric BCP.

 χ N>>10: In this case the A/B interactions are increased leading to separation of the chains to almost two different homogeneous areas divided by interfaces with very narrow thickness. The enthalpic factor is minimized leading to chains distributed away from the interface. The dimensions are larger than the unperturbed ones and the junction point is located on the very narrow interface whereas the periodicity of the unit cell of the adopted morphology is an analogue of N^{2/3}. The specific regime is called strong segregation regime (SSL). This regime depends on compositional fluctuations which strongly affect the shift of the ODT away from the microphase separation transition. For higher molecular weights of the block components (larger N values), fluctuations seem to be less dependent with segregation strength and ODT approaches the microphase separation transitions for constant χ N [Abe00]. In Figure 2.2 the morphologies based on volume fraction of the minority component are given.



Figure 2.2 Schematic of morphologies based on increasing volume fraction for the case of a linear diblock copolymer. [Mar01].

It is important to mention a third narrow region for the product χN which is within the values: **38**< χN <**100** in order to cover the phase behavior gap between WSL and SSL, known as Intermediate Segregation Limit (ISL). Using as theoretical background the self-consisting field theory (SCFT) by Helfand [Hel80], Matsen and Bates it was possible to predict more complex ordered microphases with narrow interphases between the blocks whereas time is increased experimentally confirmed [Mat97]. The most important is the double gyroid phase, in addition to the aforementioned lamellae structure followed by hexagonally closed packed cylinders of the minority component in the majority as well as bcc spheres of the minority component.



Figure 2.3: Mean field phase diagram within the SCFT approximation for conformationally symmetric diblock copolymers where f = volume fraction. The phases are: L: lamellar, C: hexagonally packed cylinders, S: spheres packed in a bcc lattice, G: bicontinuous Ia3d cubic (double gyroid), Scp: closed packed spheres. Reproduced from [Mat94]

2.2.2 Equilibrium Morphologies and Phase Diagram for Diblock Copolymers

Various equilibrated morphologies have been confirmed in diblock copolymer systems in certain composition limits, among which the most studied being the polystyrene-b-poly(isoprene) theoretically and experimentally [Mat96]. These structures are shown schematically in Figure 2.4 where the volume fraction of the B block is increased leading to alternation between matrix and minority component when f_B is low and high respectively.



Figure 2.4: Schematic illustration of the observed morphologies for A-b-B diblock copolymer upon increasing the volume fraction of the B block at the expense of the A block volume fraction. [Hiu14]

These morphologies are identified as follows:

- Spheres of the minority component arranged in a body centered cubic (BCC) lattice in a matrix of the majority component (lm3m).
- Hexagonally packed cylinders of the minority component in a matrix of the majority component (HEX).
- Double gyroid, where two independently interpenetrating and not interconnected bicontinuous networks of the minority component are formed in a matrix of the majority component (la3d).
- Alternating lamellae of the two components (LAM).

It should be mentioned in this point that the spheres in a BCC lattice, hexagonally close packed cylinders and the networks in the double gyroid morphology are occupied always by the minority component according to the volume fraction of block A or B. Of course significant role in the self-assembly is defined by the product χN which has to be large enough in order for the two segments to microphase separate.

By explaining further the scheme in Figure 2.3 when the composition is $f_A=f_B=0.5$ alternating stripes of the two components separated by flat interphases are shown, which corresponds to the lamellae structure (LAM). Upon increasing f_A at the expense of the f_B , between 0.6 and 0.7 double gyroid is evident, where two independently interpenetrating and not interconnected bicontinuous networks of the minority component are formed in a matrix of the majority component (DG). As f_A continuously increases, microstructures with lower interfacial free energy appear. At composition range 0.72> $f_A > 0.87$, hexagonally close packed cylinders of the minority component in a matrix of the majority component are observed (HEX) and finally spheres of the minority component arranged in a body centered

cubic (BCC) lattice, in a matrix of the majority component is demonstrated for values $f_A > 87$ (SPH).

As shown from the phase diagram in Figure 2.3, the phase boundaries are almost vertical for χ N values higher than 80 and it is noticeable that the DG is not an evident morphology for corresponding values higher than 60. This observation concludes to the fact that for BCPs composition range close to a phase boundary between two neighboring morphologies it is possible to obtain thermally induced order-to-order transition (OOT) since the Flory- Huggins interaction parameter χ varies as the temperature changes leading therefore to a morphology transition for the same composition. The low χ N value upon which the DG structure disappears may lead to the conclusion that the specific morphology is not stable but this case is not true since for BCPs of the PS-b-PDMS [PDMS: poly(dimethylsiloxane)] type the DG was identified at volume fractions of the minority component of 0.40 and for χ N values higher than 100 and almost equal to 200. [Pol09] In addition, cubic structures such as DG have demonstrated better mechanical properties from HEX and LAM allowing a huge perspective for potential applications [Had03]. Considering all the aforementioned structures, LAM and HEX are of high importance in terms of nanopatterning electronic templates and for membranes separation applications [Far09].

2.2.3 Microphase Separation and Self-Organization of Triblock Terpolymers

The simplest case of multiblock multicomponent polymers in terms of synthesis and morphological characterization is the linear A-*b*-B-*b*-C triblock terpolymers. Just like the previously mentioned diblock copolymers, the generating morphologies for the triblock terpolymers rely on the fundamental microphase separation regulations while the subdomains self-assemble into more complex but equally well-ordered nanostructures.

It should be mentioned that an intermediate BCP between A-*b*-B and A-*b*-B-*b*-C is the A-*b*-B-*b*-A triblock copolymer. These copolymers have been morphologically studies as well and the phase diagram produced of χ N vs. volume fraction is quite similar to that already reported for diblock copolymers. There are though important differences which should be mentioned such as the fact that the midblock B is joined with the A segments with two junction points leading to bridge and loop conformations enhancing therefore the thermodynamics involved for microphase separation. It has been also reported that in the A-*b*-B-*b*-A triblock copolymers the ODT takes place at relatively higher χ N value well above from 10.5 (as in the symmetric diblock copolymer system) and is approximately equal to 17.5. Despite these differences the adopted morphologies for specific compositions are approximately similar to those for an A-*b*-B system.

An addition of one extra block leads to larger morphological complexity as well as greater variety of morphologies for linear triblock terpolymers, due to the two independent composition variables (f_A and f_B) and three binary interaction parameters (χ_{AB} , χ_{AC} and χ_{BC}) [Bat99,Zhe95,Huc00]. However, in a three component system, more options of block sequence is possible such as A-*b*-B-*b*-C, B-*b*-A-*b*-C, A-*b*-C-*b*-B among which at least one can be synthesized with known polymerization techniques. Block sequence plays a significant role in generating different morphologies and phase transitions especially for similar compositions [Mog93].

Bates and Fredrickson have indicated the most important morphologies in A-*b*-B-*b*-C linear terpolymers [Bat99] which are exhibited in Figure 2.5. It should be mentioned that all these morphologies illustrated in Figure 2.5 depend on segment type, block sequence, molecular weight and volume fractions. Some of the morphologies shown in Figure 2.5 can be described as follows [Huc00]:

Figure 2.5a). The terpolymer is symmetric, $f_A = f_B = f_C = 1/3$ and with almost identical interaction parameters, $\chi_{AB} \approx \chi_{BC} \approx \chi_{AC}$ leading to the final morphology which is described as the 3-phase 4-layer lamellae.

Figure 2.5b). When $\chi_{AB} \ll \chi_{BC}$, the system is driven by the interaction asymmetry to adopt the hexagonal morphology of core-shell cylinders, in order to minimize the interfacial area BC relative to that of AB, resulting in an overall lower free energy.

Figure 2.5c, d, e). When $\chi_{AB} \approx \chi_{BC} \gg \chi_{AC}$ and for low values of f_B . In this case phase B becomes discontinuous allowing for increased contacts between the A and C blocks giving rise to "cylinders at the wall" (case c) or "spheres at the wall" (case d) or even the decorated cylinders (case e), depending on the proportions of A and C. Increasing the content of the B-domains give rise eventually to continuous B domains as in case (a).

Figure 2.5f, g, h, l). The most symmetric case, where $\chi_{AB} \approx \chi_{BC} < \chi_{AC}$ and $f_A \approx f_B$, can give rise to the structures shown in f, g h and l. In this case, the system tries to minimize the unfavorable contacts between A and C and gives rise to tetragonal cylinders or to the tricontinuous Gyroid morphology of case l composed of two independent networks of the A and C domains.



Figure 2.5: Schematic presentation of the most characteristic thermodynamically stable phase morphologies for linear ABC terpolymers. At the top of the scheme, blocks A, B and C adjusted in regions colored blue, red and green respectively [Bat 99].

It is easily understood from the above that by adjusting the degree of polymerization of the polymer and the composition (volume fraction, f), the length scales associated with self-assembled structures can be manipulated [Mut97].

The manner that such morphologies maybe observed depends on the preparation of the initial film from a specific solution as solvent evaporates. It is very difficult to find a solvent which equally dilutes all three segments and evaporates simultaneously from all blocks; therefore the solvent evaporation is divided into two steps (Figure 2.6). The least solvated block (e.g. A) initially begins to separate and minimizes contact with the remaining two blocks, while chain stretching occurs for block A. As the solvent continues to evaporate, B and C segments are no longer remaining mixed and thus they begin to microphase separate. In order to predict the final morphology, it is crucial to consider the position of the segments in the triblock terpolymer sequence as the mid-block or as an end-block [Yam02].



Figure 2.6: Cartoon which explains the casting of the selective solvent stepwise. In the first step, one block is separated from the other two. In the next step, the two remaining miscible blocks are also microphase separated [Had05].

2.3 Block Copolymers for Patterns and Templated Self-Assembly Applications

One of the most challenging tasks in advanced nanotechnologies is to provisionally demonstrate building block materials that can provide low-cost processes in order to fabricate large-area periodic nanostructures. The need for eliminating defects and enhance almost perfect orientation mainly in thin films led to the evolution of "bottom up" self-assembly with "top-down" patterned templates [Spa02]. Many experimental works have tried to combine both these methods in the same direction leading to templated self-assembly (TSA). The concept of TSA describes the topography of the template chemical patterns which are used to guide the organization of the BCP domains, in controversy with conventional epitaxy in which the film is mounted over the lattice of underlying substrate. Thus, for TSA induced templates, it is not necessary to exclusively adjust it only for crystalline materials. Furthermore, it is useful to distinguish the scale limits of TSA, from the atomic scale of

crystalline materials up to as high as colloidal particles dimensions ($L_0=10-100$ nm) between which the scale size of self-assembled BCPs is evident (Figure 2.7).



Figure 2.7: Schematic presentation among the most characteristic TSA systems. The characteristic feature size (L_0) of crystalline materials, block copolymers, and colloid assemblies as well as the characteristic length (L_s) of the template are exhibited [Che06].

2.3.1 Strategies for Fabricating Patterned Nanostructures

Over the last three decades, several techniques have been intensively emerged for nanofabrication in order to generate structures in controlled assembly and structuring of matter to the length scale between 1-100 nm. In a systematical effort to classify them, four strategies are emphasized: i) Electron Beam (EBL) and Scanning Probe Lithography (SPL), ii) Physical Contact enclosing techniques such as: printing, molding, and embossing, iii) Self-Assembly processes with BCPs and surfactant being the most predominant, iv) Template Deposition and v) Size Reduction strategy [Xia99].

However, it is proven that only a few of these techniques could provide good accuracy below 50 nm. The ability to create ordered structures over extent surfaces is limited by defects as well as many of these methods are limited to 2-D fabrication. High cost and time consuming paths are necessary when the feature size decreases further below 100 nm. Among these techniques, Electron Beam (EBL) and Scanning Probe Lithography (SPL) have already shown exquisite prospect in demonstrating smaller feature sizes. Although this perspective, both of these patterning tools overlay sequentially and not simultaneously the pattern and therefore the patterning time increases linearly when compared with the covered area [Zeh98]. Unlike lithographic techniques, BCP fabrication encompasses the nanoscale materials synthesis by retaining the parallel processing gain. For the most cases, covering large areas simultaneously is considered as a basic advantage for industrial applications.

2.3.2 Block Copolymers in Templated Self-Assembly (TSA)

Based on self-assembly, high-resolution BCP layers can be produced with relative low cost, ready to find use in surface patterning and offer solutions compatible with several hi-technological industrial fields such as: light-emitting diodes (LEDs), and plastic electronics. Their adequacy comes from their ability to form repetitive patterned circuits through cost effective processes, leading to interesting applications such as magnetic storage media and semiconductor microelectronics [Seg04].

Traditionally, numerous efforts for nanostructured devices have been defined using lithography/etching of bulk materials as top-down approaches finding tremendous applications in semiconductor industry. These top-down methods suffer from several intrinsic limitations including electrostatic interactions and inappropriate electron diffraction depth making them rather expensive for the semi-conductor and magnetic recording industries. In order to develop higher density circuits and data storage devices, engineers and scientists began to seek for more sophisticated approaches in micro-fabrication in order to facilitate the consumer needs for even cheaper and faster micro-fabricated devices. Consequently, novel paths to circumvent both cost and manufacturing issues should be adopted.

Designing BCPs is evaluated as a proper choice both in terms of thermodynamics and dynamics generating well-defined self-assembled systems in order to obtain large area periodic structures. Upon this effort, it is important to ensure the spatial control over the microdomains.

From an overall point of view in the nano-manufacturing field, two are the strategies which lead to spatial order and orientation control independent from the domain size structure. In the first approach, the substrates are patterned with lithographic techniques in order to produce top-down patterns, on top of which the BCPs nanopatterns can be subsequently guided along the patterned area. The formation of bottom-up block copolymer patterns within or on top-down substrate patterns is the bearer for the so-called templated self-assembly (TSA) processes. It should be noticed that TSA includes methods which intend to diminish defects and induce enhanced orientation in thin films, leading eventually to topographical and chemically patterned templates. Most importantly, well defined TSA patterns result in superior nanometer level precision and accuracy.

Describing the second approach, fabrication techniques based on this strategy involve the convergence of top-down and bottom- up patterning in the same BCP architecture for rapid patterning of functional nanostructures. Contributions by two different groups, Bal et al. [Bal02] and Spatz et al. [Spa02] took advantage of e-beam lithography in order to impose spatial organization in the microdomains of two broadly known diblock copolymers: poly(styrene)-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) and poly(styrene)-*b*-poly(2vinylpyridine) PS-b-P2VP microdomains, respectively following a simple and fast process. Their convincing results concerning time-effectiveness increased the popularity for real-time applications, such as templates in integration devices.

2.4 Nanoparticles Arrays in Block Copolymer Domains

In a pure state without any filler, BCPs nanostructures show significant impact in nanotechnology. Nonetheless, they are devoted only in applications related with ordered morphologies including stripes, holes and limited number of projections with sizes ranging from 10 to 100nm. For the sake of tuning properties, engineers and "soft matter" scientists indicated the need for more vital options in nanofabrication. As a consequence of this nano-manufacturing evolution, to enhance physical (electronic, optical) and mechanical (strength, internal stresses) properties, nanofillers distributed within the BCPs templates seemed as unique method in the bottom-up generation of polymer based nanocomposite materials (PNC).

Incorporating inorganic fillers of various chemical nature, shape (particles, rods, sheets) and size into polymer based matrices encompass different crystallization approaches since physical rules govern depending on the distribution process of the nano-filler. Employing the guideline of microphase separation, nanoparticles in colloidal state, may spatially become localized into self-organized BCP domains. Although in the past, for the formation of BCPs-inorganic nanoparticles hybrids many limitations were evident, novel synthetic routes and techniques (control living radical and anionic polymerization) have improved not only the synthesis but also the functionalization of the nanoparticles.

Except from the size and shape dependence, the spatial distribution of the nanoparticles (NPs) into BCP domains is affected by various intrinsic characteristics, taking into account the interfacial tensions between NP-NP and NP-domain of each polymer block which is actually considered as the most crucial among all these parameters affecting the NPs distribution in the polymer matrix [Har06].

2.4.1 Strategies to Control Nanoparticle Locations within BCPs Matrix

The functionalized NPs effectiveness in lowering the surface energy, compared to bare nanoparticles is very important. In some cases, the polymer protective shell anchors on the organic cores and then it is dispersed homogeneously in the polymer solution ("ex-situ" approach). By this approach and exploiting the chemical affinity between mutual polymer shell and the corresponding blocks, thermodynamically driven phase segregation forces force nanoparticles to be confined into the segregated domains [Chi05].

Another major category for nanocomposite preparation is the "in situ" approach. In this case, polymer moieties and inorganic precursors are placed simultaneously in the solution. Compared to the in-situ, ex-situ approaches provide beneficial synthetic control over the nanoparticle's size and great selectivity in spatial localization on BCP domains [Har06]. Nanoparticle templating also corresponds to less commonly used approaches such as applied external fields [Alb00] and directed chemical-binding [Mur01, Bin05] processes.

2.4.2 In situ Approach toward Polymer Based Nanocomposites

In a typical effort to highlight techniques for BCP based nanocomposites fabrication, two major pathways are appropriate: attaching the metal to the polymer chain or loading the BCP mass together with the metal salts into selective domains simultaneously. Over the last two decades, a number of important contributions are reported in the literature by various research groups specialized in NPs distributon/formation into BCPs domains using both pathways.

As a pioneer work, silver and gold precursors in form of metal salts were introduced into selectively one block at phosphine-functionalized BCP bearing Poly(norborene-derivatives) [Che92]. The TEM images given by this work verified the localization of metal crystals within specific BCP domains for three different phase equilibriums (lamellae, spheres, cylinders) as it is evident in Figure 2.8.



Figure 2.8: *TEM images from Ag (left) and Au (right) addition into phosphine-functionalized BCP indicating lamellae and cylindrical morphologies respectively after thermal annealing [Che92].*

Based on the same concept, the lamellae morphology of PS-*b*-P2VP film is used to host colloidal silver within the PVP block domain selectively. In this research work Ishizu et al. performed crosslinking of the existing BCP film by di-iodobutane (DIB). Quaternization of the pyridinium ions selectively included Ag ions throughout the PVP phase [Sat93].

Beyond functionalized monomers, the reduction of metal salts into already microphase separated BCP domains leads to a more effective control of nanoparticles deposition. Following this approach, amphiphilic BCPs derived from hydrophilic segments such as: poly(vinyl-pyridine), poly(methyl-methacrylate), poly(ethylene-oxide) can bind

precursors through diffusion into a salt solution [Soh01, Dai06, Tsu99, Son07, Abe03, Spa96]. Actually, this versatile synthetic procedure has extended to other inorganic fillers such as magnetic NPs [Abe03, Boo02, Son07] semiconductors and intermetallic alloys [Dar05] due to better chemical affinity.

The in-situ BCP-templated nanoclusters and colloidal nanoparticles still remains the most prominent approach, covering the vast majority of current interests in BCP templating applications. An outlook of the most important results which are considered as the key parameter, the spatial selectivity of nanoparticles into BCP domains is given in the following paragraphs.

In many published works where the in-situ method is adopted, the ability of poly(vinylpyridine) either P2VP or P4VP, to produce complexes with metal salts due to the presence of an N atom per monomeric unit is exploited. Titanium nanoparticles of approximately 23 nm in diameter were selectively introduced into P2VP segments using a micellar film of a PS-*b*-P2VP diblock copolymer [Li05]. Subsequent UV exposure as well as oxygen plasma treatment removed both polymer phases while the nanoparticle arrays remained onto the scaffold.

Using preformed "nanoreactor" films as previously mentioned, Horiuchi et al. infiltrated palladium and cobalt nanoparticles from selectively decomposed and reduced moieties to metallic state within PMMA and PI-OH regions as constituent blocks of PS-*b*-PMMA and PS-*b*-hydroxylated polyisoprene) with all combinations being achieved [Hor 03]. The spatial deposition of metal complexes into BCP domains was confirmed by energy filtering TEM images in a combination with electron energy loss spectroscopy (EELS) mode (Figure 2.9).



Figure 2.9: The lamellae structure as observed from TEM images of PS-b-PMMA diblock copolymer exposed to $Pd(acac)_2$ vapor. After 2h of vapor exposure, the location of Pd nanoparticles was directed from the PMMA stripes. Two different magnification images are given [Hor03].

Zehner and Sita demonstrated a new strategy for controlled fabrication of nanomettalic arrays of 20 nm repeating unit size in a direct assembled PS-*b*-PMMA pattern of

perpendicular lamellae structure [Zeh99]. This work was inspired from a previous research study of the same group, where functionalized gold nanoparticles in order to enhance the interaction with polymer domain were introduced into a well-defined diblock copolymer of the same nature but this approach was not considered as in situ method [Zeh98].

Another simple path to pattern nanoparticles is to generate them or being solubilized within the core or being located at the interphases of host micelles (Figure 2.10). Spatz et al. demonstrated the extraction of gold nanoparticles from an aqueous solution of PS-*b*-PEO micellar BCP host template over coherent and thin film [Spa96].



Figure 2.10: *TEM images which indicate: a) the micellar assembly of Au NPs into PEO core prior to annealing process of PS-b-PEO/Au NPs nanocomposite and b) the location of one single Au particle per micelle core after thermal annealing at 90^{\circ}C for 1h [Spa96].*

Exploiting this work, Spatz and coworkers extended this nanoreactor approach in other micellar diblock copolymers including PS-*b*-P2VP. In this case, gold NPs sequestered into PS phase forming the corona in a selective medium and tetrachloroaurate molecules were bound into the PS core as counterions [Spa99] as shown in Figure 2.11.

Pd and Fe nanoparticles were deposited into stable PEO-*b*-P2VP micelles in aqueous solution as reported by Broinstein et al. The key parameter in this research work which controls the nanoparticles size and shape during coordination between metal salts and P2VP segment is the pH value during the experiments [Bro99].

Using the thermal decomposition method, Rutnakornpituc et al. successively generated super-paramagnetic cobalt nanoparticles into polysiloxane templated ABA type BCP [A: poly(dimethylsiloxane and B: 3-(cyanopropyl)methylsiloxane] as steric stabilizers [Rut01]. The authors supported their results by TEM images, in which they observed well defined two dimensional arrays and in each one of them cobalt particles inside the intended micelle compartments.



Figure 2.11: *a) TEM image of PS-b-P2VP micellar structure in which Au nanoparticles are enclosed into P2VP domain, as a core of the structure. b) Schematic illustration of the same mono-micellar film which is treated by different recipe. Because of the treatment of the micellar solutions with* $HAuCl_4$, *significant alteration in surface morphology is observed* [Spa99].

Previously mentioned techniques are based on metal salts reduction which is very crucial since by completion of the metal infiltration all byproducts should be removed from the solution. Furthermore, the metal precursor's evaporation onto patterned BCP films provokes the relatively defective control of particle shape and size. Finally, it is clear that the stabilization of the particle surface cannot be fully ensured due to incomplete inter-diffusion of precursor amount for the most of the in-situ approaches.

2.4.3 Ex-situ Approach and Chemical Affinity

Rather than directly infiltrating colloidal nanofillers within phase-segregated BCP domains, a more promising approach to overcome the in-situ method limitations aroused from the ex-situ method. The perspective of this method is the desired surface chemistry of nanoparticles in order to be deposited into the target block of the BCP upon the self-organization process.

Up to date, a sufficient number of ex-situ strategies led to fabrication of BCP nanocomposites with selective incorporation of inorganic NPs within ordered domains of the polymer matrix. To impart well dispersed and non-agglomerated nanoparticle arrays, a very common strategy is to alter the surface functionality by attaching onto the NPs surface polymer chains which are properly treated by various ligands.

Small surfactant molecules such as alkanethions and citrates attribute in a more flexible synthesis approach to the nanoparticles incorporation, since various functionalities which enhance the compatibility along the BCP segments are involved. Instead of these low molecular weight surfactant molecules, controlled localization of inorganic NPs may also be achieved by grafting various polymer or oligomer ligands along the NP periphery resulting to a given structure comprised of an inorganic core and polymer shell.

The first report of such a strategy was given in the literature by Hamdoun et al. [Ham 96]. Maghemide nanoparticles of approximately 3.5 nm in diameter were initially covered by oligomer St chains which were subsequently dispersed in a lamellae structure BCP melt of Poly(styrene)-*b*-poly(butyl-methacrylate) with total weight average molecular weight of M_W = 80 kg/mol. Although the domain periodicity of the phase morphology was proven to be too small (L=32nm) to host NPs effectively into the PS domain, the final nanocomposite structure was defined from spatial domain selectivity.

To confirm mutual chemical affinity between modified NPs and corresponding polymer domains, many limitations were needed to be confronted and encountered [Chi05].

The development of highly organized hybrid material consisting of a PS-*b*-P2VP with symmetric blocks in volume fraction and gold NPs has been reported by Kim and coworkers [Kim05]. The 5 nm average diameter nanoparticles were stabilized by thiol-terminated PS-chains. The grafting of oligomer chains onto the nanoparticle surface ensured the compatibility with the PS domain. Except from the preferential localization of NPs within PS domains, it is also mentioned in this research work that the lamellae structure coexists with various morphologies along the film thickness when the particle loading overcomes a critical value.

Chemistry of capping molecules with the form of dodecanethiol ligands used was performed by Li and coworkers in order to spatially embedded gold nanoparticles (2-3 nm diameter) onto PS-*b*-P2VP templated thin films [Li08]. By varying parameters such the final ratio of dodecanethiol to 11-mercapto-1-undecanol (from 1/1 to 3/1) even the deposition method (spin-coating or dip coating) lead to the distribution of the NPs either within one of the segment or exactly at the IMDS which separates the two blocks from each other. These results are exhibited in Figure 2.12.



Figure 2.12: Comparison between the induced ratio of dodecanethiol /1, 1-mercapto-1-undecanol for NPs functionalization in a given PS-b-P2VP/gold NPs thin film. The study is supported by SFM and TEM images for a,c (1:1) and (d,e) (3:1) mixtures respectively. Films are deposited over silicon wafers and subsequent solvent annealing took place while on the same time the film is heated on a hot stage under vacuum at 170 $^{\circ}C$ for 30 min. Then, both films were quenched to room temperature under nitrogen flow [Li08].

Special attention should be devoted in ex-situ produced nanocomposites intended for semiconducting applications and therefore corresponding nanoparticles are of dominant interest. Yeh, Wei and coworkers prepared CdS nanoparticles of approximately 2.5 nm in diameter with mercaptoethanol as surfactant into an asymmetric PS-*b*-PEO diblock copolymer [Yeh 03]. In another work of similar interest by the same authors, upon increasing mercaptoacedic functionalized CdS (6 nm diameter) nanoparticles loading, morphology transitions were identified [Yeh 02]. In this contribution, nanoparticles were dispersed into P4VP cylinders or stripes over a PS-*b*-P4VP scaffold as a result of hydrogen bonding formation. The resultant morphology transitions, due to the NPs load increment, were from hpc cylinders in the pure diblock to bcc or sc spheres for the CdS/PS-*b*-P4VP composite as indicated in Figure 2.13. Upon subsequent increase of the NPs loading, additional phase transitions were also confirmed from hPC cylinders to lamellae as it was evident from TEM images.


CdS content in S4VP block copolymers

Figure 2.13: Schematic illustration of the NPs loading which induced phase transitions of CdS/PS-*b*-P4VP. Increased loading with NPs leads to a change from the hexagonal to the lamellar phase and finally to deformation of the lamellar phase [Yeh05].

Although most studies have focused on the incorporation of only one type of nanoparticle into the diblock copolymer (binary mixture), Bockstaller et al. extended the field of interest one step ahead [Boc03]. Highly organized ternary mixture consisting of two different hydrophobic (gold and silica) nanoparticles into a PS-*b*-PEP diblock system led to beneficially controlled arrangement of these two different nanoparticles array within the periodic structure. The authors conducted experimental proof of particles placement based on dimension ratio between particle size and domain periodicity where silica particles sequestered (d/L = 0.26) in the center of PEP while gold particles (d/L = 0.06) were embedded at the interface of the two segments.

More recently, Chiu et al. managed to show that by grafting different polymer ligand to particles surface, nanoparticles are directly localized at the center of the compatible domain whilst in case of mixture both of constituent polymer ligands, nanoparticles are segregated at the interphase dividing the two domains [Chi05]. This induction was experimentally verified by applying a system of PS-*b*-PVP with thiol attached gold NPs and by this manner one may exploit the interaction parameters between blocks and functionalized NPs. Particles with a mixture of PS and PVP were adsorbed at the interfaces between the PS and PVP blocks. Particles with only PS or PVP thiol therminated segments were encapsulated into the center of the compatible segment.

Another great effort on well-formed ternary mixture is focused on highly asymmetric micellar structure of PS-*b*-P4VP was demonstrated in the literature by Sohn et al. [Soh 03]. It was the first reported effort of directing two different kinds of NPs on a micellar templated structure together with explanations through both physical and chemical mechanisms. More thoroughly, they physically decorated dodecanethiol-protected gold NPs (~11nm diameter) along the periphery of micellar-cores. As a next step, iron oxide NPs (~30nm diameter) were

chemically generated at the inner part of the micellar cores. The whole formation was deposited onto a monolayer of PS-*b*-PVP scaffold which was subsequently preserved after plasma etching, revealing a well-defined ternary structure. High analysis TEM images indicated the dual nanoparticle patterning as indicated in Figure 2.14.



Figure 2.14: *TEM images of a) gold nanoparticles located at the periphery of micelles, b) placement of iron oxide nanoparticles synthesized by oxygen plasma treatment, c) coexistence of both nanoparticle kinds described as an array of iron oxide NPs surrounded by gold NPs. The insert in image b denotes a selected area of electron diffraction pattern of iron oxide NPs [Soh03].*

One of the latest reports deals with dual nanoparticle patterning of silver and gold NPs, following a two-step approach as described by Horechyy and coworkers [Hor13]. In the first step, pre-anchored with low molar mass PS-chains silver nanoparticles (~12 nm) were mixed with PS-*b*-P4VP in a neutral solvent for both segments of the BCP. By exploiting the chemical affinity, solvent vapor annealing (SVA) drives the silver NPs to the compatible PS domain. As a next and last step, three different kinds (Pt, Pd, Au with approximately 2-5 nm in diameter) of NPs are independently encapsulated into the P4VP domain by dip-coating the pre-synthesized Ag/PS-*b*-P4VP thin film into their aqueous dispersions respectively. Beyond the excellent selectivity of the NPs location into the respective BCP domains with this approach, it is of major importance to emphasize the ease of the two-step process that was followed. In Figure 2.15 scanning force microscopy (SFM) images of the NPs depositions is given by following the aforementioned two-step approach.



Figure 2.15: Dual nanoparticle deposition into PS-b-P4VP thin film illustrated by SFM images (a: symmetric lamellae structure and b) asymmetric structure of P4VP cylinder into PS matrix. The differentiation in NPs size confirms the selectivity of NPs location over the BCP thin film [Hor13].

2.4.4 Other Methods for Nanoparticles Arrangement

Beyond the above mentioned in–situ and ex-situ approaches for generating or introducing NPs within BCP blocks respectively, more sophisticated techniques involving external fields have been applied with even more advantageous contribution over the control of fabrication conditions. The detachment of one block away from the BCP structure by exposure in UV irradiation suggests a specific category in highly ordered nanoparticle arrangements. The basic concept of this patterning technique is divided in two steps according to Mathew and coworkers [Mis03]. Initially, hexagonally patterned PMMA cylinders surrounded by PS matrix were templated onto a spin coated thin film. The prepared film was subject to UV-light irradiation under vacuum conditions in order to decompose the PMMA phase into cross linked PS matrix which subsequently followed by washing with acidic acid. The resultant structure of approximately 17 nm in diameter empty cylinders was filled with the CdS nanoparticles solution. The final morphology can described as an array of sequestered NPs into a nanoporous template.

For the same diblock copolymer system (PS-*b*-PMMA), Zhang et al. applied an alternative method of external field driving the CdS NPs to be encapsulated into the nanopores. This method was named as electrophoretic deposition process [Zha05]. This method was employed over templates of 30-40 nm in thickness while equally important was the fuctionalization of CdS with α,ω thiocarboxylic acid ligands. Then, a flow pattern of electrolytes solution was induced by the electric field, driving the nanoparticles eventually into the nanopores which were modulated by a patterned electrode.

Another challenging task is demonstrated by Binder and coworkers where successfully bounded gold nanoparticles onto microphase separated BCP thin film. The procedure completed by immersing the film into solutions containing nanoparticles functionalized with the matching barbituric acid receptor [Bin05]. In particularly, selective binding of nanoparticles is due to these strong interactions (hydrogen bonds) and the thermal annealing process.

Besides these external field approaches, the selective staining of one block in order to control the NPs decoration among two non-functional constituent blocks enables the formation of organic/inorganic hybrid materials in thin film, but this is not the case for bulk films. Ansari et al. described the deposition of gold NPs along the Poly(isoprene) block as the stained block of a triblock copolymer system of PS-*b*-PI-*b*-PS [Ans01]. This strategy enables the patterning of nanoparticles by utilizing the selective chemical attack of osmium tetroxide (OsO₄) in order to increase the selectivity of the Au into stripes of the BCP substrate (Figure 2.16).



Figure 2.16: *TEM images of PS-b-PI-b-PS triblock copolymer after the first (left) and the second (right) staining step subsequently. The chemical attack of heavy metal oxide (OsO₄) enabled the deposition of sputtered gold to be patterned onto the elastomeric segment (PI) [Ans03].*

2.5 Guiding the Microphase Separation in BCP Thin Films

Under delicate conditions and by adopting proper strategies, the combination of block copolymer self-assembly with long-range order methods could potentially generate nanodomain structures of macroscopic and patterned periodicity. Based on this prospect, the effect of physicochemical constrains conditioned by interphases (surface field) on top of BCP thin films as well as the modulation of parameters including the functionality and the molecular characteristics of constituent blocks play a crucial role [Boc02, Alb10].

2.5.1 Surfaces and Interphases Effects

Thin film formation for BCP applications is of particular interest because of their challenging opportunity to develop 2-D nanomaterials with significant registry and regularity. In contrast to the bulk state behavior, BCP nanocomposites and therefore pure BCP structures fabrication takes place relative to the surface characteristics of the film. The studies

mentioned in a previous paragraph for describing the microphase separation lead to the prediction of bulk structures as developed from the melt. Actually, the morphology adopted by a neat BCP depends on molecular weight, polydispersity, composition, architecture and whether the blocks are amorphous, semicrystalline or crystalline. Also whether the morphology adopted is equilibrium morphology depends on many factors such as:

- ✓ *Solvent used* (selective or non selective) for the preparation of the solution for the casting process
- ✓ *Casting procedure*: how slow or how fast the solvent will evaporate leading to the final BCP film. An important role in this stage plays the volatility of the solvent.
- ✓ Annealing temperature and duration: Either anneal in high temperatures for very low time duration (e.g. 170° C for a few hours) or anneal in temperatures just above the highest T_g for long time duration (e.g. $110-120^{\circ}$ C for 7 days).
- ✓ Cooling process: Either quench the film after the annealing in order to freeze the structure adopted in the annealing temperature or leave the film to cool down slowly to ambient conditions. Drastic chances are evident in this process only when the BCP is within the weak segregation limit (WSL).
- ✓ *Sectioning*: Either prepare the thin sections from the initial film with ultracryomicrotoming if the BCP segments have very low T_g in order to avoid mechanical deformation from the cutting tools (glass knife or diamond knife) or environmental microtoming if the lowest T_g is well above room temperature.
- ✓ Staining procedures: Depending on the chemical nature of the blocks various stainers are used to increase the mass contrast during observation with TEM since most of the blocks involved in well studied BCP systems are comprised by blocks with similar electron densities (since most of them are hydrocarbons). The stainers in most cases induce cross-linking and therefore electron density is well increased leading to darker phases for the stained block when it is observed in the TEM.

In the case of thin films (<100 nm) almost similar parameters with those indicated for self-assembly from the melt state affect the type of morphology which will be adopted but a few more should be added such as diffusivity, interfacial width and film thickness. Especially the last parameter plays the most significant role together with the diffusivity since it has been reported that in terms of thickness and chemical nature of the substrate in thin films almost all type of morphologies may be adopted. However, even the slightest distortion threatens to disturb the delicate balance of intermolecular forces within the films. Thus, in addition to driving forces determined in the bulk state, it is necessary to consider these two parameters which plays a major role in the BCP thin film formation and relate to diffusivity and film thickness [Seg04]. In Figure 2.17 the possible morphologies adopted for thin films from simple BCPs are schematically illustrated.



Figure 2.17: Schematic presentation of self-organized BCP thin films and principal axial orientations with respect to the substrate surface: A) Lamellae structure of two phase patterned parallel to the substrate, B) lamellae oriented perpendicular, C) cylinders embedded parallel, D) cylinders normally oriented and E) dispersed spheres [Seg04].

BCP thin films are confined by surface (air atmosphere or vacuum) or interphase (to the substrate) energy which is interpreted from the surface tension γ , measuring the energy cost per units area between the air-polymer and polymer-substrate. In both cases the patterned film undergoes surface relaxation and surface reconstruction and depends on the diffusivity between BCP and substrate. The second factor that determines the morphological development of a BCP system and relates to the film thickness is the domain periodicity L₀ of the bulk state microphase separated structure and the tendency of each constituent block to occupy an interphase. By this means, the ultimately induced morphology considering all these parameters is additionally convoluted with the particular BCP morphology. For example, symmetric or less symmetric compositions (lamellae or cylinders respectively) exhibit shapes of long axes and their orientation with the surface film dominates the observed morphology [Fas01].

In the simplest case of a diblock copolymer thin film, the interaction of each block with the interphase may be described by two interfacial tensions γ_A and γ_B respectively. Differences in these values (surface field) indicate which of the block segment will reside at the interphase, e.g. the block with the lower interfacial tension is in most cases preferentially absorbed at the interphase. Many limitations in the preparation of thin films arise from surface phenomena leading to hindrance of the nanodomain formation and desired orientation, which in the case of BCP melts self-assembly do not exist. Thin film formation is considered as the most practical technique for self-assembled BCP deposition due to its recognized ease and time-effectiveness in creating a surface pattern and due to the efficacy of this pattern to be transferred to a new polymer substrate. Taking into account the physical and thermodynamic regulations that govern the resulting morphology, several practical restrictions must be confronted for well controlled topologies with good orientation, order, minimizing

discrepancies and defects throughout the thin film. These restrictions are described thoroughly below.

At first, regarding the deposition process, the most widely used methods in order to produce a BCP thin film are the spin-coating and dip-coating process. In both cases, BCP thin film is cast from a solution (copolymer with neutral solvent for both blocks in most cases) onto the scaffold surface and as a consequence disordered, thermodynamically trapped and uncontrolled in shape morphologies are formed. In the BCP disordered state, the connectivity of the chains drives the whole system to compositional oscillation among two polymer moieties completely different when compared with the bulk state/melt case. To provide the highest density of the domain (rich component for each block segment) and an equal distance between them, sufficient mobility of the polymer chains should be evident to allow the sub-domains reorganization, until a thermodynamically stable structure is achieved [Fas01].

The preservation of phase equilibrium can be obtained upon increasing the mobility of the chains along the polymer nanodomains. To prompt such conditions by enhancing chain mobility, it is necessary to anneal the films. Annealing mechanisms are noted for their crucial role since they enable an increase in order, which is induced by enthalpically driven thermodynamics [Bat90]. Thermal annealing (TA) and solvent vapor annealing (SVA) are demonstrated as the two most commonly applicable mechanisms to facilitate the long range order and the improvement on lateral confinement of regular and uniformly sized nanostructured patterns [Fos02]. Both of these mechanisms are going to be thoroughly explained in the following paragraphs.

Secondly, another challenging issue in BCP thin film patterns includes the knowledge of the manner that the two blocks are aligned onto the substrate, as previously explained. For axial compositions such as cylindrical or lamellae, perpendicular domain orientation is required. The lateral confinement of the film is affected by the tendency of each block to preferentially wet the substrate. That comes in contradiction with the thermodynamically driven normal orientation as it is evident by experimental and theoretical studies [Van95]. Therefore, several strategies have been utilized in order to accomplish long range order and domain alignment in block copolymer thin film patterns.

One contribution of high importance in this field is given by Morkved et al. under T. P. Russell guidance who introduced the cylindrical alignment in asymmetric diblock copolymer of the PS-*b*-PMMA type BCP by applying external electrical voltage [Mor96]. The minority PMMA component which according to the BCP compositions gives PMMA cylinders is oriented parallel or perpendicularly along the electrical field lines over a critical amount of 30 kV/cm. Thermal treatment of the film at 250 ^oC is preceded prior to this process. Depending on the applied electric field orientation, the cylinders are aligned either in

plane (C||) or normal (C^{\perp}) ideally suited to the spatial control of highly regular structures (Figure 2.18).



Figure 2.18: *TEM images of electric field induced alignment of cylinder-phase, diblock copolymer PS-b-PMMA films. Minority component of PMMA cylinders (bright stripes) surrounded by PS majority component (dark regimes) and cylinders domain periodicity ranged to 60 nm. Scale Bar 500 nm. (A) Gradual transition from highly aligned cylinders left side, (E - 37 kV/cm) near the central electrode gap to random cylinder orientations to right side (20 kV/cm) upon electrical field intensity decrease. (B and C) TEM images of regions located close to the corner of one electrode induced by the force of applied Electron field (B) and without (C) field [Mor96].*

The third limitation towards formation of the desired BCP thin films relies on the confinement and film thickness effects. Upon the uniform film deposition over a substrate area, even for the simplest case of equally volume fraction segments of a diblock copolymer films are subject to appreciable degree of confinement. In general, highly symmetric composition of lamellae morphology is described by stripes that oriented parallel under the influence of surface field [Mat99].

The thermodynamically driven tendency of a BCP system to self-assemble into morphologies prevails in entropic penalty which is induced by the stretching or compression of the polymer chains as a result of confinement between polymer-air and substrate-polymer interphases. Moreover, the orientation of morphological features (stripes) may alter their direction from parallel to perpendicular orientation when the intrinsic domain periodicity of lamellae is proportionless to the deposited film thickness. In more details, to adjust the domain periodicity and symmetry of BCPs towards substrate supported conditions, two basic options of confinement can be defined: "hard" and "soft" confinement [Alb10].

By considering soft confinement conditions, a lamellae or cylindrical structure of A*b*-B diblock copolymer is formed through fitting the domain array into the confined space. According to the surface interactions and in order to relieve the effect of synergy among the chains stretching/compression, asymmetry may provide either normally axial formation like lamellae or cylinder, or formations such as islands or holes of not well-organized structures. A key parameter that indicates the induced morphology upon deposition is the degree of confinement either named as the deviation of the ratio t/L_0 (where t is the film thickness and L_0 is the domain periodicity) as governed by the symmetry conditions.

The majority of theoretical studies concerning the physics of thin film equilibrium phases emphasize mostly in the case of symmetrical boundary conditions [Smi01, Fas01, Pic97]. Considering these thin film surface boundary conditions, the most preferential to the surface interacted block is creating an initial layer over the substrate. Possible configurations of the lamellae structure can be formed once the BCP thin film is subject to preferential surface interactions. Furthermore, a major conclusion which is evident in thin films is that for film thickness greater than the domain periodicity, lamellae axes are aligned parallel to the substrate.



Figure 2.19: Potential conformations of lamellae phase equilibrium for the case of symmetric BCP films confined at one surface: (a) parallel lamellae with symmetric wetting, (b) asymmetric wetting and (c) perpendicular lamellae (neutral surface) [Seg02].

To the question which of the constituent blocks wets the respective surface, symmetric or anti-symmetric conditions of wetting distinguish two different situations (Figure 2.19). In the case where one of the two blocks wets simultaneously substrate and free surfaces (symmetric wetting), equilibrium conditions are given when: $t=nL_0$, with n receiving always integer values (n = 1, 2, 3...). On the other hand, anti-symmetric wetting conditions are described as one block wets the substrate surface and the other block wets the free surface independently, equilibrium conditions are then given when: $t=(n+1/2)L_0$. According to symmetric wetting, the achieved structure derives from entropic penalty which is imposed on the chains when surface–parallel lamellae are constrained by film thickness, which will be multiplied by integer values of L_0 . If the entropic penalty exceeds the enthalpic gain from preferential wetting, lamellae structure will be evident. When the film thickness is not proportionate with the stripes domain periodicity (L_0), islands or holes are nucleated on the substrate film and in order to adopt the preferred values the film thickness needs to be adjusted [Seg02].

2.5.2 Solvent Vapor Annealing

Annealing of the film is performed by two predominant ways. One of these effective mechanisms in order to adopt highly organized structures which may be considered equilibrium topologies, is thermal annealing (TA). Upon thermal treatment exceeding the highest glass transition temperature (T_g) of the BCP, TA can be successfully applied in order to create sufficient degree of chain mobility. One major drawback for the TA method is the fact that the equilibrium state of the BCP system is not easily reached especially when the BCP total molar mass is not high. Additionally, the lack of time-effectiveness renders its utilization especially when short time procedures are required.

To face this weakness of TA for short time procedure, it is preferred to use the solvent vapor annealing (SVA) process. In this case, the solvent transmits mobility to the system by exposing the as prepared BCP thin films to one or more solvent vapors, without any thermal treatment above the highest T_g of the BCP blocks. Moreover, exploiting the plasticizing effect (incorporation of solvent molecules in the BCP texure improves the self-assembly), relaxation of the nanostructure into lower energy is evident while both of domains size increase and defect free orientation can be successfully achieved [Elb02]. Regarding the thin film formation the solvent vapors favor the reduction of interactions between the nanodomains reducing their surface energies even at room temperature.

The widespread use and proven capability of SVA treatment began to show vigorous signs by many efforts that have been applied in fabricating highly organized assemblies on BCP thin films since the late 1990s. One of the first studies introduced the significance of SVA impact towards BCP thin films long-range order was made by Kim and Liberia [Kim98]. The authors described the morphological development employed by a PS-*b*-PB-*b*-PS triblock copolymer system (with PS 30% w/w) as a function of solvent evaporation rate from thin films casted onto NaCl substrates. By comparing the solvent evaporation rate and the diffusion of the segments, three different morphological options were observed. In the most rapid evaporation rate (~200nL/s), a disordered nanostructure was adopted due to kinetically ''trapped'' macromolecular chains. Intermediate evaporation (~5nL/s) guided the thin film into hexagonally packed and normally oriented PS cylinders on top of the NaCl substrate. Finally, at even lower solvent evaporation rate (~1.5nL/s) in plane PS cylinders on top of the film were reported.

Looking as well on the evaporation rate, the same morphology dependence in a PS-*b*-PEO cylindrical sample (PEO minority segment) was reported by Lin et al. from the Russell group [Lin02]. In both articles ([Kim98], [Lin02]) the BCP thin films have been prepared by using specific conditions such as: a) toluene was the spin-casting solvent, b) toluene was a preferential solvent for the PS blocks in both cases and c) high immiscibility between the two chemically different blocks was necessary.

Due to the considerable potential of the SVA technique, apart from the solvent evaporation rate, special consideration is also given in other technical parameters. For example, in accordance to the film preparation method, film thickness is proven to be of substantial importance on the adopted morphologies. In 2004, Knoll et al. showed that thin film morphologies depend on local film thickness and polymer concentration by studying a PS-*b*-PB-*b*-PS triblock copolymer system of the composition as Kim and Liberia did in the late 1990s [Kno04]. A phase diagram is derived from their specific system by plotting the observed phases in accordance to the film thickness and polymer concentration solution.

Russell and coworkers explained the non-uniform solvent evaporation phenomenon and how the gradient of solvent concentration progress normally to the film thickness [Kim04] which is analytically described in Figure 2.20. As the solvent diffuses directly from the top of the deposited film, solvent evaporation is interpreted as highly directional. When solvent vapors gradually remove from the free surface, the noticed ordering propagates normally from the interphase through the internal thickness of the film. As a consequence, the solvent flow has the ability to direct the alignment of the domains (PB cylinders in a PS-*b*-PB BCP system) in a direction perpendicular to the solvent flow.



Figure 2.20: Schematic view of the solvent vapors removal in a thin BCP thin film. In the illustration the concept of ordering while solvent evaporates is given as well as the manner this order propagates through the internal film width [Kim04].

When a BCP thin film is subject to SVA, in order to achieve well-organized structure in the film exhibiting high degree of orientation, two basic considerations should be taken into account. In addition to thermodynamic considerations which govern the bulk state behavior, kinetic considerations associated with the transition from a swollen state to the dried film should also be included. The whole SVA procedure can be divided in two steps. During the first step, the potential selectivitity of solvent vapors for each block provokes the swelling of one or both domains leading to equilibrium or non-equilibrium structures accordingly. At the second step, the removal of the solvent from the atmosphere (e.g autoclave chamber) causes hasty and non-equilibrium conditions (deswelling). As a result, key parameters for each of the steps should be emphasized: understanding of domain swelling and control of the dried morphology. These parameters are considered as the most decisive points on the final thin film resulting morphologies.

The quality of the solvent is sovereign factor in order to absolutely control the formation of the BCP thin film nanostructure during the SVA method. Harant and coworkers investigated the influence of phase transition with several domain orientations by applying different solvents as well as combination of these solvents with different ratios [Har05]. Cylindrical PI microdomains of a PS-*b*-PI diblock copolymer which were normally aligned to the substrate under methyl ethyl ketone (MEK) vapors were reported. By altering the solvent from MEK to toluene, a fingerprint texture is depicted. Also, by changing for the same diblock copolymer system the spin-coating solvent without further annealing, MEK induced led to a hexagonal structure while the toluene spin-coated thin film led to a disorder state.

In a more specialized SVA strategy, the addition of a small amount of homopolymer to improve the orientation perpendicular to the surface along large domain thin film area was adopted by Kim et al. [Kim04]. The deposited film was comprised from a cylindrical structure in a PS-*b*-PEO diblock copolymer with PEO homopolymer enhancing the already preexisting tendency for propagation of cylinders alignment through the film thickness, following the same mechanism shown for the pure BCP swelling conditions. In the last stage of the procedure, the selective removal of the homopolymer is necessary in order to produce nanoporous templates with long-range order.

2.5.3 Basic Considerations for SVA Process Optimization

During the thin film formation the removal of the solvent depends upon functions that highly influence the final state of the dried film. There is a sequence of very important factors which contribute to the efficacy of the annealing method. Therefore, at any seemingly minor perturbations, decisive changes up to irreversible conditions may occur towards the overall process.

Beginning to reveal these factors, the nature of the blocks on the BCP system determines the temperature induced texture of the film after solvent exposure treatment. By comparing observations related with morphology features through thickness either surface microscopy measurements, bulk and thin film structures can be displayed respectively. Studying a typical A-*b*-B diblock copolymer in a thin film state, upon thermodynamic considerations, chain mobility or immobility of a particular block is dictated by its corresponding glass transition temperature (T_g). For BCPs which contain at least one crystalline and one glassy segment at ambient conditions, the microphase separated morphology results from the interplay of incompatibility between blocks and the BCP

system consists of two amorphous blocks, the dynamics driven by solvent exposure are related with the chain rearrangements, from the disorder swollen state, passing through several swollen metastable states to finally ordered state of clear symmetry upon drying of the thin film.

Except from the chemical nature, the total molecular weight should also be considered in BCP type selection in order to be involved in direct self-assembly studies. With similar behavior as in the bulk state, high molecular weight systems require longer time to come in phase equilibrium when compared to lower molecular weight. Thermodynamic explanations illustrate that the larger the length of the macromolecular chains of each block, the more enhanced with the chain diffusion be, accompanied with a greater interfacial area per junction point with respect to the two chemically dissimilar blocks. Going from low to higher total molar mass systems, the induced energy cost is translated as longer duration in the solvent exposure process. During this additional time, the swollen state of the solvent exposed may affect the final morphology or in the best case, extend the time required to achieve the respective phase equilibrium (Figure 2.21).



Figure 2.21: Schematic illustration depicting five fundamental considerations in BCP thin films during SVA procedure: **a**) block copolymer selection, **b**) substrate treatment, **c**) film texture which appears a microphase separated but disorganized formation, **S**) under solvent vapor exposure a homogeneous solvent film shown d) and ultimate deswelling by solvent evaporation results in normally oriented cylinders along the film as a typically produced perpendicular cylinder structure [Sin13].

To this very common comparison between bulk and thin film copolymer specimens, composition of the BCP system is the most important from all these parameters that determines the existence of symmetry to the ultimate morphologies for both cases. By controlling the ratio of volume fractions for each block within the polymer film, one is able to predict and experimentally confirms the final structure. Furthermore, in any attempt to compare BCP systems even for very small compositions, it is important to ensure that the segregation strength remains stable. Besides the molar mass, changes in segregation strength may be due to the Flory-Huggins interaction parameter (χ). As a result, any potential change

in BCP composition presupposes the manipulation of highly controlled polymerization procedures at fixed degree of segregation strength.

Beyond the BCP composition and the chemical nature of the corresponding blocks in a BCP thin film, solvent and surface effects can constrain the bulk morphology away from the surface itself [Kim98]. The choice of the solvent content for the deposition of a block along the surface film is of a major concern. The tendency of each block to lay in parallel orientation to the film surface is also a matter of interfacial energies, due to competition between them and the solvent. Upon swelling, the interaction parameter χ for each pair of adjacent blocks drives the specimen, especially in the case of axial compositions (lamellae, cylinders) in order to adopt a specific orientation [Jun07]. This tendency originates from the free surface film and is developed toward the inner thin film area.

Nonetheless, solvent quality affects the induced orientation by the solvent vapor pressure perspective significantly. The effective parameter between blocks dissolved in a solvent is constrained by limitations since there will likely be a solvent vapor pressure dependence indicating which particular block will lie down the surface. This specification for specimens of lower film thickness renders their morphological characterization further. Small angle X-ray scattering methods and thicker film samples sectioned by random locations from the bulk film through microtoming are aids to overcome such setbacks.

Prior to the SVA procedure several deposition methods have been used with spin coating being the most widely known. Spin coating high popularity in polymer coating applications comes from practical simplicity even for high impact BCP thin films, intended for nanopatterned fabrication where anti-fouling surfaces is a prerequisite (controlled environmental conditions, acceleration). A spin coating instrument imposes a rotational movement on the surface to be coated. At the same time, drops of sample solution are deposited onto the rotated stage, converting the solution on a thin film. During the spinning procedure in order to predict the film thickness with accuracy, it is essential to control two variables: solution concentration and rotation speed. Under appropriate conditions, thickness is produced. Practically at fixed polymer concentration, high speeds lead to depositions of lower thickness, as well as the control of roughness is favored, since it is often crucial in surface analysis by AFM and SEM [Dim12].

Under appropriate conditions, the film thickness can also be controlled through the volatility of the casting solvent which also influences the surface roughness. Using volatile solvents (high boiling point) the perspective of controlled spinning process is limited since the solvent content is rapidly driven off. The less volatile the solvent, kinetic constrains may induce trapped morphologies.

Nonetheless, the BCP structure also remains of primary importance for the solvent choice including any functional groups of constituent blocks. The solubility parameter of solvent during the casting procedure should be significantly considered. There various organic solvents with a solubility parameter almost similar to the respective value of block in a specific BCP system. By varying these solvent media, homogeneous solution ensures the equal deposition on top of the surface substrate. Otherwise, if an organic solvent is used with a solubility parameter which does not approach the value for one of the blocks, micellar structures may arise. Practically, BCP thin films are well known to self-assemble into spherical reverse micelles, if a non-solvent for one of the blocks is used. Consequently owing to this superior size uniformity as well as sufficient kinetic stability upon coating process, monolayers or multilayers of such individual micellar blocks can be produced [Boo02] (Figure 2.22).



Figure 2.22: AFM height image of micellar thin film (~22nm thickness) from polystyrene-bpoly(acrylic acid) or (PS-b-PAA) (Mn=16.400 g/mol & Mn=4.500 g/mol respectively). The A-b-B diblock thin film was spin coated from toluene solution on top of silicon nitride substrates. The given structure is being described as lateral hexagonal arrays of PAA micelle cores into PS matrix ([OO02].

Beyond the lab-scale, polymer and in particular BCP deposition over larger depositing areas can be made through other techniques in order to fabricate uniform thin films. Dip-coating [Bok01] and spray-coating [Ho13] contribute in this field with really encouraging results. For dip-coating, induced plate is rinsed into polymer solution while subsequent drying drives to the solidification of a coating. The film thickness is set by several parameters, including viscous force surface tension, gravity and lifting speed. Consequently, the faster the plate is withdrawn, the thicker would be the deposited film. The lifting of the substrate can be achieved either manually or automatically. For obvious reasons, to control all these variables, controlled thin film coating requires specialized instrumentation.

Indeed, in the recent years the spin-coating method seems to predominate in comparison with the other two (dip-coating and spray-coating respectively). This preference

is explained by the fact that thickness and uniformity are sensitive to speed as well as the spin-off deposition does not include any respective rheology study as in the case of the dipcoating method.

Chapter 3: Instrumentation-Synthesis-Functionalization

3.1 Characterization Techniques

3.1.1 Atomic Force Microscopy (AFM)

In the early 1980s, the discovery of scanning force microscopy (SFM) has rapidly emerged as a powerful technique equipped to investigate surface morphological features with resolution as low as the nanometer scale. Atomic force microscopy (AFM) is the most widespread instrument among these advanced microscopes. Its success is based on two specific advantages in comparison with electron microscopes such as SEM and TEM. The first involves the easy sample preparation and the second one its use in different environments such as ultra high vacuum, inert atmosphere or even liquids. Over the last twenty years, AFM emerged as a multifunctional technique suitable for characterization of topography and adhesion of various types of materials [Mag 97].

The basic operation of an AFM is related to repulsive forces between the tip and the sample. The investigated surface is scanned with a probe and at the edge of the surface a miniature cantilever and a sharp tip are mounted. In terms of cantilever bending (contact mode) or damping its oscillation amplitude (tapping mode), the tip-sample interaction data is collected by an optical lever. The overall electric circuit is connected with a laser beam that reflects into the center of a photodiode. The resultant information is converted to two dimension view of the scanned surface through an output signal. Consequently, even the smallest forces between the tip and the sample can be measured. Any forces acting on the tip result in bending (vertical forces) or twisting (lateral forces) of the cantilever and therefore in a different reflection angle. The piezoelectric crystal (crystal which changes dimensions when a potential difference is applied) is kept in a horizontal plane over the tip-surface encounter while the vertical resolution is controlled by a feedback mechanism. Upon AFM measurement vertical resolution can be lowered down to a few tens of nanometers. In contrast, lateral resolution is depending on the tip radius (sharpness).

A variety of AFM modes have been established in accordance with environment of scanning and the source of forces acting on the tip. The applied on the tip force is determined by the texture of the investigated surface and all these modes mainly are classified in two distinct categories: contact (CM) and tapping mode (TM). The operation of an AFM is illustrated in **Figure 3.1**.



Figure 3.1: Schematic representation of the atomic force microscopy operation.

In contact mode (CM-AFM) the tip is placed to oscillate close to its resonance frequency approaching really close with the surface. The piezoelectric element checks the difference of the photodetector output in order to push the cantilever over the sample surface, maintaining a constant repulsive interaction between tip and surface. This output difference as generated from the photodetector attributes to deflection (output signal) which is continuously sharpened by the additional piezoelectric crystal and is compared with the set point value as a feedback signal. A feedback loop continuously controls the feedback signal and if deflection differs from the setpoint value then the feedback amplifier forces a voltage and adjusts the height of the tip over the sample in order to minimize the difference. The desired deflection value is effective, only if the feedback signal is constantly monotonous over the tip-surface distance. Keeping the tip at a height corresponding to a permanent interaction over the scanned area enables the mapping of the topography for every scan point along the scanned surface sample. Therefore in CM-AFM, feedback is responsible for the regulation of impact force on the sample. Except from measuring this force value, the modulation of this magnitude permits the acquisition of images at very low values. When the cantilever and the optical lever are combined they both contribute to the calculation of local height between surface and tip. This facilitates the feedback circuit in keeping constant the deflection of cantilever by adjusting the piezo-voltage to raise or lower the sample relative to the cantilever [But05].

In order to investigate the surface of soft materials and especially elastomers, the CM-AFM is not suggested due to the continuous touch of the tip with the scanned surface, during the measurement. In most cases, these measurement conditions cause irreversible distortions on the surface film due to the presence of various types of forces [Wan03]. That is the reason why *tapping mode* AFM (TM-AFM) has replaced the CM-AFM and is considered

the standard tool for studying polymer and biological sample surfaces. Consequently, it is of major importance to mention that surface deformation by applying short intermittent contacts between tip and surface must be avoided and by such an approach the inelastic distortion is minimized. The variation of the tip-to-surface force is affected through the variation of real-time measurement parameters which are: drive amplitude and the set-point amplitude (A_0 , A_{sp} respectively). The amplitude signal serves as the feedback signal that normally decreases accordingly with the tip-sample distance. TM-AFM facilitates the imaging of surface topologies that are loosely attached on their substrate and such imaging is difficult to conduct by contact mode techniques. One main obstacle that arises during the scanning procedure is the force associated with friction, adhesion or electrostatic forces between the tip and the sample especially when the measurement is made at ambient conditions. Such a limitation is surpassed by the utilization of rather stiff cantilevers (spring constants 40N/m) and more dynamic vibration amplitudes (10-100 nm). These characteristics allow the restoring force to exceed the adhesion force.

To perform TP-AFM instable conditions beyond amplitude setpoint, one might also consider another additional essential parameter which is drive frequency. Amplitude setpoint is very crucial since it determines whether the tip-surface forces are repulsive or attractive. For this method and during scanning, the oscillating tip amplitude is implemented by taking large amplitude values only slightly below the free amplitude of the tip. Alternatively, the oscillating tip starts tapping or lifting toward the surface at frequencies larger than the resonance frequency (40-450 kHz). While the cantilever intermittently contacts the sample surface, established scanning provokes reduction of oscillation and only forces between tip and sample indentation are calculated. The resultant energy loss caused from this interaction determines frequency shifts and by this way phase contrast of different materials provides output information concerning the surface topography.

Simultaneously with height image recording, phase images showing the variations of different point of the scanned area are also taken. The output phase data are interpreted as local variations of multicomponents by analyzing phase curves, generated by plots of previously mentioned phase versus A_{sp}/A_0 .

Up to now, the universal interaction of repulsive forces between tip and sample developed a variety of scanning probe modulations with high-resolution profile. This rapidly growing materials characterization field has to boast similarly modern instrumental facilities like magnetic force microscopy (MFM), tunneling force microscopy (TFM), scanning probe microscopy (SPM), scanning tunneling microscopy (STM) and force modulation microscopy (FMM).

The instrument used for conducting the experiments in the framework of this thesis generated from Bruker Multimode 3D Nanoscope using silicon microfabricated cantilever type TAP-300G, with a tip radius <10 nm and $\sim 20-75$ N m⁻¹.

3.1.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a technique where electron beams are used in order to magnify sample images. This requires operation in vacuum since air scatters electrons. The main advantage of using electrons instead of light is that they provide at least 3 orders of magnitude increased resolution since they are smaller than atoms. The resolution provided by a visible-light microscope is approximately 200 nm, while for an electron microscope can go as low as the scale of 0.1nm or below. Many of the features that control the properties of materials are on a scale well below of 200 nm. Thus, there is a need in nano/materials science and engineering to image details, all the way down to the atomic level, in order to understand and ultimately control the properties of materials. That is a major reason why TEMs are so useful, especially in polymer science. In electron microscopy, the sample is exposed to an electron beam and through the interaction of the electrons with the sample, information for its structure are received. Electron microscopes are available for microscopic polymer analysis since 1930 where Knoll and Ruska first proposed the idea for which Ruska received the Nobel Prize in 1986.

Transmission electron microscope is a powerful instrument for studying the structure of biological and polymeric materials. The potentials of this technique are not limited only to high resolution images, but also to the creation of small dimension domains for studying local changes of the chemical composition or the crystalline structure which can be verified via spectroscopy or scattering techniques respectively. Nevertheless, in order for the electron beam to penetrate the sample as well as to secure restricted inelastic scattering (resulting in better images), the sample is required to be quite thin regardless its type.

In reality, the resolution of a TEM is limited due to the spherical aberration of electron lenses but a new generation of aberration correctors has been able to partially overcome this problem in order to increase resolution. Hardware correction of spherical aberration for the high-resolution transmission electron microscopy (HRTEM) has allowed the production of images with resolution below 0.5 angstrom (50 picometers) and magnification above 50 million times. The general set up of TEM is similar to that of an optical microscope with only major difference being that the lenses are coils. A schematic through thickness image of a TEM instrument is given in **Figure 3.2**.



Figure 3.2: A schematic figure of a typical TEM instrument.

The transmission electron microscope consists of two basic systems, the illumination system and the image projection system. The illumination system comprises from the gun and the condenser lenses and its role is to take the electrons from the source and transfer them to the specimen. The electron gun is normally fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at 100-200 keV, while advanced TEMs can reach up to 1MeV which provides better examination of thicker specimens. The image projection system comprises from the objective lens, the intermediate lens, the diffraction lens, the projection lens, the viewing luminous screen for observation of the sample is performed by the objective lens where the rest of the lenses create the final magnification.

The transmission electron microscope can produce the image of the specimen by either the bright-field imaging method or the dark-field imaging method. In bright-field imaging method, by inserting an objective aperture into the back focal plane (BFP) of the objective lens, only the direct-beam electrons are collected while the scattering electrons are excluded. In this way, the areas of the specimen that does not cause electron scattering appear bright, while those that cause electron scattering appear dark. In dark-field method, by inserting the selected area diffraction (SAD) aperture into the image plane of the objective lens, only the scattering electrons from a specific diffracted beam are collected.

The creation of the image that appears on the viewing screen of a TEM depends on the image contrast. The electron wave can change both its amplitude and its phase as it goes through the specimen and both kinds of change can give rise to image contrast.

There are two principal types of amplitude contrast, mass-thickness contrast and diffraction contrast. Mass-thickness contrast results from variations in mass or thickness of the specimen or a combination of the two because the electrons interact, by incoherent elastic scattering, with more or less material which means more or less mass. Alternatively, diffraction contrast rises from coherent elastic scattering and can only vary locally because the specimen is not a perfect, uniformly thin sheet. Consequently, thicker or less crystallized areas of the specimen scatter electrons more and appear darker.

There are several ways to increase mass-thickness contrast and it is by using smaller objective apertures, by alternating the beam accelerating voltage or by chemically staining the sample with heavy atom compounds such as osmium tetroxide or ruthenium tetroxide. By decreasing the dimensions of the objective aperture, more scattered electrons are excluded. But by decreasing the objective aperture size, the radiation intensity is decreased, thus the intensity of projecting image is decreased. When the beam accelerating voltage is reduced, the beam energy is reduced also resulting in increased scattering and image contrast because electrons remain more time in the structure of the sample. The disadvantage of this case is the possible destruction of the specimen due to the increased remaining time of electrons in its structure leading to increased interactions between electrons and sample molecules.

The third method for increasing image contrast and most commonly used in polymer science is staining with heavy atom compounds. Staining involves the incorporation of electron dense atoms into the polymer structure in order to increase the density and thus enhance image contrast. In block copolymers where one of the blocks is a diene, the most commonly used staining compound is osmium tetroxide (OsO_4) which reacts with the carbon-carbon double bonds enhancing the image contrast by the increased electron scattering of the heavy metal compared to the unstained material. The reaction is very important as it both stains and fixes the polymer. This fixation is a chemical cross linking or bridging which causes hardening and increased density. The high vapor pressure of OsO_4 is beneficial, making vapor staining of sections viable. However, this vapor pressure, along with the toxicity of the compound and the limited exposure time, makes it extremely dangerous to use and appropriate care must be taken by any means. The reaction that takes place is shown in **Figure 3.3**:



Figure 3.3: Reaction of osmium tetroxide (OsO₄) with the double C-C bonds.

The result of this staining is that the polydiene phases appear darker while the phases of the other blocks appear brighter. This method is commonly used in polystyrene-polydiene copolymers as OsO_4 does not react with polystyrene. Similar results also are provided with ruthenium tetroxide (RuO₄) which reacts with polystyrene and it is primarily used for staining copolymers of polystyrene with polyolefines.

The observation of the samples was performed in a JEOL JEM-2100 transmission electron microscope (TEM) operating at 200 kV in bright field mode equipped with a LaB_6 filament. In order to study the morphology of the copolymers prepared in the framework of this thesis, the preparation of thin films that exhibit microphase separation was required.

Casting-Annealing: Initially, for the preparation of the thin films, a 5% w/v solution of each sample in toluene was prepared. The solvent should be non-selective for all blocks of the copolymer. The samples were casted for approximately 7 days in a properly established saturated environment under a beaker in a hood. In this manner, the solvent is evaporated slowly from the solution. Thin films with thickness approximately 1 mm were formed and half parts of them were placed in an oven for thermal annealing (120^oC) for 5 days. **Ultramicrotomy:** Cryo-ultramicrotoming was performed in a Leica EM UC7 Ultramicrotome. Cryogenic conditions (-100^oC) were employed for the reason that the hardness of each sample was improved, since the microtoming was accomplished below the lowest T_g of all blocks: PS, PB and PI_{3,4} (~100^oC, -90^oC and -10^oC respectively).

3.2 Supplementary Analytical Techniques

3.2.1 Size Exclusion Chromatography (SEC)

For the control of molecular characteristics during and completing the anionically synthesized BCP matrices, size exclusion chromatography (SEC) or gel permeation chromatography (GPC) plays a significant role. SEC is demonstrated as a time-effective technique with easy modulation enabling the separation of different size molecules based on their hydrodynamic volume. As a liquid chromatography method, except from the quantitative results, it may also afford qualitative indications (success of the polymer synthesis, success of linking reactions, solvent purity). SEC belongs in the indirect methods of molecular characterization, since calibration with polymer standards of various molecular

weights (e.g. polystyrenes) is required in order to real-time control the elution volume time of novel monodisperse polymers. Depending on their hydrodynamic volume, these novel polymers (standards) will elute at different elution volumes resulting in the calibration curve described as $\log M = f(V_e)$ where M is the molecular weight per sample (M_{peak}) and V_e the elution volume. It can be easily understood that macromolecular separation is directly associated with hydrodynamic volume of the polymer. The main reasons which make this method so widely used are the simplicity, the fast rate of its analytical potential and the ability

to estimate the molecular weight distribution ($I = \frac{\overline{M}_w}{\overline{M}_n}$) of the studied polymer as well as the

number and weight average molecular weights (\overline{M}_n and \overline{M}_w respectively). The basic separation mechanism of the instrument relies on the correlation between size of pores of the cross-linked polymer which acts as the filling material of the columns and dimensions of the polymer macromolecules.

Separation columns are the most important part of the instrument together with the isocratic pump which keeps the mobile phase flow constant (e.g. 1ml/min) and the pressure constant as well. Columns of crosslinked polystyrene with well-known pore size or specially treated silica gel are applied for organic solvents. The liquid mobile phase (e.g. THF) is passed through the column at a fixed flow rate, setting up a pressure across its length and the sample polymer molecules pass into the column as a result of this pressure. The smaller macromolecules are able to penetrate the pores as they pass through the column but the larger ones are too large and remain mainly in the space between the pores. The smaller molecules are only temporarily retained and flow down the column until they encounter other pores to enter. The larger molecules flow more rapidly down the length of the column since they cannot reside inside most of the pores. Finally the two molecular sizes are separated completely.

A size exclusion chromatograph (SEC), equipped with an isocratic pump (SpectraSystem P1000), column oven (LabAlliance) heated at 30^{0} C, three columns in series (PLgel 5 mm Mixed-C, 300×7.5 mm), refractive index (RI, Shodex RI-101) and ultraviolet absorbance (UV, SpectraSystem UV1000) detectors, and tetrahydrofuran (THF) as the eluent, was calibrated with eight PS standards (M_p: 4.300 to 3.000.000 g/mol). In every case, prior to calculating the polydispersity indices (PDI) of the synthesized polymers as well as prior to making estimation on the average molecular weights (\overline{M}_n and \overline{M}_w), a series of standard PS solutions were always tested in order to examine the accuracy of the measurements.

3.2.2 Proton Nuclear magnetic Resonance Spectroscopy (¹H-NMR)

Proton nuclear magnetic resonance spectroscopy, commonly referred to as ¹H-NMR. is one of the most versatile tools for characterizing molecular structure, and its application to polymer solutions has provided qualitative and quantitative information concerning these materials. Although larger amounts of sample are needed than mass spectroscopy, NMR is non-destructive, and with modern instruments much information can be obtained from samples weighting less than a milligram. The nuclei of many elemental isotopes have a characteristic spin (I). Some nuclei have integral spins (e.g. I = 1, 2, 3...), some have fractional spins (e.g. I = 1/2, 3/2, 5/2...), and a few have no spin, I = 0 (e.g. ${}^{12}C$, ${}^{16}O$, ${}^{32}S$...). Isotopes of particular interest are 1 H, 13 C, 19 F and 31 P, all of which have I = 1/2. The nucleus that has been widely used and studied in NMR is that of the hydrogen atom (proton). In order to obtain a good NMR spectrum, except from the external magnetic field, homogeneity of the opposing local magnetic field near the sample is also required, which means that the same power of magnetic field must be applied on the sample. In order to take the NMR spectra of a solid, it is usually necessary to dissolve it in a suitable solvent. This solvent must be deuterated in order to avoid extremely sharp resonances of the solvent. Commonly used solvents are chloroform-d (CDCL₃), acetone-d₆ (CD₃COCD₃) and DMSO-d₆ (CD₃SOCD₃).

Proton nuclear magnetic resonance (¹H-NMR) spectroscopy was used for determining the composition and the potential geometric isomerisms of polydienes blocks independently and was carried out in $CDCl_3$ at 30^oC using a Bruker AVANCE II spectrometer. Data were processed using UXNMR (Bruker) software.

3.2.3 Spectroscopic Ellipsometry (SE)

Spectroscopic Ellipsometry was used to determine the films thickness and values of the refractive index at wavelength of 532 nm (green light). A phase modulated ellipsometer (UVISEL from JOBIN YVON-HORIBA) operating in the spectral region 1.0-6.5 eV with a step of 20 meV and at angle of incidence of 70° was implemented. The measured Psi-Delta spectra were modeled using a three phase model (semi-infinite Si substrate/polymer film/air) of varying thickness of the polymer layer; the optical properties of the transparent polymer film was fitted by a single Lorentz oscillator located at an energy position E_0 (free parameter that converged to values between 6.31 and 6.56 eV for all samples). The combined three phase model and Lorentz oscillator model resulted in a fitting procedure using 5 free parameters (polymer film thickness, dielectric constant at infinite wavelength, and the spectral position, strength and broadening of the Lorentz oscillator). This fitting procedure rendered the values of the thickness and the refractive index of the polymer films.

3.2.4 X-Ray Diffraction (XRD)

By this method, significant structural characteristics of crystallinity of either natural or composite material under non-destructive conditions may be obtained. The determination of crystallinity is primarily useful when the wave length of the X-rays is comparable with the interatomic distances (distance between crystal lattices) of a crystal.

XRD measurements involve the constructive interference of monochromatic radiation and a crystalline sample. Radiation is generated by a cathode ray tube with an intermediate filter in order to concentrate the monochromatic beam at specific wave length, collimated and directly bombs on the specimen. Upon interplaying of the beam with the specimen and when conditions satisfy the Bragg's law as a prerequisite ($n\lambda=2d \sin\theta$), the production of constructive interference occurs. A typical X-ray diffraction pattern provides a uniquely formed print consisting of several crystallographic lattices, as periodically arranged according to standard Miller indices. Concerning nanoparticles, XRD has a good potential for the analysis of several size particles, due to the fact that width and shape of reflections yield information concerning the size of crystallites, dislocations of structure and the intrinsic crystal structure of the powder.

3.2.5 Thermogravimetric Analysis (TGA)

As a method definition, the mass of a substance is monitored in a relation with time or temperature while the specimen is subjected to a heating circle at controlled atmosphere conditions. TGA can quantify loss of water, solvent, plasticizer or weight % of nanofillers. The utilization of this technique towards the nanocomposites prepared in this research work was devoted in determining the organic tethered polymer layer at the periphery of the chemically functionalized particles. Heating circle was ranged from 10 C⁰ to 800 C⁰ with applied heating rate of 5 C⁰ K/min . All measurements were conducted at nitrogen flow. The instrumentation used in order to study the weight loss of this thesis functionalized NPs was from the company Perkin-Elmer, type: Pyris-Diamond with the ability to reach temperatures up to 1500 0 C.

3.2.6 Substrate Treatment

To perform AFM measurements, pure BCP and PNCs are dissolved in toluene. The solutions are applied on top of specially treated silicon (Si) wafer with (100) orientation. Prior to the spin-coated process, Si wafers were cut into appropriate size (1.5 x 2.0 cm) and were kept in a dichloromethane (DCM) ultra-sonication bath for 15 min. After rinsing these pieces of Si wafers with deionized water, they were treated with a "piranha" solution for 35 min at 80° C within an ultra-sonication bath consisting of a mixture of H_2O_2/H_2SO_4 in a 3:1 ratio.

Afterwards, the substrates were rinsed three times with deionized water and were dried under pressurized nitrogen flow.

3.2.7 Annealing Process

For these experiments, the essential adjustment of a glass-formed reactor to an autoclaved chamber of identical capacity (250 ml volume) was used (**Figure 3.4**). Primarily spin-coated films were placed for various periods of time into the chamber and were mounted on a glass flat surface. By adjusting a metallic ring and clamp, around the lid of chamber, autoclave conditions are achieved. Except from the typical constant temperature in all cases (ambient conditions), no further control of the solvent vapor pressure could be performed.



Figure 3.4: Side (a) and top (b) view of the improvised apparatus for the solvent vapor annealing procedure. Within this autoclave chamber, a glass substrate is evident up on which the Si wafers are deposited beneath which the solvent resides which stands on top of solvent deposit in a specific smaller chamber.

3.2.8 Film Thickness Measurements

To estimate the film thickness dependence on the resultant morphologies as obtained from the AFM studies, 1% w/v polymer solutions in toluene were prepared and 5 different thicknesses of thin films were calculated through ellipsometry measurements. The combined three phase model and Lorentz oscillator model resulted in a fitting procedure using 5 free parameters (polymer film thickness, dielectric constant at infinite wavelength, and the spectral position, strength and broadening of the Lorentz oscillator). This fitting procedure rendered the values of the thickness and the refractive index of the polymer thin films leading to the graph given in **Figure 3.5.** From this graph it is evident that at 2500 rpm the thickness is approximately equal to 50 nm whereas at 3750 rpm the thickness of the polymer thin film is even smaller (~40 nm).



Figure 3.5: Film thickness calculations depending on the spin casting rate. It is evident that at 2500 rpm the thickness is approximately equal to 50 nm whereas at 3750 rpm the thickness of the polymer thin film is even smaller (~40 nm).

3.3 Molecular Characterization of BCP hosts and Functionalized Nanoparticles

3.3.1 Overview

Polystyrene/poly(butadiene) and polystyrene/poly(isoprene) block copolymers as diblock or triblock copolymer systems are thermoplastic elastomers (as long as the rubbery block is the midblock one of B in the ABA triblock copolymer sequence). Their ability to self-assemble adopting specific morphologies arises from the microphase separation of the constituent blocks taking into account their immiscibility (Flory-Huggins interaction parameter, χ , well above zero) and the copolymer composition. A special characteristic of such copolymers is focused on their behavior with regard to the change of temperature: at room temperature they behave as cross-linked rubbers whereas at elevated temperature they exhibit processability equal to that of thermoplastics [Hen13]. As an important industrial BCP product, they are mainly formed by the linear combination of a hard phase of polystyrene and a soft rubber segment of either poly(butadiene) or poly(isoprene) demonstrating a number of products where each one possess its own importance in industry: SBS, SEBS, SIS (EB corresponds to poly(ethylene-r-butylene) which is the hydrogenation product of PB). These styrenic-elastomer BCP materials are normally obtained by anionic polymerization synthesis procedures.

In recent years, these neat BCP systems have been used to host different kind of nanofillers and the SBS triblock copolymer is known to be the most popular choice for such applications. Although the addition of nanofillers has contributed in enhancing the pure BCP properties, the induced molecular level by such a combination is disadvantageous mainly due to the poor matrix/filler compatibility. This limitation is more emphatic when the objective is to spatially incorporate nanoparticles within particular BCB domains. Except from few exceptions, the nanofillers incorporation by physical blending does not agree to what has been reported up to date in the literature. To functionalize the surface of nanoparticles with various homopolymers has proven to be a reliable synthetic pathway. However by avoiding any etching or lithographic patterned mask procedure, anionic polymerization remains as a costeffective technique, not only for the BCP preparation but also to increase the nanoadditives surface chemistry and particularly that of various types of nanoparticles.

Moreover the absence of atmospheric air (oxygen, humidity, CO, CO₂) and impurities from the initial monomer, solvent, initiator throughout the anionic polymerization procedure leads to predicted molecular characteristics both for the matrices and for the dispersed nanoparticles. This accuracy in molecular characteristics as achieved by anionic synthesis ensures well-defined BCP hosts with desired molecular weight for the involving blocks and desired volume fraction. The significance of precision in molecular characteristics such as desirable molar mass and low polidispersity index becomes more important in the case of adding an extra block and going from the simple diblock copolymer A-*b*-B sequence to the more complicated one A-*b*-B-*b*-C sequence (**Figure 3.6**). Regarding the polymer chain attached onto the periphery of the nanoparticles, similar anionic procedures are adopted in order to equally control the polymer functionalized NPs.



Figure 3.6: In this schematic, the co- and ter-polymers of successfully synthesized block sequences are illustrated. All synthetic attempts followed the anionic polymerization standards.

The synthetic novelty of the present work is focused on the incorporation of nanoparticles into diblock copolymer and triblock terpolymer materials by converging both of most common rubbery segments such as poly(butadiene) and poly(isoprene) and the thermoplastic polystyrene phase. All purification methods and polymerization procedures were conducted under high vacuum technique standards. All respective synthetic procedures were carried out in Pyrex glass apparatuses constructed via scientific glassblowing. Size exclusion chromatography showed the progress of the polymerization despite the number of reactions steps involved in the polymerization. If the resultant molecular weight coincides with initially calculated, the experiment is continued until the desired material is prepared. As a complementary technique to control the volume fractions of the constituent blocks in BCP systems proton nuclear magnetic resonance (¹H-NMR) spectroscopy is necessary to calculate in accuracy the composition as well as the geometric isomerisms of the polydienes involved in the polymer matrix (either PB or PI or both).

Monomers and solvents required for the BCP matrices polymerization and surface nanoparticles functionalization were purified and distilled by attaching properly constructed glass flasks on the high vacuum line. Details for the protocols used in order to purify and degass all reagents used (monomers, solvents, initiators, linking and termination reagents) are thoroughly presented at the following paragraphs.

3.3.2 Anionic Synthesis of Diblock Copolymers and Triblock Terpolymers Consisting of Chemically Different Polymer Segments

For the needs of this dissertation, diblock copolymers of the PS-b-PB and triblock terpolymers of the PS-*b*-PB-*b*-PI_{3,4} and PB-*b*-PS-*b*-PI_{3,4} sequences were synthesized. According to the initial monomers amount, phase equilibrium morphologies emerged such as: three phase four layer lamellae. The domain periodicity for each block and the morphology of the final structures can be controlled from the blocks volume fractions and the Flory-Huggins interaction parameters (χ) of adjacent pairs of segments (A-*b*-B, B-*b*-C, A-*b*-C). The block composition was calculated by ¹H-NMR, and SEC was used in order to follow the various steps of the synthesis procedures.

3.3.3 Introduction to Anionic Polymerization

Anionic polymerization was used under high vacuum conditions in order to synthesize the diblock copolymers and triblock terpolymers respectively. As a living polymerization procedure, it involves an ionic propagating species. In the field of polymer science, "control-living" anionic polymerization has attracted significant attention as a synthetic approach for preparing materials with well-defined architectures (linear and non-linear) and accurately designed molecular characteristics.

3.3.4 Solvents and Materials

All chemicals used for the synthesis of the final materials were purchased from Sigma-Aldrich and Fluka while procedures involving purification steps and distillations took place on a high-vacuum system (vacuum as low as 10^{-5} - 10^{-6} mm Hg) by following specific protocols and reactions as described in the following paragraphs.

3.3.5 Purification of Solvents

Benzene (C_6H_6)

Benzene as purchased is thiophene free. It is transferred into a round bottom flask containing fresh finely grounded CaH₂with a proper size magnetic stir bar. Then it is attached carefully on the vacuum line, degassed and left overnight in order for the CaH₂ to react with any traces of moisture. Then it is degassed again twice and distilled in a calibrated cylinder containing n-BuLi and styrene in approximately a 7:1 weight ratio. The maintenance of the bright orange color of the produced PS⁽⁻⁾Li⁽⁺⁾ (by the reaction of styrene and n-BuLi) indicates the purity of the solvent. Various quantities of the purified benzene are distilled into polymerization, initiator or other apparatuses when necessary.

Tetrahydrofuran (THF)

Tetrahydrofuran was refluxed for at least 3 hours over a flask containing sodium (Na) small pieces and then it was collected in a round bottom flask containing fresh finely grounded CaH₂. Then, by attaching the flask on the vacuum line, it is degassed and left overnight for reaction with CaH₂ in order to remove any moisture. The next day, THF is degassed again 2-3 times while in the meantime a mixture of sodium and potassium pieces (weight ratio 1:3) is prepared in another flask and connected in the vacuum line through a stopcock nearby to the THF/CaH₂ flask. By using a reducing flame, the two metals are melted in order to create a reactive Na/K alloy. The THF is distilled in this flask and is degassed again. Upon defreezing, a bright blue color appears which is attributed to the existence of free potassium electrons and indicates that the solvent is free from impurities and can be used as long as this blue color is present.

3.3.6 Purification of Monomers

Purification of styrene (St)

Prior to stirring with dibutylmagnesium (Bu₂Mg), styrene was transferred into a round bottom flask containing fresh finely grounded CaH₂, attached on the vacuum line via a short path distillation apparatus (because of its high boiling point, bp: 145 0 C), it is degased once and is left overnight under stirring in order for CaH₂ to react with any traces of moisture.

Then it is degassed again and is distilled in a round bottom flask containing an appropriate amount of Bu_2Mg in heptanes ([monomer]/[Bu_2Mg] = 25/1) which has been introduced through an elastic septum. Styrene is left to react with Bu_2Mg for 3 hours over stirring, degassed one more time and finally distilled in calibrated ampoules which are kept in -20^oC for future use. The Bu_2Mg is preferred as purifying regeant due to its higher solubility in hydrocarbon solvents. It is also important to mention that styrene should not be kept in the Bu_2Mg solution for many hours since it can react as an initiator and can anionically polymerize styrene.

Purification of Isoprene (Is)

Isoprene (Fluka, stabilized with *tert*-butylpyrocatechol) was dried within a flask containing CaH₂ overnight. The mixture was degassed prior to the isoprene being distilled into flasks containing n-butylithium (1.6 M in hexanes, Acros Organics). The solution (Is/n-BuLi) is kept under stirring for 25-30 minutes at 0° C ([monomer]/[n-BuLi] = 4/1). The purification with n-BuLi is performed twice and isoprene is kept in the organometallic compound for a small amount of time since n-BuLi is a really good initiator for the anionic polymerization of isoprene. Degassing prior and after any distillation improved significantly the internal vacuum conditions. Finally, isoprene is distilled and collected in calibrated ampoules, which are kept in -20^oC for future use.

Purification of Butadiene (Bd)

At ambient conditions, this monomer is stored in a gaseous phase and is kept into specifically formed gas cylinder. For this reason, it is condensed into a glass apparatus constructed via scientific glassblowing which involves a calibrated cylinder and a round flask. Both cylinder and flask contain n-butylithium (1.6 M in hexanes, Acros Organics). The monomer amount is firstly stirred for 25-30 minutes at -10° C (ice/salt bath) into the calibrated cylinder. The monomer has been distilled into the calibrated cylinder from the initial gas cylinder by creating a freezing bath of -78° C (liquid nitrogen/isopropanol). The monomer amount is afterwards distilled into the flask and is kept for additional 25-30 minutes under the same conditions. While the butadiene amount is stirred into the round flask, the main polymerization apparatus is appended to the vacuum line. The necessary amount of Bd is finally distilled in the main apparatus containing the solvent or the preformed "living chains" and is subsequently polymerized.

Purification of Methanol (MeOH)

Methanol is widely used as the terminating agent in anionic synthesis and is usually purified by the following method. Methanol amount is stirred in a round bottom flask together with fresh finely grounded CaH_2 for overnight, attached in the vacuum line, degassed and left for reaction of CaH_2 with moisture overnight. The next day, the amount into flask is distilled and deposited in a few quantities (0.5-1.5 ml) into ampoules and then sealed from the vacuum line.

Dilution and Titration of Initiator (sec-Butyllithuim)

This organometallic compound (sec-BuLi) is very reactive, especially with air components such as CO_2 , O_2 and H_2O . These undesirable reagents can lead to deactivation of the initiator, and therefore, uncontrolled polymerization might take place leading to non-model polymers, as well as to increased molecular weights and molecular weight distributions. The initiator *sec*-BuLi, as commercially received, is in high concentration (1.4M in hexane or cyclohexane solution) and a dilute solution is needed in order to be used sufficiently for the required experiments. The dilution of the initiator is accomplished in a suitable apparatus with pre-calibrated ampules.

3.3.7 Synthesis of Triblock Terpolymer BCP Systems

All polymerization steps were accomplished with benzene as a solvent media and only before the initiation of isoprene polymerization, a small amount (~1 ml) of tetrahydrofuran is added in order to change the polarity of the solution and synthesize the PI segments with increased ratio of -3,4 microstructure (~55-60%). A glass apparatus was applied with the central section being the polymerization flask reactor while several ampoules and a "purge section" were attached on the apparatus before the whole procedure begins. It is worth to mention that each glass ampoule and flask of the whole apparatus was attached to the main apparatus through scientific glassblowing in terms of high vacuum technique standards.

After completing the whole polymerization apparatus construction where all necessary ampoules and flasks are attached, it is of major importance to test the apparatus for any eventual pinholes by attaching it to the vacuum line. At this point, flame drying with a hand torch in order to accelerate degassing and remove any moisture traces is very useful. The apparatus is checked for pinholes through a Tesla coil which is operated in specific Volts and Watts. If there is no pinhole the noise of the tesla coil gradually diminishes. After the completion of degassing, a small amount (2-3 ml, depending on the solvent volume) of n-BuLi in hexanes is added with a syringe through the elastic septum which is attached in a side arm of the purge section. The elastic septum is rinsed with the hexanes and detached afterwards by sealing off the specific constriction and the small amount of hexane is distilled from a purified cylinder reservoir, by using liquid nitrogen into the main reactor flask of the purge section through the vacuum line and as soon as the mixture is degassed, it is detached from the vacuum line by sealing off the constriction at the joint through which the apparatus

was connected in the vacuum line. Then, the solution of n-BuLi and benzene defrosts and is transferred 2-3 times in all the inner glass surface of the apparatus by careful subversion. In this manner, n- BuLi reacts with any possible impurities that could exist in the apparatus and were not removed during its purification at ambient conditions. Then, the solution is collected at the purge recovery flask (which is placed into a hot bath of water (~45^oC) in order to rinse the apparatus and condense the solvent through it. This solvent is concentrated in the reactor flask and poured back into the purge recovery flask by carefully tilting the apparatus. Repeating this procedure periodically 10-15 times allows the collection of the remaining n-BuLi, along with its reaction products with impurities on the surface of the glass, back to the recovery flask). Then, the solution is collected in the purge recovery flask and the pure solvent is gently distilled in the reactor flask where the temperature is below ambient conditions (~0^oC) and in the purge section flask the temperature is slightly above ambient temperature (~30-35^oC).

3.3.8 Synthesis of PS-b-PB-b-PI_{3.4}

The synthesis of the PS-*b*-PB-*b*-PI_{3,4} type linear triblock terpolymers was accomplished by sequential anionic polymerization of styrene (4 g, 38,46 mmol), butadiene (1,95 g, 36,10 mmol), and isoprene (4.6 g, 67,65 mmol) in benzene, using *sec*-BuLi as initiator (0,147 mmol). After the polymerization of styrene in benzene (300 mL) at room temperature conditions, appropriate amount of butadiene is distilled in the apparatus in order to successfully prepare the necessary intermediate block B of the PS-*b*-PB-*b*-PI_{3,4} linear terpolymer sequence. Prior to the addition of the third monomer (isoprene) a small quantity of THF (1mL) is inserted in the reactor in order to improve the kinetics of the living ends and gain the favorable 3,4- microstructure (~55-60%) for the PI segments. The reactions for the synthesis of the triblock terpolymers are shown in **Figure 3.7**.



Figure 3.7: Synthesis reactions for the preparation of the linear triblock terpolymer of the required $PS-b-PB_{1,4}$ - $b-PI_{3,4}$ sequence.

3.3.9 Molecular Characterization of the Diblock Copolymer and Triblock Terpolymer Matrices

For all the samples as already mentioned, during their synthesis, SEC is adopted to calculate their molecular characteristics among which the most prominent is the polydispersity index or molecular weight distribution ($I = \frac{\overline{M}_w}{\overline{M}_w}$). SEC with THF as the eluent at 30°C was used extensively in order to verify the narrow molecular weight distributions of the polymers and to receive information concerning the number average molecular weights. The instrument was always calibrated with PS standards. Only the molecular characteristics for the PS block were considered accurate, when styrene was polymerized first (as in the cases of the PS-b-PB and PS-b-PB-b-PI_{3,4} sequences). As already mentioned in a previous chapter SEC is a unique tool in order to follow up the progress of a reaction (polymerization or linking) if it involves more than one steps. In Figures 3.7 and 3.8 the results directly from SEC are given for two samples used as polymer matrices which are: PS₅₀-*b*-PB₅₀ and PS₄₅-*b*-PB₃₄-*b*-PI₇₄ respectively. By observing the SEC chromatographs, it is clearly understood that the molecular weight distributions of either the intermediate living polymer chains or the final co- and terpolymer products are narrow and monomodal leading to well-defined materials. The verification of the intermediate product molecular characteristics was made by membrane osmometry (MO) in aliquots taken from the reactors.



Elution Volume (mL)

Figure 3.8: SEC chromatographs of the initial PS precursor (black line) and the final diblock copolymer of the PS-b-PB type (dashed line). The absence of any side peaks is evident in the chromatograph of the final diblock leading to a well-defined copolymer.



Figure 3.8 SEC chromatographs of the initial PS precursor (black line) the intermediate diblock copolymer of the PS-b-PB type (bold dashed line) and the final triblock terpolymer of the PS-b-PB-b-PI type (simple dashed line). The absence of any side peaks is evident in the chromatograph of the final triblock leading to a well-defined terpolymer.

The molecular characterization via proton nuclear magnetic resonance (¹H-NMR) spectroscopy was necessary in order to verify the composition results. By combining the results from SEC and MO as produced by the average molecular weights of both blocks followed the calculation of the weight fraction that can be derived from ¹H-NMR spectra, as well as to confirm the microstructure of the PB block in the diblocks as well as of both polydienes (PB and PI) in the final triblock terpolymers. In **Table 3.1** all the proton chemical shifts for PS, PB and PI are exhibited. As it is evident, the ratio of each geometric isomerism adopted by the polydienes can be estimated via ¹H-NMR spectroscopy since different protons generate different chemical shifts in a corresponding ¹H-NMR spectrum.
Polymeric	Geometric	Type and	Chemical Shift (ppm)	
chain	Isomerism	Number of Protons		
PS		Aromatic (5)	6.3-7.2	
PB	1,4	Olefinic (2)	5.35	
	1,2	Olefinic (1)	5.60	
		Olefinic (2)	4.95	
PI	1,4	Olefinic (1)	5.12	
	3,4	Olefinic (2)	4.70	
	1,2	Olefinic (1)	5.82	
		Olefinic (2)	5.00	

Table 3.1: Type and number of protons with the corresponding chemical shifts for protons incorporated in the monomeric units of PS, PB and PI blocks.

A ¹H-NMR spectrum, except from the molar ratio of the microstructure, can also provide information for the composition of a copolymer since through specific proton chemical shifts the molar ratio for the segments maybe calculated and therefore eventually the calculation of the number average molecular weight is possible. Such a procedure is possible by calculating the molar ratio (% moles) of each block through the following equation:

$$X_A = \frac{a_A}{\beta}$$

where X_A is the molar ratio (% moles) of A block, α_A is the area of the peaks corresponding to the specific chemical shifts in the ¹H-NMR spectrum for A block and β is the number of protons that cause the particular chemical shift.

Specifically in the case of PB and PI_{3,4} blocks, overlapping effect is inevitable in some proton chemical shifts, especially for those corresponding to the one olefinic proton of 1,2-PB at ~5.60 ppm with the one olefinic proton of 1,2-PI at ~5.82 ppm. Furthermore, the chemical shifts that correspond to the one olefinic proton of 1,4-PI at ~5.12 ppm, the two olefinic protons of 1,2-PI at ~5.00 ppm and the two olefinic protons of 1,2-PB at ~4.95 ppm are as well overlapped leading to rather difficult calculations of the various microstructures content for each segment. However, after careful assignment of the specific chemical shifts to corresponding protons, it was possible not only to calculate the composition of the two polydienes in the terpolymers but also the ratio of their corresponding microstructures (-1,2 and -1,4 for PB and -1,4, -1,2 and -3,4 for the PI). The ¹H-NMR spectra for two of the samples used as polymer matrices (PS₅₀-*b*-PB₅₀ and PS₄₅-*b*-PB₃₄-*b*-PI₇₄) are given in **Figures 3.9** and **3.10** respectively.



Figure 3.9: ¹*H-NMR spectrum of the final diblock copolymer of the* PS₅₀-b-PB₅₀ type. The assignment of the corresponding protons for specific chemical shifts is shown. More specifically the chemical shifts at 7.0-7.5 ppm are attributed to the five (5) aromatic protons of the aromatic ring per monomeric unit of the PS block whereas the chemical shifts in the area from 5.3-5.9 ppm are attributed to specific protons as identified in the spectrum for the two microstructures per monomeric unit of the PB block.



Figure 3.10: ¹*H-NMR spectrum of the final triblock terpolymer of the* PS_{45} -b- PB_{34} -b- PI_{74} type. The assignment of the corresponding protons for specific chemical shifts is shown. More specifically the chemical shifts at 6.5-7.3 ppm are attributed to the five (5) aromatic protons of the aromatic ring per monomeric unit of the PS block whereas the chemical shifts in the area from 4.8-5.9 ppm are attributed to specific protons as identified in the spectrum for the two microstructures per monomeric unit of the PB block and for the three microstructures per monomeric unit for the PI block respectively.

3.4 Functionalization of Nanoparticles

3.4.1 Nanoparticles Characterization

Within the framework of the research activities of this thesis, two sets of noble metals (Ag, Au) and iron oxide (Fe₃O₄, γ -Fe₂O₃) nanoparticles were incorporated into several copolymer and terpolymer matrices. Except from the γ -Fe₂O₃ batch which was prepared at the Polymers Laboratory, Department of Materials Science Engineering, University of Ioannina, the remaining NPs batches were kindly donated by another collaborating Laboratory (Ceramics and Composites Laboratory, Department of Materials Science Engineering, University of Ioannina). Prior to the surface treatment step and after the preparation of pure NPs, several characterization methods were used to conduct measurements in order to validate the crystallinity of the inorganic core and the geometrical features such as: shape and size of the NPs. After completion of the functionalization step, thermogravimetric analysis (TGA) experiments led to significant information such as confirmation of the successful modification of the NPs surface. Molecular characteristics for certain functionalizations as given by SEC were really illustrative for the progress of polymerization was accomplished.

As a first task of NPs characterization, structural analysis for γ -Fe₂O₃, Fe₃O₄ and Ag batches were supported by X-ray diffraction measurements as indicated in **Figure 3.11**. Small amount from all batches was pulverized and inserted in the sample holder at the form of powder (since the equipment used was a powder XRD). X-ray diffraction patterns were recorded at room temperature using a Brucker D8 instrument equipped with copper filament (Ka_{Cu} λ =0,145nm). Measurements were performed by using Bragg-Brendano geometry and copper filament in order to produce the X-ray beam. By the calculated positions of the characteristic intensity peaks, the cubic structure of spinel was confirmed (for the case of iron oxide particles) as indicated from the XRD pattern plotted as angle (20) versus intensity (**Figure 3.11a,b**). According to the database of JCPDS (No. 04-0755) the created oxides correspond to particles of maghemite or magnetite with characteristic reflections corresponding to Miller indices for permitted crystallographic planes: [220], [311], [400], [422], [511], [440] and are evident between 20° and 70°.

Also, the XRD pattern plotted as angle (2 θ) versus intensity is also given (**Figure 3.12 c**) for the synthesized silver nanoparticles. According to the database of JCPDS (No. 04–0783) the formed NPs corresponds to Ag particles since characteristic reflections are evident between 20° and 80° corresponding to Miller indices for permitted crystallographic planes: [111], [200], [220], [311] which distinguish significantly the Ag particles.

Raman spectroscopy was used to identify the successful formation of maghemite nanoparticles. Figure 3.11d shows the μ -Raman spectrum of γ -Fe₂O₃ NPs sample. In the

Raman spectrum three bands at710 cm⁻¹ (A₁), 494 cm⁻¹(E) and 381 cm⁻¹ (T₁) are observed which can be assigned in active modes of γ -Fe₂O₃



Figure 3.11: X-Ray diffraction patterns of nanoparticles synthesized within the framework of this thesis corresponding to: (a) γ -Fe₂O₃, (b) Fe₃O₄ and (d) Ag nanoparticles. In these patterns, except from the measured reflections, an assignment of the characteristic Miller indices are given corresponding to permitted crystallographic planes per particle.(C) Additional Raman spectrum for the batch of γ -Fe₂O₃ also indicates the successful formation of maghemite nanoparticles.

3.4.2 Surface Functionalization of Nanoparticles

Iron oxide nanoparticles of maghemite and magnetite with approximately 10-11 nm in diameter were kindly offered and were synthesized following the Massart coprecipitation method [Mas81]. Exploiting the chlorosilane-chemistry method, these magnetic nanoparticles have been functionalized by attaching onto the particles surface polystyrene chains of low molecular weight ($M_n = 6.5$ Kg/mol). Of particular interest of this type of functionalization is that the homopolymer exhibits functional groups (chlorine atoms) due to the linking reaction with dichlorodimethylsilane [(CH₃)₂SiCl₂] since it has been transformed from PS⁽⁻⁾Li⁽⁺⁾ to PS-SiCl through the reaction with [(CH₃)₂SiCl₂.

Initially by following the same procedure as already described for the synthesis of the PS first block for both diblock copolymers (PS-*b*-PB) and triblock terpolymers (PS-*b*-PB-*b*-PI_{3,4}) the polymerization of styrene took place in benzene using sec-butyllithium as the initiator. More specifically, styrene was polymerized in order to obtain a homopolymer with

desired molecular characteristics. Afterwards, by using large excess (250:1) of (CH₃)₂SiCl₂, the substitution of only one chlorine atom in the linking chlorosilane reagent is performed leading to the formation of PS-Si(CH₃)₂Cl, which will be denoted from here on as PS-SiCl. The excess amount of (CH₃)₂SiCl₂ is removed through the high vacuum line by distilling it into a waste flask and in order for the whole reaction to be successful it is necessary to remove even very small traces of the linking reagent in order to avoid side reactions such as gelation. As a result in the reactor flask (after continuous rinsing with pure solvent at least two or three times and removal) remains only the desired product of the PS-SiCl type. The reaction is schematically illustrated in **Figure 3.12** where the wanted (PS-SiCl₂) are given. The approach used for this type of reactions is very well handled by using high vacuum techniques and anionically synthesized polymers in combination with chlorosilane chemistry and many reports of complex architectures are evident in the literature by research groups dealing with anionic [Fra06, Uhr10].



Figure 3.12: Two step reaction leading to the functionalization of the magnetic NPs surface by the modified with the suitable chlorosilane $[(CH_3)_2SiCl_2]$ PS chains.

For the surface modification of silver and gold nanoparticles, quite different functionalization process was followed. The termination of the PS⁽⁻⁾Li⁽⁺⁾ was accomplished for these two NPs with ethylene sulfide in order to prepare the desired thiol end group, leading to thiol terminated polystyrene which is denoted as PS-SH. The initial synthesis step for preparing PS living chains was similar to the procedure already described above involving anionic polymerization of styrene under high vacuum techniques. Subsequently, the living PS⁽⁻⁾Li⁽⁺⁾ solution was mixed with ethyl sulfide in order to modify the living end into a thiol group. The sulfide was used in a 1.5-fold excess compared to the concentration of the PS living ends. The reactions involved in the preparation of the thiol terminated PS are exhibited in **Figure 3.13**.

$$PS^{(\cdot)}Li^{(+)} + CH_2 \xrightarrow{C_6H_6} PS - CH_2 - CH_2 \xrightarrow{C_6H_6} PS - CH_2 \xrightarrow{C_6H_2} CH_2 \xrightarrow{C_6H_2} PS - CH_2 \xrightarrow{C_6H_2} CH_2 \xrightarrow{C_6H_2} MeOH$$

$$PS - CH_2 \xrightarrow{C_6H_2} CH_2 \xrightarrow{C_6H_2} PS - CH_2 \xrightarrow{C_6H_2} SH$$

Figure 3.13: Reactions adopted in order to modify the PS living ends to thiol terminated ends which are denoted as PS-SH.

The TGA measurements were performed in order to evaluate the quantity of the functionalized polymer grafted on the surface of the NPs in order to quantitavely calculate the number of polymer chains attached to the NPs surface. Through the TGA thermographs, it is possible to calculate the weight loss of the modified and pure NPs and through that weight loss in combination with porosimetry (BET) the area of NPs with polymer chains on their surface can be estimated. For the magnetic nanoparticles (Fe₃O₄ and γ -Fe₂O₃) the surface area was found to be equal to 85 m²/g, whereas for the Ag NPs the relevant surface area was estimated 92 m²/g and for the Au NPs 95 m²/g respectively. By using the following equation the grafting density of chains per nm² can be calculated as long as the Δ weight is estimated from the TGA thermographs which are exhibited in **Figure 3.14**.

$$ho(ext{chains/nm}^2) = rac{\Delta ext{weight}(rac{g_{ ext{polymer}}}{g_{ ext{MN}}}) imes 6.022 \cdot 10^{23}}{M_{ ext{W}_{ ext{polymer}}} imes S_{ ext{BET}}(rac{nm^2}{g_{ ext{MN}}})}$$

From the above equation, ρ corresponds to the grafting density (chains/nm²), $Mw_{polymer}$ is the molecular weight of the homopolymer and S_{BET} is the characteristic surface in m²/g.

Sample (homopolymer/NP)	Molecular weight (g/mol)	Nanoparticle diameter (nm)	Weight Loss or ∆weight (%)	Grafting density (Chains/nm ²)
PS_Fe ₃ O ₄	6.500	11	33,5	0.52
PS_γ - Fe_2O_3	6.500	11	12.7	0.17
PS_Ag	2.300	13	10.9	0.79
PI_Au	1.775	12	19.5	1.12

Table 3.2: Molecular and structural parameters that control the grafting density for each particle batch.

Table 3.2 includes all the necessary values (molecular weight of homopolymer, NPs diameter and Δ weight) for each one of the four different particles used whereas on the final column the grafting density is calculated leading to values ranging from 0.17 chains/nm² (PS_ γ -Fe₂O₃), 0.52 chains/nm² (PS_Fe₃O₄) 0.78 chains/nm² (PS_Ag), to 1.12 chains/nm² (PI_Au).



Figure 3.14: TGA thermographs for the three out of four NPs (only the Au NPs case is not appearing). In all thermographs the pure NPs (P-NPs, black curves) and the polymer functionalized NPs (PF-NPs, red curves) are shown. In all cases the weight loss has been calculated and the Δ weight value is estimated by the following equation: Δ weight = (Weight loss)_{PF-NPs} – (Weight loss)_{P-NPs}.

Furthermore, in order to verify the small dimensions of the functionalized NPs and minor or not any agglomerations, transmission electron microscopy studies were made for all four different batches. The homopolymer/NPs system was dissolved in toluene and a concentration of approximately 1 w/v % was prepared. The solution was sonicated for 30 minutes in order for the NPs to be well dispersed. After the sonication procedure two drops of each solution were deposited into carbon coated 150-square mesh Cu grids for TEM investigation. It is crucial at this point to evaporate the solvent completely in order to avoid problems with the high vacuum involved in the TEM column. The carbon coated Cu grids were used in order not to lose the homopolymer/NPs thin layer formed after the solvent evaporation. The results from the TEM studies are observed in **Figure 3.15** It is clear that the dispersion for all four cases of NPs, even for the magnetic ones, is excellent and furthermore the dimensions are kept almost constant with those calculated for the pure NPs prior to functionalization.



Figure 3.15: TEM images for the homopolymer grafted nanoparticles of different polymer nature and molecular weight as indicated from the **Table 3.2.**

Chapter 4: Morphological Characterization

4.1 Overview

On the frame of present dissertation, a one-step method is followed for the nanoparticles (NPs) incorporation into diblock and triblock copolymer thin films. The convergence of the self-assembly process and the chemical affinity of functionalized nanoparticles towards pure polymer blocks considered to be the major pathway for the successful incorporation of NPs onto the polymer chains as it is evident from this thesis results.

Regarding the chemical nature, four different batches of nanoparticles were incorporated into several combinations of diblock and triblock systems adopting different sequences. Prior to the NPs incorporation, the surface chemistry of nanoparticles was tuned using two different tethering procedures. Noble metal NPs of silver and gold are functionalized with thiol terminated polystyrene and poly(isoprene) chains of low molar mass. Towards iron oxide NPs modification, a chlorosilane chemistry approach was adopted. For this dissertation, independently of the block sequence and the incorporated nanoparticles, the solvent vapor annealing method was used in order to reach on potential equilibrium state for the respective BCP system.

Morphological observations for the as-prepared and solvent annealed pure BCP matrices were also accomplished. It should be noted that incorporation of the NPs into the corresponding BCP host influences the morphology of the neat samples, driving the overall composite system to structural transitions or even complete collapsing of the self-assembly. Important effects that must be considered when preparing these composite materials includes the phase transitions depending on the segregation strength of adjacent blocks and molar mass [LoC07], the swelling of the blocks [Sin13], the size ratio between nanoparticles' diameter and domain periodicity [Boc03]. The presence of nanoparticles into BCP domains requires the consideration of additional parameters relative to their final placement [May12] and grain boundaries stabilization [Ryu12, Lis09].

The displacement of nanoparticles into a block copolymer matrix is also affected by their geometrical characteristics (size and shape) and by the efficacy of the functionalization step prior to their mixture with the BCP system (diblock or triblock). The inclusion of both noble metal and iron oxide nanoparticles in the available BCP matrices, as they were performed for this dissertation and the morphological changes in bulk or in thin films have been basically studied by TEM and AFM techniques respectively.

Taking into account the fabricated ensemble of diblock and triblock copolymer matrices to independently host all kinds of NPs and to perform all possible combinations was proved as a time consuming process. The BCP matrices utilized for the composites preparation were of the following sequences: PB-*b*-PS, PS-*b*-PI, PB-*b*-PI, PS-*b*-PB-*b*-PI and PB-*b*-PS-*b*-PI. These matrices were investigated by TEM in order to study the neat morphology and the domain features for each matrix separately. The basic principle in order to achieve well dispersed nanocomposite mixtures relies on the common organic solvent (toluene) used for the homogenation of both organic and inorganic phase for all mentioned experiments. Otherwise, when nanoparticles and BCP hosts were dispersed in different solvents, the solubility parameters should be close (Toluene-THF). Prior to the NPs deposition step, gentle stirring of the composite solutions for at least 24 hours at ambient conditions ensured the homogeneity of the system with respect to the solvating media.

Obviously, separate protocols for thin and bulk composite films preparation were followed. For the preparation of thin films, drops of 1% wt. of polymer solutions were spin coated at 2.500-4.200 rpm and were deposited onto pretreated SiO_2 substrates (silicon wafer) whereas for bulk films, 50-60 nm sections were taken and deposited in Cu grids through the ultra cryomicrotoming procedure. The initial bulk film was prepared through casting (slow removal of solvent at room temperature) from an initial 4-5 wt% BCP solution in good solvent for all segments.

4.2.1 Morphologies of Pure Diblock Copolymer Matrices

For all BCP samples which were used as scaffolds, it was necessary to study their microphase separation in order to perform a comparison between pure BCP and composite (BCP+NPs) material.

For symmetric lamellae structure and with BCP film thickness in the order of a few times the lamellar thickness, the surface tension of each block is a prominent parameter for both the surface/film and the film/air interfaces. By controlling the effect of surface tension and the volume fraction ratio of the respective blocks, several combinations of diblock and triblock copolymer consisting of polystyrene, poly(butadiene) and poly(isoprene) segments could be analyzed by AFM measurements. Based on the work already reported in the literature for solvent vapor annealing (SVA), the results below are divided in two distinct categories: Study of the as-span films and study of the annealed films by solvent vapor annealing in vapors of toluene or benzene.

The most applied diblock copolymer matrix for embedding specific nanoparticles into its domains selectively was the PB₄₀-*b*-PS₄₀ (where the subscript in each block denotes the respective average molecular weight per number, \overline{M}_n , per block in kg/mol) with total \overline{M}_n equal to 80 kg/mol. In **Figure 4.1**, AFM images (height and phase) are shown for the asprepared thin film. The BCP thin film was generated by spin coating upon solubilization of the respective toluene diluted sample on top of a silicon wafer substrate.



Figure 4.1: Height and phase images from AFM studies of as-span PB_{40} - PS_{40} with total \overline{M}_n equal to 80 kg/mol. The thin film was cast from toluene and the spin coating method was used for the film deposition on silicon wafers. (Scan size: $2x2 \ \mu m$)

The specific BCP surface characterization by AFM studied in contact mode has led to surface distortion even for low applied forces (1 nN). By using the tapping mode when conducting AFM experiments, it has been reported in the literature [Van94] that the morphology may be observed without any non-destructive effects.

In tapping mode AFM (TP-AFM) imaging for a diblock copolymer matrix thin film, which consists of almost identical surface tension PS and PB domains, incompatibility between these chemically different blocks is evident, leading to poor well-defined morphology. Generally, PS and PB are non polar blocks (they are consisting exclusively from C and H) and the silicon wafer substrate behaves almost like a non selective surface. Thus, the lack of substantial tendency for preferential absorption of one of the two blocks to the polar surface of SiO_X of treated silicon wafer permits vertical orientation equally for both blocks. Even for lower total \overline{M}_n equal to 50 kg/mol of a diblock copolymer film with the same segment sequence and similarly almost symmetric composition, the observed topology led to similar images where the observed morphology could not be recognized as the alternating lamellae structure.

No evidence of ordered morphology was observed even for a higher molecular weight PS_{50} -*b*- PB_{50} sample as-span thin film (**Figure 4.2**). In this case, the different sequence with respect to the former sample (PB_{40} -*b*- PS_{40}) did not affect the final topology, although the block sequence involves a different synthesis protocol. The higher in total $\overline{M}_n PS_{50}$ -*b*- PB_{50} sample appears to exhibit features which resemble the lamellae morphology. In this case the specific paradox may be explained by considering the slight variations in film thickness between the different diblock copolymers.



Figure 4.2: Height and phase images from AFM studies of as-span Ps_{50} -PB₅₀ with total \overline{M}_n equals to 100 kg/mol. The thin film was cast from toluene and the spin coating method was used for the film deposition on silicon wafers. (Scan size: $2x2 \ \mu m$)

In addition to the aforementioned samples, another almost symmetric diblock of the PS_{25} -b- PB_{25} type with even lower total \overline{M}_n equal to (50 kg/mol) revealed the same features significantly deviating from the alternating lamellae structure as well. None of the three different samples exhibited equilibrated phases and not very well-ordered lamellae grains were evident at least for sample Ps_{50} - PB_{50} .

Considering lamellar phase equilibrium in a symmetric thin film with film thickness equal to few times the value of the lamellae domain periodicity, the lamellae orientation is governed by several surface parameters. Among all the key parameter is the surface tension of each block. These values control the interfacial energy of each block both at the substrate-film and film-free surface interfaces.

Similar measurements to determine the level that the topology order is being influenced by the solvent has been made for Poly(isoprene) instead of Poly(butadiene). Asspan polystyrene-*b*-poly(isoprene) thin films revealed as well nanoscale discrete features, but none of the adopted morphologies could be validated as a phase equilibrium structure. Considering the case of poly(butadiene) in PS-*b*-PB thin films, already mentioned above, the spin coating process contributes to the formation of non-equilibrium in–frozen structure. The explanation for this result may be attributed on the very different T_gs of the corresponding blocks. At ambient conditions PS blocks are the glassy part (T_g of PS: 100 C⁰), while PI chains correspond to the rubbery part (T_g of PI: -65 C⁰). In this manner taking into account the AFM basic operation principle of a "hard-soft", BCP system is identified by the AFM tip in terms of hardness. Upon imaging such a diblock thin film, the viscous PI segments dissipate more energy when compared to the glassy PS blocks. For this reason in a height AFM image, the PI blocks appear as the darker stripes since they can be strongly identified from the AFM tip when compared to the hard PS segment (lightly colored phase) of higher height [Kop03]. The striped surface structure of the following PS-*b*-PI thin film is consistent with an asymmetric cylinder structure as depicted in **Figure 4.3**.



Figure 4.3: Height (left) and phase (right) images from AFM studies of as-span PS_{25} - PI_{15} total \overline{M}_n equal to 40 kg/mol. The thin film was cast from toluene and the spin coating method was used for the film deposition on silicon wafers. (Scan size: $2x2 \ \mu m$)

By depositing polymer film onto Si or SiO_x substrates, PI blocks seem to exhibit stronger affinity with the coating surface due to their lower surface tension compared with that of the PS segments (γ_{PS} :40mN/m, γ_{PI} :32mN/m, γ_{PB} :45mN/m of 92% 1.4-microstructure) [Bus03]. Nonetheless, AFM imaging exhibits significant sensitivity for such polystyrene-bpolydiene thin films. For example, in a typical A-b-B diblock material thin film, both symmetric and asymmetric topologies are exhibited which are described as islands or holes on their free surface, while the as-span film thickness does not exhibit comparable size with a particular number of deposited layers [Seg02]. Additionally, after the SVA process, one might expect that typical terracing (either islands or holes) would be formed taking into consideration the wide range of produced thickness. Actually, microphase separation of nonequilibrium structures for as-span and phase equilibrium structures for SVA treated films are shown respectively. Similar morphological results have been reported for commercial PS-b-PB-b-PS [Har00] and for several mixtures of PS-b-PI with homopolymer of majority component (PI) in the literature [Myk04]. The explanation is given upon studying the interactions between the native oxide occupying the surface substrate and the carbon-carbon double bond of the polydiene block. The native silicon oxide created by the exposure of the substrate with the atmosphere prior to the BCP deposition chemically attacks the carboncarbon double bond of the polydiene blocks. This spatial pinning prohibits the diffusion which leads to terracing phenomena and permits the surface separation of chemically different blocks.

For this dissertation experiments with variable rounds per minutes (rpm), ranging from 2,000-4,200 rpm, induced spin-coated PS-*b*-PB films revealed significant differences in

the resultant topology due to different film thicknesses. Especially, PS-*b*-PI thin films appeared to exhibit film thickness dependence and morphology distortions due to terracing effects in the final structure formation. Furthermore, in PS-*b*-PB films, the higher surface tension of PB component (γ_{PB} : 45 mN/m) introduces better affinity with the substrate when compared to the PS segments. Consequently for slightly thicker PS-*b*-PI films the PI tends to wet the Si substrate and also creates a wetting layer at the polymer-air interface in order to minimize the total interfacial free energy.

Apart from the as-span thin films, in order to realize the conditions of equilibrated and well microphase separated morphologies, different thermodynamically effected techniques have been reported in order to study BCP thin films with the most widely applicable being the SVA method. For the experiments of this thesis, the SVA process was carried out in an autoclave chamber saturated by solvent vapors (toluene or benzene). Obviously, most stable and distinctly microphase separated morphologies were observed for the same films which were exposed in solvent vapors for different time duration. This behavior can be attributed on the gradual variation between the rapid evaporation of the solvent in ambient conditions (as-span state) to more slow and controlled evaporation of the solvent in the autoclave solvent saturated vapors conditioning. Consequently, not only the thin film preparation but also the SVA parameters influence the finally adopted morphology [Bus03]. Annealing treatment for most of the BCP materials impacts positively the topology since spatial sharpening of the phase boundaries and enhancement of phase contrast is the result from this time-dependent thermodynamically driven ordering method [Van95].

The dependence of the orientation of lamellae domains or axial feature orientations as examined by TP-AFM reveals a specific repeat spacing of the domain structure which is known as domain periodicity (L₀). On exposing as-span films of neat PS-b-PB and PB-b-PS sequences in either toluene or benzene vapors significant changes on the adopted structure and on the long range order have been observed. After exposure of films on solvent (toluene) vapors of the same as-made film for 2 hours, the film surface developed a more defined structure while gradually after 6 hours, well-defined lamellae structure for symmetric BCP films is finally obtained. Similar morphology occurred from thin films exposure on benzene vapors except that in this case the required time was reduced to 4 hours. Considering previously published research work on similar BCP thin films, even symmetric compositions depicted the lamellae morphology as expected. The stripes of the corresponding blocks lie normally with the substrate since the difference on their surface tension does not indicate any particular tendency for any of the two blocks to occupy the substrate surface exclusively. Such occupancy by only one segment onto the substrate area can be accomplished from PS component due to its lower surface tension. For such measurements no preferential absorption for any of the two blocks was observed even when untreated silicon wafers were used.

In addition, the annealing treatment may attribute to the development of surface morphology which is interpreted as higher phase contrast and more longitudinal curvatures [Van94]. On TP-AFM imaging, vibrational motion of a tip along the tested surface is governed by viscoelastic interactions which identify a damping and phase shift of the cantilever vibrations in comparison with vibrations attributed to zero interactions. To record data for given height images, damping remains constant while the tip mounted on the probe eventually scans the surface. At the same time, the AFM instrument collects data of recorded phase shifts by capturing any local change of viscoelastic behavior on the film surface. At room temperature, subdomains of rich component in PS-glassy or PB-rubber texture are discriminated as different domains owing to dissimilar viscoleastic features [Bus03].

As given below **Figure 4.4** (**a,b,c**) a set of two different scan size TP-AFM images upon SVA process completion are shown. Although different preparation protocol and conditions are followed, the corresponding bulk films measurements through TEM imaging is presented as a complementary technique (**Fig.4.4,d**). This deployment of both measurements (AFM and TEM) in thin and bulk film serve as identifiers of domain periodicity for lamellae structure samples. With a careful observation of both samples, alternative stripes of constituent blocks may describe as a meandering lamellar [Pot07].



Figure 4.4: AFM and TEM images for PB_{40} -b- PS_{40} after proper treatment for thin and bulk films separately. Images a and b represent the height and phase of the produced morphology after 6 hour exposure in toluene vapors respectively at scan size: $2x2 \ \mu m$. In image c similarly conditioned film at scan size $4x4 \ \mu m$ is given. Image d depicts the cross section TEM image after 5 days thermal annealing at 115 °C followed by ultramicrotomy treatment. Scale bar: 200 nm.

Lamellae structured BCP thin films from a PS-b-PB type copolymer by AFM has been reported in the early 90's in the literature [Sch92] since by that time AFM was considered a relatively new technique and was employed as a structural complementary method for cross-sectional TEM analysis. Primary in bulk state, the microphase separation of a compositionally symmetric system was considered an easy task. In thin films, the generated morphology encloses additional factors in order to predict the confinement of the polymer domains with respect to the substrate and free surface boundaries. In terms of thermodynamic stability, two distinct orientations have been demonstrated: perpendicular and parallel relative to the substrate.

Apart from the relatively similar surface tensions, PS and PB are rather non-polar and therefore the tendency for preferential absorption of one of the two blocks towards the polar SiO_x as a native oxide substrate promotes a perpendicular orientation as it has been mentioned in the literature [Fas01]. Such a behavior is in agreement with the observed images adopted

by the SVA treated PS-*b*-PB and PB-*b*-PS copolymers respectively. In a more extensive investigation for symmetric PS-*b*-PB thin films, Busch and Papadakis reported the molecular weight dependence of lamellae alignment toward the respective substrate [Pot07]. Whereas for molecular weights larger than 90 kg/mol, they observed in plane lamellar structure with respect to the substrate surface, for lower molecular weights than 50 kg/mol, only one component covers preferentially the sample surface and the resultant formation adopts the parallel orientation. Any convergence effort with this thesis results could not be indicative since different annealing process for the samples was followed.

The long range topography of AFM images is accompanied by the highly organized and axially oriented lamellar texture as given from cross-section TEM analysis, for the two diblock copolymer samples of PS_{40} -*b*- PB_{40} (**Figure 4.4**) and PS_{50} -*b*- PB_{50} (**Figure 4.5**) type respectively. Alternating stripes of PS (grey) and PB (dark) domains exhibit almost equal widths consistent with ¹H-NMR spectra calculated volume fractions for both the samples. It is possible to notice morphological features of lamellae structures with excellent lateral and depth resolution. The observed phase contrast is enhanced since the sections on the TEM grids were stained with OsO₄ vapors in a 4 % wt. aqueous solution for 45 minutes.

The contradiction between AFM and TEM images is also introduced to support domain periodicity (L_0) distances. The digital micrograph software available by Gatan Inc. permits the determination of the stripe width for several areas of the long range ordered structure. By comparing unstained and stained samples for determining L_0 of similar composition upon unstained conditions, imaging does not provide sufficient mass thickness contrast which is evident in stained sections. On the other hand, staining may cause chromatic distortions on structural characteristics such as the lamellar period L_0 . Thus, it is of major importance to corroborate TEM images of stained grids with the relative AFM results [Sch92].



Figure 4.5: AFM and TEM images for PB_{50} -b- PS_{50} after proper treatment for thin and bulk films separately. Images **a** and **b** represent the height and phase of the produced morphology after 6 hour exposure in toluene vapors respectively at scan size: $2x2 \ \mu m$. In image c similarly conditioned film at scan size $4x4 \ \mu m$ is given. Image d depicts the cross section TEM image after 5 days thermal annealing at 115 °C followed by ultramicrotomy treatment. Scale bar: 100nm.

Table 4.1: List of molecular and composition characteristics for the dib	olock copolymers used
as BCP host matrices in the framework of this thesis.	

Sample	\overline{M}_n Block A	\overline{M}_n Block B	<i>₩</i> n ^{total} g/mol	(% v/v) Block A	(% v/v) Block B	L ₀ from TEM
	g/mol	g/mol				nm
PB ₄₀ -b-PS ₄₀	40.000	40.000	80.000	0.54	0.46	40
PS ₅₀ -b-PB ₅₀	50.000	54.000	101.000	0.44	0.56	48
PB ₂₈ - b - PI ₃₂	27.800	32.640	60.450	0.55	0.45	54
PS ₂₅ - b - PB ₂₅	25.000	31.000	56.000	0.40	0.60	30

4.2.2 Morphological Study of Diblock Copolymer Nanocomposites (diBCP/NCPs)

Film Preparation

After measurements of the pure BCP films, several NPs incorporation efforts were attempted. Through the SVA method the effect on the structure of the nanocomposite thin film was proved to be really decisive in understanding the BCP orientation and intrinsic domain features. This knowledge in optimizing conditions and materials was necessary in order to accomondate the NPs into only one specific segment of the two involved in a diblock copolymer by means of chemical affinity. Previous experimental studies on surface interactions between the substrate and the BCP blocks introduced various unwanted phenomena such as terraces, holes and other dewetting defects.

As it was already mentioned above for the neat BCP films, in order to form the diblock nanocomposites a solution based method was also used. Diblock copolymer samples were diluted in 1% w/v polymer concentration in toluene. The functionalized NPs were already well-dispersed and dissolved in the same solvent. After mixing the two solutions, the homogeneity of the nanocomposite (NCP) solution was enhanced by automatic stirring for at least one day. A sonication step (lasting only a few minutes), just prior the spin coating procedure, improved the NPs dispersion. For the majority of the BCP/NP mixtures the NPs load remained constant at 5 and 10 % w/w. In specific occasions different NPs loads (from 1 to 20%) were applied in order to observe the resultant morphological features. A few drops of the NCP solution were placed on the substrate (from a precalibrated pipette) while the substrate is rotated on top of the spin-coater stage with predetermined rate (in rpm). To record the spatial placement of the NPs within the copolymer segments, selected films were investigated in terms of SVA treatment time. The higher the spin rate, the lower was the film thickness. All applied films were span cast in a spin rate ranging from 2.800 to 4.200 rpm.

4.2.3 Morphological Study of Magnetic Nanocomposites (BCP/ Iron NPs)

Magnetic nanocomposites were initially examined by incorporating iron oxide NPs (IONPs) within the diblock matrices. The basic purpose of this study is to display the spatial arrangement of surface modified NPs while at the same time to confirm the self-assembly of the amorphous BCP matrix. It should be mentioned that the maghemite and magnetite NPs have been evenly coiled with PS chains exhibiting low average molecular weight per number (~6.3 kg/mol). The ultimate goal was to verify both the dispersion and the affinity of NPs with one of the blocks in the PS-*b*-polydiene system. All nanocomposite thin films were prepared via one step assembly process and as a following step TP-AFM imaging on the film surface was accomplished. For the same reason, as mentioned for the neat BCP films, TP-AFM mode (also called non-contact) was applied in order to prevent any surface damaging between the AFM tip and the scanned surface.

For each sample investigation, different areas of the film surface were recorded by collecting topographical and phase images data. During all measurements, the AFM instrumentation was placed in room temperature and ambient conditions. As to concern pixel analysis for the recorded micrographs, both height and phase scanning were conducted at 512

lines since the applied scan rate ranged from 0.5 up to 0.8 line/s with the latter exhibit as the most commonly used.

The combination of PS-grafted IONPs ($12 \pm 2 \text{ nm}$) within PB₄₀-*b*-PS₄₀ was initially examined in order to study any possible self-assembled nanostructured morphology. This batch of IONPs was added to the solution in a concentration of 10 wt. % when compared with the BCP matrix concentration. The same film is measured after being conditioned in three different states: as span, SVA for 1.5h, 3h and 6h hours remaining within the autoclaved chamber during the SVA process.



Figure 4.6: AFM height (**a**,**c**) and phase (**b**,**d**) images for as-span PB_{40} -b- PS_{40} _PS- γ -Fe₂O₃ composite thin film. Two different scan size (**4x4 & 2x2 µm**) views depict the NPs arrangement with loading rate 10% wt.

Beginning with as-span film images, yellow spots are clearly observed which are randomly distributed throughout the scanned area corresponding to the PS-grafted IONPs of maghemite. Although the particles appear to incorporate within both yellow (PS domain) and dark phases (PB domain), the lack of distinct microphase separated domains cannot lead to a substantial conclusion whether spatial selectivity of the NPs is performed. Furthermore, the lack of phase separation is obvious leading to the inference that the NPs introduction has clearly distorted the surface segregation since even the few lamellae grains have completely disappeared. Figure 4.6 shows the TM-AFM height and phase images obtained by two different scan sizes 4x4 (top images) and $2x2 \ \mu m$ (down images) in order to describe the asspan formation of the studied thin film.

By analyzing further the **4x4** μ m scan size image, it seems that the γ -Fe₂O₃ NPs were incorporated into the PS domains but without exhibiting uniform distribution. The perpendicularly oriented surface texture is different from either the as-span or the SVA film of the neat BCP where well-ordered lamellae morphology was evident. At the lower scan size image of **2x2** μ m, bright and dark areas are more clearly depicted while the yellow spots may be denoted as two different formations in shape and size. Thus, individual NPs and small NPs aggregates are evident at height and phase images. A significant amount of deposited NPs are located into the PS phase in the form of agglomerates while it is evident that individual NPs are being dispersed in both segments (PS and PB).

By observing the adopted structure in higher magnification, a different conclusion may be supported. In **Figure 4.7** images (**a**,**b**) reveal short length stripes with NPs being spatially distributed. By looking at higher magnification images one might support the formation of PB cylindrical domains in irregular sizes surrounded by the PS rich narrow rings decorated with NPs.

However, after 90 minutes of SVA in toluene vapors treatment, the same film demonstrates significantly different morphological behavior. Most of the IONPs were segregated within the brighter stripes corresponding to the PS domain. Unlike the as-span film results where individual NPs were distributed in the PS segment, in this case again individual NPs emerged indicating the tendency to occupy the PS phase within a row and/or line (**Figure 4.7**). Phase image illustrates more prominently the phase contrast between the two segments whereas the NPs presence defines "guidelines" towards surface scanning by the probe.



Figure 4.7: AFM height and phase (a,b) images after SVA treatment for 90 min of PB_{40} -b- PS_{40} _PS- γ -Fe₂O₃ composite thin film. Phase images (c) correspond to SVA treated film for 6 hours (film thickness ~35nm). Phase image (d) depicts the morphology for 24h SVA treatment in different film thickness (~45nm). The NPs loading is kept constant at 10% wt.

The phase image (**Figure 4.7 c**) depicts the arrangement of NPs after 6 hours SVA treatment in toluene vapors. In this case, the surface shows both tortuous and circular features formed from the PS phase. Nearly all IONPs have been embedded within the brighter stripes but the relatively larger size of the yellow spots clearly displays the tendency for agglomeration leading therefore to irregular grains. Inevitably, these aggregates are unable to fit into the narrow stripes corresponding to PS domains and tend to unsettle the boundaries of the lamellae structure. Compared to the image after 24 hours SVA treatment, a larger amount of such NPs aggregates are shown on the limits of the PS stripes but not for the whole surface. As a result, there is not any proof of long range order. Another remarkable feature is the successful embedding for individual NPs or even for their aggregates led to the swelling of the spatial lamellae thickness [Lau10]. Finally, at areas where even larger aggregated clusters of NPs are localized, the collapse of the structure is evident.

The same tendency of γ -Fe₂O₃ IONPs to phase segregate along the film surface also occurs for the same NPs loading (10% wt.) but in another diblock copolymer (higher in total molecular weight) of the PS₅₀-*b*-PB₅₀ type.



Figure 4.8: *AFM* images indicating the morphology evolution from as-span to 200h SVA treatment of PB_{50} - PS_{50} - PS_{7} - Fe_2O_3 composite. The SVA treatment finally induced morphology is shown through topography (**g**,**h**,**i**) and phase images (**j**,**k**,**l**) for 200 hours respectively. The NPs loading is kept constant at 10% wt. (film thickness ~40 nm)

Here, AFM mesurements proved that for slightly higher molar weight BCP system significantly longer time is required in order to observe perpedincularly oriented microdomains where NPs occupy only one of the two phases selectively. In the first column of **Figure 4.8**, images of $3x3 \mu m$ scan size are observed (**a**, **j phase** and **d**, **g height**), whereas on the other two columns $2x2 \mu m$ scan size are exhibited (**b**, **e**, **f**, **k height** and **i**, **l phase** respectively). In the case of the as-span images, besides the fact that individual NPs and small size NPs aggregates are randomly incorporated, it is visually impossible to verify their distribution due to lack of phase contrast for the two domains. Through SVA treatment for approximately 90 hours, the texture of homogeneous NPs deposition on top of the thin film is evident probably due to the chain relaxation of both blocks. Additionally, an early stage of macrophase separation is shown. Such a thermodynamically driven tendency is validated from topography (height) of two different areas of the film surface (**e**, **f**).

By increasing the SVA duration time from 90 to 200 hours, a well-ordered structure arises for the same thin film. Expect from specific regions of the image (top area, **image g**) the NPs arrangement is still problematic due to the formation of aggregates, whereas in a large area of the same image great affinity of PS-grafted IONPs with the PS domain is evident, leading eventually to the swelling of the PS stripes. Moreover, for even such long SVA duration both domains are consistently oriented in plane with the substrate. It is also important to mention that for most measurements, phase images led to more distinct analysis of the topographical features. A phase image highlights the edges of particular stripes, since it is not affected from large scale height deviations. This is the reason why phase images provide more clear observation of phase contrast when compared to the corresponding height image. To shortly summarize for this first incorporation effort, because of SVA annealing, solvent acts as a plasticizing effect increasing noticeably the chain mobility.

Slightly smaller IONPs of Fe_3O_4 (diameter of approximately 11 nm) were also mixed with the PS_{50} -*b*- PB_{50} diblock matrix. In this set of experiments, better spatial arrangement of NPs was observed attributed to the improved chemical affinity between NPs and PS segments. A highly ordered polymer template is performed directly onto the film without the aid of SVA treatment. A specific benchmark for this case is that the majority of the dispersed NPs are not evident.



Figure 4.9: *AFM images for* PB_{40} -*b*- PS_{40} _*PS_Fe*₃ O_4 *NCP from the as-span sample. Scan size is* 2x2 μm (*a*, *b*) while a slightly lower scan size (Phase 1.4x1.4 μm) is also given for higher analysis imaging. The film is prepared by spin coating in 3.400 rpm (film thickness ~40 nm). The NPs loading is kept constant at 10% wt.

In **Figure 4.9**, the phase image of as-span texture depicts the phase contrast between the two blocks of the PB₄₀-*b*-PS₄₀. The number and the volume fraction of yellow spots do not correspond to the NPs load (10 % wt.) as initially mixed with the BCP solution. By observing more carefully image from **Fig. 4.9 c**, it is clear that a large number of NPs can be seen which are disorderly embedded within the PS phase. Therefore, the bright spots correspond to aggregates with spherical diameter significantly higher than the average diameter of typical NP or to individual NPs. To improve imaging clarity none of the AFM mode parameters was altered. In order to investigate this system further, a new thin film was prepared by spin coating drops of the same solution at higher speed and specifically 4.200 rpm (leading to lower film thickness (~32 nm) since all preparation parameters are kept constant for the film preparation). The AFM images are exhibited in **Figure 4.10**.



Fig 4.10: AFM images for PB_{40} -b- PS_{40} _PS_Fe₃O₄NCP from the as-span sample. Height and phase of different scan size includes $3x3 \ \mu m$ (a,b) and $2x2 \ \mu m$ phase. Corresponding height and phase profile as an inset in image a. The film is prepared by spin coating in 4.200 rpm (film thickness ~32 nm). The NPs loading is kept constant at 10% wt.

Obviously, NPs arrangement emerges on the film surface with most of them being incorporated within the PS domain despite the fact that a small amount of individual NPs occupies the PB domain. The occurred surface segregation of the two domains does not lead again to a well-ordered structure.

Studying the same NCP system, but reducing the NP concentration in half (5% wt.), the AFM imaging for the as-span thin film revealed similar texture but most importantly longer and narrower PS stripes were evident. Many research groups have demonstrated that NPs inclusion retard the kinetics of the microphase separation in BCP films [Des07, Chu10]. Based on this suggestion, the lower the percentage of the NPs will lead to lower kinetic constraints. The topography and the phase images (**Figure 4.11 a, b**) indicate a "hodgepodge" of separated bright stripes and disordered regions including both domains whereas the NPs are slightly hosted into PB domains. It is also believed that in specific regions bright rings are observed which can be considered as PB rolls surrounded by PS shells with IONPs being embedded onto them.

After being exposed in benzene vapors at four different time durations, AFM results are given for the nanocomposite. Initially, cylindrical formations are exhibited as indicated from the AFM imaging of the as-span sample. This phase contrast is no longer evident after SVA treatment for 18 hours (**Figure 4.11 c, d**). In this case the PB rolls were replaced by more elongated PS stripes which are perpendicularly oriented with the substrate surface. A large number of individual and spherical shape NPs are located closer to the stripes and the PB domains do not host any NPs.



Figure 4.11: *AFM* height (left) and phase (right) images for PB_{40} -b- PS_{40} _PS_ Fe_3O_4 NCP for as-span (*a*,*b*) and SVA treatment on benzene vapors for 18 hours (*c*, *d*). Scan size $2x2 \ \mu m$. The film is prepared by spin coating in 3.400 rpm (film thickness ~40 nm). The NPs loading is kept constant at 5% wt.

By performing SVA for 68 hours in benzene vapors, surface segregation is more evident. Bright stripes cannot be marked as longitudinal but they are only noticeably expanded in lateral thickness. At $3x3 \mu m$ scan phase image (Fig. 4.11 a,b,c) the structure of irregular bright coils coexists with individual NPs denoted as demarcated lines. Thus, one might realize that the number of isolated NPs has been significantly reduced. Based on the increase in coil width, it is speculated that most of amount of IONPs is gradually embedded within PS domain.

By increasing the duration of SVA method for additional 48 hours, different morphology is observed (total SVA for 6 days). The phase contrast between chemically different blocks has nearly disappeared and possibly the selective deposition of PS-grafted magnetite NPs leads to the distinct observation of spatial phase contrast (**Figure 4.12 d**). Similar selectivity is also evident mainly from the AFM phase image corresponding to the SVA for 8 days film (**Figure 4.12 f**) since the resultant AFM height image cannot lead to

significant conclusions. In this final stage, except a slightly improved BCP phase segregation eventually resulted, no morphological changes are presented.



Fig 4.12: AFM images for the SVA for 68 hours, 6 and 8 days treated film of PB_{40} -b- PS_{40} _PS_ Fe_3O_4 nanocomposite. Scan size, type of image (height or phase) and conditioning is iindicated in **Figure 4.11.** (film thickness ~40 nm).

4.2.4 Bulk Film Studies for diBCP/IONPs Composites

In addition to the AFM characterization, a study of the diblock nanocomposites was performed with transmission electron microscopy (TEM) as the characterization tool. Thin sections of thick films (1mm thickness) from diblock copolymers of the PS-*b*-PB type were studied. The initial films were prepared from solutions in non-selective solvent (toluene) through simple casting. 2mls of the solution were placed in specific ceramic crucibles and the solvent was left to slowly evaporate for approximately 7 days. This specific solvent was used since it can be considered an almost non-selective solvent for the blocks of the diblock copolymer studied (PS and PB) and also has a slow evaporation rate since it is not a very volatile solvent. The overall concentration of the solution was 4% wt for the mixture of the

diblock copolymer with the respective NPs. The weight fraction of the NPs in the mixture was approximately 5% wt.

With inclusion of different nature NPs, morphological changes in the bulk film have been analyzed by observing the adopted morphologies. As-cast composite films required annealing in order to adequately justify the nanofiller dispersion and the thermodynamically driven phase separation between polymer chains of chemically different segments. TEM imaging revealed the domain preference or not for the NPs as indicated in samples of the PS*b*-PB_IONPs hybrid materials. In controversy to the AFM, TEM has the ability for higher magnification images leading to very good justification of the spatial NPs dispersion since their in-plane orientation is not affected from the film depth.

The unique concept of exploiting surface modification of NPs and how they can be placed within the bulk nanostructured film, PB_{40} -*b*- PS_{40} and PS_{50} -*b*- PB_{50} diblock_IONPs nanocomposites were investigated. In contrast with the AFM results, different images are seen with the TEM concerning the NPs dispersion. The TEM results were taken from both unstained and stained specimens. By staining it should be clarified that vapors of OsO₄ in an aqueous solution were used to selectively stain (through cross-linking) the PB blocks.

To begin with the unstained samples of the PB_{40} -*b*- PS_{40} - Fe_3O_4 composite material, a homogeneous dispersion is achieved along the bulk BCP matrix. The lack of phase contrast cannot determine any potential thermally induced microphase separation of the two domains (**Figure 4.13 a,b**). Despite this weakness to verify a well-ordered structure for the diblock copolymer (as expected), a slight natural contrast is distinct and attributed to the uniform dispersion of NPs without extensive particle agglomerations. Two representative images of this observation representing two different magnifications are shown below (**Figure 4.13 a,b**).

In order to increase the contrast, staining with vapors of OsO_4 in an aqueous solution was used in different time frames (10 minutes, 20 minutes and 30 minutes respectively). Since phase separation is now evident, the regular placement of particles is more clearly detectable (**Figure 4.13 c,d**). More specifically, several grids were slightly exposed for 10 minutes on OsO_4 vapors to enhance phase contrast (**Figure 4.13 c,d**). The images in **Figure 4.13 e,f** correspond to the larger time frame (30 minutes) of staining. After this treatment, dark regions reflect to the PB domains while bright regions to PS respectively.



Figure 4.13: TEM micrographs of unstained (a, b) slightly stained (c, d) and more extensively stained (e, f) PB_{40} -b- PS_{40} $PS_{Fe_3}O_4$ composite specimen of 5% wt. Micrographs of stained sample show PS (bright) and PB (dark) domains oriented vertically to the electron beam. The scale bar of each image is located at the lower left.

The adopted morphology is apparently identified as the alternating lamellae structure. Inspired by the AFM results, it was expected that the PS-functionalized particles will be localized at the PS phase. Unexpectedly, uniform dispersion of particles at both phases PS and PB is observed. Thus, the surface grafting of INOPs prior to incorporation did not impose any selective deposition exclusively within the PS phase in the BCP matrix although significant long-range order is indicated throughout the examined samples. Also, apart from improved domain ordering, in terms of composite texture, the annealing process did not allow any kinetically trapped particles to segregate within the energy favored domains. Particularly, for regions where higher sharpness of stripes is detected, particles appear to have a slight tendency to localize at border lines between the two phases but also within both phases. In a more focused effort to realize this non preferential affinity, additional factors that govern the state of mixing should also be considered. Basically, the BCP phenomenon of macrophase separation may be described as a balance of interfacial area between the chemically different domains and chain-stretching. Regarding the polymer brush formed from the ordered BCP as well as the interactions with the functionalized particles, the self-assembly driven by chain stretching probably is qualitatively more complicated. By means of spatial placement of the NPs, the reorganization and phase separation have as a prerequisite the block chains diffusion. Although polymer chains can be diffused, they cannot pass through solid particles leading to distorted local chain packing. In this specific case of the PB₄₀-*b*-PS₄₀-Fe₃O₄ composite material it is evident that 2R << d/2 (R is the radius of the NPs and d is the thickness of the PS lamellae phase) therefore the particles are very small in dimension. It is known that very small particles behave just like the solvent does and in this limit a facile mixing it is expected.

For particles of such low dimensions, constraints associated with particles accommodation may be affected by lower molecular weight diluent and solvent amount. Likewise, Lan and Bates have reported in the past, that this maybe the cause and the driven force for PS-grafted iron oxide particles (PS-grafted silica) being incorporate almost equivalently within both domains (PS and PB). The authors also suggested that by approaching the limit of 5-10 % of BCP where the ordering phenomenon takes place, the swelling of the grafted chains due to toluene mixing is the governing factor leading to enthalpic interactions with the nanoparticles. Such steric effects may impose the particles dispersion inside both domains. Upon segregation and successive drying, the NPs are to be stabilized among both domains. Any kinetic tendency for relocating the particles from one segment to another is considered as very slow and even impossible in terms of thermodynamic driving force.

For the same composite BCP/IONPs, a quite different protocol approach resulted in different morphological texture, since the lamellae structure remained unprocessed. In this case, copper grids are covered from drop-casted NCP solution of the same concentration (5% wt.). After that, the solvent vapor treatment on toluene vapors was carried out by placing the grids within an autoclave chamber for approximately 40 hours. Before doing any TEM studies, the grids were thermally annealed overnight a 130 C^0 under vacuum. In these images (**Figure 4.14 a,b,c**), the magnetite particles are found unequally distributed again within both phases. Surprisingly, the tendency to favor mostly the PB phase is evident.



Figure 4.14: *TEM* micrographs from PB_{40} -b- PS_{40} - $PS_{-}Fe_{3}O_{4}$ composite specimen of 5% wt. Micrographs of lightly stained in order to reveal the underlying lamellae structure. Magnetite NPs are equivalently located at both PB and PS domain. One might be able to claim that NPs reside more at PB domain.

Similarly, migration of the maghemite NPs within the same A-*b*-B diblock matrix generated another ordered self-assembled pattern (**Figure 4.15**). It is well understood from the TEM results that even for similar solvent casting conditions, the unstained samples images reveal a significantly lower homogeneity on the NPs dispersion (**Figure 4.15 a,b**). Moreover the grafting of a homopolymer ligand on the particle surface has been found effective in avoiding the formation of agglomerations. This observation may be attributed to the higher grafting density of the magnetite over the maghemide NPs. By comparing the two different NPs (γ -Fe₂O₃ vs. Fe₃O₄), more efficient discrepancy arises from the stained samples. The segregation behavior of underlying structure suffers from lack of domain order. Describing the structure alternatively, macrophase separation occurs in the system and in that case the NPs prefer to distribute within both phases of the BCP.



Figure 4.15: *TEM micrographs of unstained* (a,b) *and stained* (c,d) *from* PB_{40} -b- PS_{40} - $PS_{-}\gamma$ - Fe_2O_3 *composite specimen of* 5% *wt.*

4.2.5 Morphological Study of Noble Metal Nanoparticle Nanocomposites (BCP/ Noble Metal NPs)

A comparative study on the self-assembled nanocomposite structure by incorporating noble metal nanoparticles within one of the two previously investigated diblock copolymers is given below. Similarly in order to obtain selective placement and good dispersion, the surface of silver and gold NPs was grafted with PS and PI of low molar weight chains respectively. Details on the preparation method are thoroughly explained in the nanoparticle synthesis and functionalization part.

PS_grafted silver NNPs (13 \pm 3 nm) with the grafted PS exhibiting an average molecular weight per number approximately equal to 2.300 g/mol were incorporated into the PB₄₀-*b*-PS₄₀ in order to control the self-organization of the generated hybrid structure. Prior to the analysis of the SVA nanocomposites in different time sequences the as-span thin film was studied by AFM. Although the phase contrast of the constituent blocks is evident the NPs are non-preferentially located within both domains. In comparison with the aforementioned diblock copolymer magnetic NPs system, more individual NPs are evident since agglomerations are not formed (**Figure 4.16 a, b**).



Figure 4.16: AFM height (left) and phase (right) images for the as-span prepared thin film of the PB_{40} -b- PS_{40} - PS_{Ag} composite containing 5%wt NPs. Different scan size of $3x3 \ \mu m$ (top) and $2x2 \ \mu m$ (down) are shown respectively.

At lower scan size (**Figure 4.16 c,d**) the PS domains appear as bright regions surrounding the dark holes of the PB blocks. In this topology, NPs have the tendency to avoid being placed into strongly segregated PS regions.

By treating the as-span film for 24 hours under SVA conditions, the surface displays enhanced phase contrast, whilst large size NPs and agglomerations are mainly governed by macrophase separation (**Figure 4.17 a,b**). Besides the darks regions, the remaining surface in which the NPs are located appears slightly blurred. Exploiting the phase data imaging, more information is evident for the blurred regions leading to worm–like features in which the NPs are not incorporated.



Figure 4.17: *AFM* height (left) and phase (right) images after SVA treatment of the as-span PB_{40} - PS_{40}

By repositioning the same film for additional 40 hours into the autoclave chamber, identical features were observed with an exception of diminished phase boundaries for adjacent domains. Significant morphological alternation was evident after SVA treatment for 6 days. Unexpectedly, more dense NPs arrangement is observed (**Figure 4.18 a,b**). It can be concluded in this case that the time increase of the SVA treatment has led to the observation of larger NPs quantity on the surface without corresponding to the initially calculated loading (5% wt) in the nanocomposite solution. Although microphase separation cannot be again confirmed for the BCP, the narrow PB dark stripes are not covered with NPs.



Figure 4.18: AFM height (left) and phase (right) images after SVA treatment of the as-span PB_{40} - PS_{40} - PS_Ag composite containing 5% w.t NPs for 6 days. Two different scan size are given 4x4 (*a,b,c,d*) and $2x2 \ \mu m$ (*e,f*).

In order to compare these results with the previously studied magnetic BCP/NPs, it is evident that improved surface morphology is obtained for the corresponding SVA treatment for 6 hours. These results verify the capability of A-*b*-B or A-*b*-B-*b*-A copolymers consisting
of polystyrene and poly(butadiene) segments to induce confinement of functionalized with polymer brushes silver NPs. In the same manner, this confinement is in agreement with past studies that validate the elective incorporation of NPs within specific domains. It is interesting to note that such type of matrices begin to lose this host capacity for loading rates greater than 7% wt for the most cases. Upon higher NPs loading, self-assembly of the BCP domains, no longer exists and as a consequence disordered regions are prominent [Pep08]. In a more extented study, Kramer and coworkers demonstrated that the lamellae structure remains unchangeable only when the NPs loading is below a characteristic weight value [Kim05]. Above this critical value, the spatial NPs concentration varies along the film thickness resulting to various different morphologies depending on film depth.

The utilization of chemical affinity as an important pathway similarly adopted in case of polyisoprene chains anchored onto gold nanoparticles surface as a final aim to localize them preferentially into BCP domains. Here, the role of structure guiding-matrix scaffold plays a polydiene-polydiene system consisting of poly(butadiene) and poly(isoprene) 3,4microstructure components.

Upon TP-AFM imaging, except the observation of topographical differences, one might has also the ability to distinguish between hard and soft segments. Basically, the surface segregation induced phase contrast is visible due to the difference in modulus of the soft and rigid domains. Similar viscoelastic properties of Polyisoprene and Polybutadiene render their mutual separation potentially difficult. By incorporating directly NPs inside PI domain, the phase contrast of constituent polydienes appears to enhance. Due to the weakness on imaging PB-*b*-PI_{3,4} surface film texture by TP-AFM microscopy, consequently lamellae structure is confirmed via TEM characterization (**Figure 4.19**).



Figure 4.19: Cross sectional FE-TEM image of pure PB-PI_{3,4} BCP domain with total molar mass 60.450 g/mol. Lammellae phase equilibium morphology of neat system is supported only from TEM imaging because no meaningfull measurement resulted from AFM imaging. Scale Bar is **100 nm**

Solvent vapor annealing procedure for 68 and 90 hours were applied to control the spatial distribution in lamellar forming BCP. PI_grafted gold NNPs of (14 \pm 2 nm diameter) were found to segregate uniquely inside one domain. As shown at **Figure 4.20**, topography image shows an "islands and holes" formation. Despite this featureless texture, a phase separation hardly appears since no indication of NPs takes place. Structural ordering in BCP/NCP is apparently denoted from phase image data. Scan size of **5x5 µm** witnesses the long-range organization of scanned surface as well as NPs evenly mounted and well dispersed at top of the surface. At lower scan size (Scan size **2x2 µm**) individual spots and elongated agglomerations of gold NPs are indicated. Owing to such a spatial localization of particles, perpendicularly oriented stripes formed leading to the possible conclusion of a periodic scaffold.



Figure 4.20: *AFM* height (left) and phase (right) images of solvent annealed on tolyene vapors after 68 hours of $PB_{28}PI_{33}/PI_Au$ composite loaded with 5%wt. Two different scan size of (top) 4x4 & (down) $2x2 \mu m$ are included.

The additional stay of similarly conditioned film has profound effects of the overall morphology as depicted from imaging for 90 hours SVA annealing. In contrast with the previously investigated film state, an ordered structure disappeared. Instead of this, the SVA

induced film substantially interpreted as a macrophase separated NPs arrangement templated above disorder scaffold. This phase separation motivates the direct placement of NPs atop of the surface. That is the reason where microphase separation of polydienes domain is no longer invisible.



Figure 4.21: AFM images of toluene annealed $PB_{28}PI_{33}/PI_Au$ composite for 90 hours. The BCP isNloaded with 5% wt NPs.Left image (**a**) depicts the phase at **5x5 µm** while the other two images (middle,**b** and right **c**) indicate **2x2 µm**.

Annealing process gradually leads to swelling of PB domain although NPs preferentially distributed into PI phase as distinguished from image **Figure 4.20 d.** Chemical affinity between corresponding domain and anchored chains at NP periphery as well as the thermodynamically driven self-assembly mechanism are combined. Diligent localization of NPs engraves intuitively sharp lines as none so far NCP system attributed before. Since that perpendicularly domains orientation could not be confirmed directly, the texture of NPs deposition on top of the surface film render this hypothesis really possible.

4.3.1 Morphological Study of Triblock Terpolymer Nanocomposites (tri/NCPs)

The previously discussed diblock copolymer/NPs composites are used as an intermediate BCP system prior to the investigation of the NPs nanocomposites with linear A*b*-B-*b*-C triblock terpolymers as a host. This investigation involving diblocks was performed in order to aid in understanding of the NPs distribution within the blocks.

At the main part of this PhD dissertation, triblock terpolymer systems of the following sequences: PS-*b*-PB-*b*-PI and PB-*b*-PS-*b*-PI are utilized as the polymer matrix for the particles incorporation within at least one of the three blocks. Undoubtedly, an A-*b*-B-*b*-C polymer based composite represents an equally important class of PNC materials as a structure directing agent. More complicated phenomena are involved at the resultant structure, since additional parameters related to the volume fraction and the corresponding Flory-Huggins parameters included, as to compare with diblock PNCPs [Hoh14]. For a given A-*b*-B-*b*-C system, in order to keep constant the parameter χ for each pair of adjacent blocks,

morphology prediction can be partially manipulated from variables including the composition (volume fraction of each block) and the total molecular weight of the system. It should be pointed again here that the two polydienes in the two different sequences are of specific geometric isomerisms. More specifically the PB exhibits approximately 92% -1,4 microstructure and 8% -1,2 whereas the PI is enriched in -3,4 microstructure (~60%), ~25% corresponds to -1,4 and ~15% to -1,2 microstructures respectively.

By exploiting the composition of nearly symmetric A-*b*-B-*b*-C hybrid compounds, the transition from two-domain to three-domain polymer morphologies will be studied through the incorporation of similar nanoelements as already reported in the case of the diblock copolymers. As an additional block (compared to the PS-*b*-PB system), $PI_{3,4}$ with ~60% of -3,4 microstructure is used leading to the unique combination of polydiene/polydiene microphase separation in order to form a three-component and well-microphase separated terpolymer material [Avg02]. For these hybrid materials consisting of triblock terpolymers and specific nanofillers a convergence between AFM and TEM studies concludes to significant results concerning the manner of the nanoparticles incorporation within complex ABC terpolymer structures.

More analytically, the difference between symmetric and asymmetric compositions of diblock copolymer is consecutively expanded to A-*b*-B-*b*-C linear terpolymers [Sar15]. Thus, this symmetry affects in the same way the interfacial curvatures, attributing to more complex morphologies than the diblock copolymers arise (spheres, cylinders, gyroid). Within a similar perspective, the resultant morphologies for the A-*b*-B-*b*-C depend on both end blocks with the midblock pair symmetries (A-*b*-B, B-*b*-C). For equally symmetric composition for the three chemically different blocks ($f_A=f_B=f_C$), and almost equal Flory-Huggins interaction parameters ($\chi_{AB}\approx\chi_{AC}\approx\chi_{BC}$) a 3-phase 4-layer alternating lamellae structure is found [Bat99]. In contrast, for different volume fractions and interaction parameters of specific values, much different morphology with curved grain boundaries of adjacent blocks have been already reported in the literature.

Prior to inducing the thermal/solvent annealing step, similarly with di/BCP samples, the preparation of tri/BCP materials for TEM involved a casting solvent procedure. A solvent of slow evaporation (toluene), due to its low volatility, was chosen. The terpolymer together with the relative NPs had a total solution concentration of 5 % w/w. Upon slow evaporation of the solvent amount (takes places in ~7days), a thick (~1 mm) sample is prepared in the specific ceramic crucibles and specimens are easily detached with liquid nitrogen flow. Toluene is an almost non-preferential solvent for the three blocks involved in the A-*b*-B-*b*-C sequence (PS, PB and PI_{3,4}). Taking into account the solubility parameters of the present segments and that of toluene, a slight preferential affinity of toluene for PS exhibits [Sch92]. Initially the morphological results directly from the TEM studies for the initial A-*b*-B-*b*-C terpolymer will be given followed by AFM results of the composite material in order to justify the NPs incorporation in one of the blocks at least. Basic principles for such NPs incorporation will be described and the microphase separation together with the chemical affinity between a specific domain and pre-grafted NPs will be given.

Two different samples of the same block sequence but with different total number average molecular weight were used. These two different samples were of the PS-*b*-PB-*b*-PI PS-*b*-PB-*b*-PI_{3,4} sequence and are denoted from here on as: PS_{45} -*b*-PB₃₄-*b*-PI₇₄ and PS_{25} -*b*-PB₂₃-*b*-PI₁₂ respectively. The index next to each block indicates the number average molecular weight of each block as they were calculated by the various molecular characterization methods (**Table 4.2**). In a pure state, for both samples bulk casting films were prepared following the same protocol and the same morphology was evident (3-phase 4-layer alternating lamellae structure) [Avg02]. The TEM images of both samples are observed in **Figure 4.22**.

To enable microphase separation for a terpolymer of the PS-b-PB-b-PI_{3,4} sequence containing two polydiene blocks, the corresponding geometric isomerisms or microstructures for each polydiene should be considered. This phase separation dependence from the potential combination of polydiene/polydiene is attributed to the value of the Flory-Huggins interaction parameter between PB and PI blocks. This value that dictates whether or not the system will undergo microphase separation (PB-1,4 and PI with high -3,4 microstructure) rather than a mixed polydiene system (-1,4/-1,4, -1,2/-1,4, -1,2/-3,4 for PB/PI blocks) [Avg02, Zap15]. The ratios mentioned above are those which as reported in the literature do not microphase separate and only one case (the one adopted within the framework of this PhD dissertation) leads to extremely good microphase separation. The images shown below were taken by ultra cryomicrotoming at -100°C by sections of thickness varying between 50 and 70 nm. All sections were placed in 600-mesh Cu grids and were stained with vapors of OsO_4 in an aqueous solution for approximately 45 minutes in order to be able to distinguish between the dark phase (PB) and the grey phase (PI) and avoid overstaining where both polydienes would appear dark. PS domains are not stained with OsO_4 and therefore they appear white in the TEM images.



Figure 4.22: *TEM* images for the two linear triblock terpolymers of different total molecular weight indicating the PS-b-PB-b-PI_{3,4} sequence. Image (a) corresponds to PS_{45} -b- PB_{34} -b- PI_{74} and image (b) to PS_{25} -b- PB_{23} -b- PI_{12} respectively. The indices next to the blocks in both samples indicate the number average molecular weight of each block respectively.

Similar morphology for the sequence poly(isoprene)-*b*-poly(styrene)-*b*-poly(ethylene oxide) ABC terpolymer has also been reported in the literature by Stefic, Bates et al. [Ste09]. This group simply named the specific morphology a three domain lamellae.

Table 4.2: Molecular characterization results and TEM domain spacing as well as PS layer thickness for the triblock terpolymers synthesized in the framework of this PhD dissertation of the PS-b-PB-b-PI_{3,4} sequence and were used as the polymer matrix for the formation of the nanocomposite with specific nanofillers (nanoparticles).

Sample	$\mathbf{M}_{\mathbf{n}}$	$\mathbf{M}_{\mathbf{n}}$	$\mathbf{M}_{\mathbf{n}}$	$\mathbf{M}_{\mathbf{n}}$	(%v/v)	(% v/v)	(% v/v)	\mathbf{L}_0	PS layer
	Block A	Block B	Block C	Total	Block A	Block B	Block C	from TEM	from TEM
	g/mol	g/mol	g/mol	g/mol				(nm)	(nm)
<i>PS</i> ₄₅ - <i>b</i> - <i>PB</i> ₃₄ - <i>b</i> - <i>PI</i> ₇₄	45000	34000	73700	152700	0.28	0.33	0.39	104	40
PS_{26} - <i>b</i> - PB_{23} - <i>b</i> - PI_{12}	25800	23400	12000	61200	0.39	0.33	0.28	33	11
PS ₃₅ - <i>b</i> -PB ₂₈ - <i>b</i> -PI ₃₉	35000	28000	39000	102000	0.34	0.28	0.38	43	14
PB ₃₈ - b - PS ₂₄ - b - PI ₃₆	38000	24000	36000	98000	0.28	0.31	0.41	38	12

The location of the NPs and how their incorporation affects the generated terpolymer-NPs structure is discussed below. In order to prepare the thin films, in relation to the PS-*b*-PB diblock host matrices, the NPs concentration has also been proven to be decisive in controlling their placement with the PS-*b*-PB-*b*-PI_{3,4} terpolymer. Initially, PS-grafted IONPs were mixed with both PS-*b*-PB-*b*-PI_{3,4} samples in order to incorporate the NPs within the PS domain. Unfortunately, on following the same characterization route through AFM imaging as for the diblock prepared nanocomposites, detailed analysis of the morphological features was not possible [Kub08]. All samples exhibited the characteristic phase-separation by revealing bright and dark domains. However, distinctive phase separation for the two polydiene blocks was proven impossible by AFM.

For the tri/BCP composite patterned materials several morphological transformations are addressed from electron and force probe microscopy [Wan03]. For such complex PS-b-PB-b-PI_{3.4} matrices, the surface topography and the local phase determination of three chemically different components from the recorded image of the pure PS-b-PB-b-PI₃₄ topology is of primary importance. In Figure 4.23 the surface structure with height and phase AFM images of the two symmetric triblock terpolymers systems of the PS-b-PB-b-PI_{3,4} sequence after 24 hour exposure in benzene vapors are illustrated. Due to the fact that the two polydiene components seem to be even slightly compatible, the surface topology microphase separates on the microscopic scale among pure rubbery and glassy domains. For the lower molar mass PS₂₅-b-PB₂₃-b-PI₁₂ film, a phase separated but not highly organized pattern is observed. The whole formation could easily be identified as a short-length discontinuous lamellar structure. However, discrete areas of the scanned pattern appear in a disorder state. For the terpolymer PS_{45} -*b*- PB_{34} -*b*- PI_{74} which exhibits higher total average molecular weight per number significantly minor tendency for self-organization is noticed. Indeed, for this sample, annealing treatment of 25 hours duration shows that the swelling of PS domain over the polydiene blocks is prominent, since dark circular regions of rubbery domains are surrounded by the PS matrix. The surface morphology in this case can be described as a weakly organized domain without remarkable morphological features, e.g. domain periodicity [Kub08].



Figure 4.23: *TM*-AFM height (*left*) and phase (*right*) images for the neat samples of PS_{25} -b- PB_{23} -b- $PI_{12}(a,b)$ and PS_{45} -b- PB_{34} -b- $PI_{74}(c,d)$ respectively after 24 hours annealing in benzene vapors inside the autoclave chamber (solvent vapor annealing).

Also, an additional major setback arises from the preparation of the thin film concerning the degree of microphase separation. During the bulk casting for constructing a relatively thick film (~ 1mm thick), the different domains probably exhibit sufficient chain flexibility to form equilibrium and well-organized patterns (as it is evident in **Figure 4.23**) TEM images for the neat triblock terpolymers). In the bulk film casting, a long time scale process, which was adopted, favors the slow solvent evaporation and chain mobility is facilitated due to large time duration and more controlled conditions. On the other hand, when thin films are generated by the spin-coating process, time and space are significantly diminished against chain mobility leading to relatively not well-ordered structures. For the composite thin films (terpolymer and naofiller), the aggressive exposure in solvent vapors must not necessarily be interpreted as a disadvantage. Very slow exposure rate drives the system to kinetically trapped morphologies, as well as hides the nanoparticles within the polymer entanglements [Lan07].

4.3.2 Morphological Study of Iron Oxide NPs Nanocomposites (triBCP/IONPs)

As in the case of di/NCPs, the study of tri/NCPs begins with the iron oxide NPs incorporation. Both PS-*b*-PB-*b*-PI_{3,4}/PS-grafted_Fe₃O₄ thin films were prepared by following the same protocol. **Figure 4.24** exhibits images from the as-span film as well as the same film for different time durations of SVA in benzene vapors leading to specific morphologies and significant observations.



Figure 4.24: *TM*-*AFM* phase images gallery of as-span and after specific time duration for SVA treatment of sample PS_{45} -b- PB_{34} -b- $PI_{74}/PS_{grafted} Fe_{3}O_{4}(10\% \text{ wt.})$. The time of treatment in benzene vapors was: (a) as-span, (b) 2h, (c) 4h, (d) & (e) 18h, (f) 60h, (g) 4d, (h) 5d, (i) 8d. Scan size for all phase images is at $2x2 \ \mu m$, except from image (e) which corresponds to higher magnification ($1x1\mu m$).

Although the phase separation of polydienes is not distinct, lamellae phase characteristics vary in the above images probably due to the particle localization within the terpolymer matrix. It should be mentioned that the absence of height images from **Figure 4.24** is due to the fact that they did not reveal clear morphological features [Agi13]. Unlike height images, the corresponding phase data enabled imaging of distinctly separated phases

and simultaneously particle segregation within one or two polymer domain phases or on the interphases distinguishing the different domains, depending on the film conditioning (time duration).

As for di/NCPs AFM imaging, bright portions correspond to the hard PS phase while the dark portions to the polydienes due to the thermodynamically driven phase separation [Gan06]. Starting with the as-span film image (**Figure 4.24 a**) a self-organized formation due to microphase-separation is observed. Although the surface pattern comprises of uniformly separated nanodomains, the IONPs cannot be distinguished from the underlying stripes texture. Almost the same description fits with the next two images (**Figure 4.24 b,c**) as the SVA time increases to 2 and 4 hours respectively. Stripes of PS domain are shown more elongated for 2 h, whereas at 4h, they seem to have acquired larger width and length (better order). Over the stripes morphology until the first 4 hours, no sign of distinct nanoparticles is evident.

The first indication of typically organized and well distributed particles arrangement is observed after 18h in SVA benzene vapors exposure (Figure 4.24 d,e). After 18h (Figure **4.24** e) the good dispersion of the NPs is evident without though any affinity for any domain. The AFM images for 60h (Figure 4.24 f) and 4 days (Figure 4.24 h) SVA treatment indicate an increase in phase intensity between the blocks and the hard texture of the NPs is again evident but distinction of the NPs is hardly visualized. Despite this observation, the NPs are directly located within the PS segment. The last two images corresponding to 5 days (Figure **4.24 h)** and 8 days (Figure 4.24 i) reveal a decent arrangement of individual NPs and small size agglomerations. Interestingly, below this inorganic texture formed from the NPs, one might faintly observe the underlying microphase separated scaffold. Analogous imaging features have been demonstrated in the literature from Garcia, Mondragon et al. by sequestering PS grafted magnetic NPs (4% wt) [Gar08]. In contrast with our results, the A-b-B-b-A triblock copolymer material [A: polystyrene, B: poly(butadiene)] which is used as the BCP host in the aforementioned reference yielded to better organized domain features. On the other hand, the Garcia et al. reported system did not show such a good selectivity when compared to the triblock/NPs nanocomposite system used in this dissertation.

In contrast with the di/BCP hosts, the time effectiveness in the tri/BCP annealing process plays a significant role [Jeh14]. Indeed, the process entirely can be divided in two stages. Initially, the nanoparticles emerge on top of the surface (for the first 4 days) and then the swelling of the domains steams from the chemical affinity of the homopolymer grafted NPs with domain in the terpolymer exhibiting mutual chemical nature (PS). The reason is probably that benzene is an almost non-selective solvent for all three blocks involved in the PS-*b*-PB-*b*-PI_{3,4} sequence. As already mentioned for the toluene, benzene as well exhibits a slight selectivity towards PS. Such a mutual affinity provokes the polymer mobility in the

swollen state due to solubility constrains. As a result this structural rearrangement facilitates the NPs to be distributed within chemically mutual domains [Jan14]. This assumption is even more strongly confirmed by presenting a higher analysis image (**Figure 4.25**) in which the last composite film after SVA for 8 days is exhibited.



Figure 4.25: *TM-AFM* height and phase images of sample PS_{45} -b- PB_{34} -b- $PI_{74}/PS_{grafted}$ Fe₃O₄(10% wt.) corresponding to the 8 days SVA treated composite film.

The majority of the functionalized with PS inorganic particles are distributed along the PS regions either as independent NPs or as slightly agglomerated. The underlying phase separated structure may be interpreted as discontinuous lamellae or not well ordered cylindrical formation. In any case, the resultant formation cannot be recognized as phase equilibrium morphology. Additional SVA time led to ineffective structure improvement.

On the basis of annealing time, typical self-assembled nanostructure of the second PS_{45} -*b*- PB_{34} -*b*- PI_{74} host containing same nature and percentage of filler (10% wt PS_grafted Fe₃O₄) was also investigated. The mixture of the same batch of particles with a different triblock terpolymer of higher total molecular weight yielded to different morphological characteristics, despite the fact that the preparation and treatment of the film protocol remained the same. In the as-prepared composite film, a soft microphase separation can be observed (**Fig. 4.26 a**). Even for this sample, due to toluene being an almost good solvent for all the three segments, a perpendicularly oriented texture is immediately formed after the deposition on the corresponding substrate. Irregular formation of bright continuous lines or circular spots of the PS domain emerged with no distinctive particle illustration on top of the terpolymer surface. In order to enhance the microphase separation and visualize the NPs, the typical procedure of SVA is progressively repeated in the same manner as for the lower molecular weight triblock terpolymer PS_{25} -*b*-PB₂₃-*b*-PI₁₂.



Figure 4.26: *TM-AFM* phase images of thin films for sample PS_{26} -b- PB_{23} -b- $PI_{12}/PS_{grafted} Fe_{3}O_{4}$ (10 % wt.) (a) before exposure in benzene vapors, (b) after 5h, (c) 25h, (d) 50h, (e) 3d, (f) 4d. Scan size: $2x2\mu m$

After 5 hours of SVA in benzene vapors treatment, the swelling of the PS phase is observed (**Figure 4.26 b**). The slight selectivity of the solvent vapors (benzene) towards one of the blocks (PS domain) provokes the swelling of microdomains. As a result, upon changing

the effective volume of the domains in this second triblock terpolymer with higher total molecular weight (and higher molecular weight per block) leads to constantly variable features due to the thermodynamically driven process of annealing. Regardless this morphological change, particles are still not evident on top of the scanned surface.

After a period of 25 hours of similar annealing process, a significant amount of IONPs are evident along the PS domain preferentially (Figure 4.26 c). Here, it is not so noteworthy to control the selectivity, since induced phase separation cannot lead to narrow nanophases and long-range order. By the completion of 50 hours of SVA, one might distinguish the coexistence of a more defined underlying scaffold and satisfactory NPs distribution within the PS domain (Figure 4.26 d). Most of the NPs are not located as individual features but mostly as small elongated aggregates crowded along the PS canals. By extending the annealing process, it is worthy to mention that the most interesting results are obtained after SVA in benzene vapors for 3days (Figure 4.26 e). The surface topology macrophase separates by adopting the structure of dark holes surrounded by PS coils. It was found from AFM images that on top of these coils, The NPs exhibit great affinity being sequestered inside these regions. Interestingly, particles are strongly aggregated but only within the outlines of the PS regions. Similar texture is also revealed by extending for one more day the SVA process (Figure 4.26 f). However, the localization of bright spots corresponding to the PS_grafted NPs was achieved in a better manner when compared to the 3 days SVA treatment.

As can be seen in the last AFM image (**Figure 4.26 f**), obviously bright spots are located on the PS domain. Taking a closer look in the last two phase images (**Figure 4.26 e,f**), it is clear that these spots size is not comparable with the NPs size calculated by the TEM analysis. Indeed, the particle diameter is too small to achieve such big bright spots. It is assumed that NPs aggregation occurs as it was certified for extensive SVA time periods, even for the di/NCP composite films. The second important variable that should be mentioned is the difference in total molecular weight between the two triblock terpolymers. Basically, this difference results to variable domain periodicity (L₀) as depicted from the TEM images of the respective neat specimens (**Table 4.1**). Upon incorporating the same batch and volume fraction of PS_Fe₃O₄ particles which means that dimension and concentration remains constant (10 % wt), the size of the PS lamellae (11 nm) is not big enough to host the particles in the PS₂₅-*b*-PB₂₃-*b*-PI₁₂ sample. On the other hand, by using sample PS₄₅-*b*-PB₃₄-*b*-PI₇₄ for the same purpose, the domain size of PS is much larger (40 nm) enabling therefore more effectively the particle deposition within the PS domain.

For experimental results related with the second sample series and by altering the available combinations of tri/BCP host and IONPs, PS_{45} -*b*- PB_{34} -*b*- PI_{74}/PS_{74} grafted γ -Fe₂O₃ is studied as well. In a similar manner with the previous composite film, the height image of the

as-span image was captured initially (**Figure 4.27 a**). Although the surface is covered by a layer of dark holes, an underlying phase separated formation cannot be easily distinguished. The phase image seems more enlightening in clarifying the poor phase separation of the topmost surface formation (**Figure 4.27 b**).



Figure 4.27: *TM*-AFM height (**a**) and phase (**b**) images of the as-prepared thin film of the PS_{45} -b- PB_{34} -b- $PI_{74}/PS_{grafted} \gamma$ - Fe_2O_3 composite material. Load of particles is 10% wt and for scan size 2x2 μm

In order to motivate the emergence of particles atop of film surface as well as to provoke the domain phase separation, systematic SVA treatment was again employed. SVA time induced structures are also investigated at the same periods of time as for the previous relevant sample with the other triblock terpolymer host. Swelling of the PS domain after five hours of SVA is evident (**Figure 4.28 a**), whereas significantly organized arrangement of narrow PS domains (bright regions) and polydiene dark regions are depicted (**Figure 4.28 b**) after 15 hours of SVA. No remarkable indication of particles can be proven at these SVA conditions. The first sign of individual particles or small agglomerated of them is indicated after 45 hours of similar treatment (**Figure 4.28 c**). The AFM image depicts a preformed discontinuous cylinder-like texture of adjacent blocks oriented perpendicular to the surface. The appearance of larger bright dots (~25nm) may be attributed to the larger in size IONPs or to the formation of sporadically emerged agglomerates due to the lower grafting density of PS_ γ -Fe₂O₃ (0.17 chains/nm²) over the PS_Fe₃O₄ (0.28 chains/nm²) batch. Furthermore, even for these larger clusters, it is distinguishable that they thoroughly avoid their incorporation within the dark regions.

In order to improve the existing structure of the composite film, it was placed again inside the autoclave chamber for more than one day for SVA and yielded to significantly different adopted morphology (**Figure 4.28 d**). Particles are not found any more at individual state or slightly aggregated. Instead the particles arrangement is generated atop of the film

surface. This phase separation is governed not upon the underlying microphase separated structure, but due to macrophase separation of the segregated particles at the surface. Similar tendency was previously mentioned for the PS_{25} -*b*- PB_{23} -*b*- PI_{12} /Fe₃O₄ nanocomposite sample.



Figure 4.28: *TM-AFM*) phase images of the as-prepared thin film of PS_{45} -b- PB_{34} -b- $PI_{74}/PS_grafted \gamma$ - Fe_2O_3 (10 % wt.) composite for (a) 5h, (b) 15h, (c) 40h, (d) 3d, (e,f) 4d SVA treatment. Scan size 2x2 μm except from image d which is $4x4 \mu m$

In the case of SVA treatment for 4 days, the observed morphology has not been radically affected. Beyond the typical scan size $2x2 \ \mu m$ (Figure 4.28 f), a wider area of composite surface was captured at $4x4 \ \mu m$ (Figure 4.28 e). One additional morphological detail that must be kept in mind is the slightly elongated and narrower PS stripes. These surface features attribute to a gently organized structure in a long-range order.

Up to date literature, many similarities and differences arise as to compare with the abovementioned results. For a triblock copolymer with maghemite nanoparticles as nanofiller system incorporated in poly(styrene)-b-poly(butadiene)-b-(polystyrene) host [Gar07]. To preferentially embed within PS domain, particles are decorated onto their surface with PS brushes by ATRP method. Although the low amount of particles load (1%wt.), AFM images did not form a continuous microphase separated structure. Comparing with investigated composite film of present work the morphology of Garcia neat BCP structure did not significantly affect by the addition of particles, but only a small disposition of lamellae structure indicated.

To shortly compare the annealing treatment induced nanocomposite morphologies instead of benzene toluene was used for SVA method under similar conditions for sample PS_{45} -b- PB_{34} -b- PI_{74} /PS_grafted IONPs. As indicated from **Figure 4.29**, toluene SVA treatment reflects at completely different resultant structure. There is no sign of particles texture not even underlying within the microphase separated pattern (**4.29 a,b**). Taking into account the greater scan size of the taken images, for γ -Fe₂o₃ the larger morphological features as appeared can be described as a typical phase separation state with greatly swelled bright regions. In contrast, the respective composite of Fe₃O₄ nanofiller correspond to highly agglomerated clusters of particles which is supported from disorganized formation at the bottom of scanned surface (**4.29 c,d**).



Figure 4.29: AFM height (left) and phase (right) images of PS_{45} -b- PB_{34} -b- PI_{74} / $PS_grafted IONPs$ after SVA treatment at toluene vapors for 5 days. Top images (**a**,**b**) correspond to γ - Fe_2O_3 and down images (**c**,**d**) to Fe_3O_4 composite with 10 % wt. respectively. Scan size: 6 μm

It is important to be mentioned that such a difference on resultant morphologies is proved to not similarly respond for pure BCP films as thoroughly studied in previous studies.

4.3.3 Block Sequence Relation with the Particle Placement for Preferentially Grafted Particles

At the last part of tri/BCP_NPs study, the incorporation of PS_grafted Ag particles as a function of block sequence is investigated. The incorporation of the same particles batch (PS_ grafted Ag) is made in two different triBCP matrices which are differentiated by the block sequence: PS_{35} -b- PB_{28} -b- PI_{39} and PB_{38} -b- PS_{24} -b- PI_{36} respectively. It is clear by the block sequence as well as by the molecular characteristics of the two triblocks that in the former triblock the NPs will be incorporated in an end block whereas in the latter they will be dispersed in the middle block. The molecular characteristics and especially the composition plays a significant role on the adopted morphology in bulk which as evident in the following figures (Figure 4.30 a and Figure 4.32 a) is the three-phase four layer lamellae which might cause a problem especially if the domain sizes are not big enough for the incorporation of the NPs especially in the case where the PS is the middle block. To perform an efficient comparison between the triblock terpolymers the same particles load is used in both cases. In order to avoid particle agglomerations which was found a really common phenomenon for high particle loads (>5% wt) in these composite bulk films, this amount did not exceed 3% wt. Regarding the above studied sequence of PS₃₅-*b*-PB₂₈-*b*-PI₃₉, the prospect of controlled particles placement by tuning the surface chemistry of the Ag particles with PS grafted chains is also examined. Taking into account the results from the literature, it has been demonstrated that the particle position depends significantly on the grafting density of the corresponding surface functionalization [Kim07]. To control their precise location, the block sequence of a host matrix involves a critical prerequisite for domain periodicity (L_0) determination (Figure **4.30** b). Tto specifically tailoring and based on this spatial correlation, domain periodicity indicates the width of domain that is to host the particles.



Figure 4.30: Cross sectional TEM image (**a**) for PS_{35} -b- PB_{28} -b- PI_{39} in bulk and a schematic (**b**) of generated composite film after incorporation of 3% wt particles load. In order to describe the optimal dispersion of particles within PS domain, particles placement is given.

For this particle incorporation, the NPs with the highest grafting density of PS_grafted Ag exhibiting 0.79chains/nm² were chosen. From **Figure 4.31**, it is clear that PS_grafted particles are mainly dispersed within the bright stripes which correspond to the PS domains (end block in this type of triblock terpolymer sequence). Although chemical selectivity between PS segment and particles is evident, at locations where particles are placed, it is obvious that local distortions of the underlying self-assembled structure occur. These distortions provoke dramatic changes on the structure especially for the polydienes

phase separation. The segments of PB and PI seem (**Figure 4.31**) in some areas in the TEM images to lose their immiscibility while the phase contrast of PS domain with the other two blocks is ideally maintained. Additionally, the lack of directed self-assembly may also be attributed to the steric effects which hinder the dispersion during solvent evaporation near or on the ODT [Lan07]. In these observations the ratio of particle diameter/microdomain dimension should be considered as a really important factor. It should be noticed in this case that **Figure 4.31** corresponds to the same block sequence and triblock terpolymer and PS_grafted Ag NPs (again in a 3% wt. loading).



Figure 4.31: TEM micrographs of stained PS_{35} -b- PB_{28} -b- $PI_{39}/PS_grafted Ag NPs containing 3%wt. filler, at different magnifications. Micrographs revealed significantly lower load particles due to strong agglomerations on specific grids area. Ultramicrotomy method did not lead to well NPs dispersed nanocomposite films.$

Three-phase four layer lamellae of the PS_{35} -*b*- PB_{28} -*b*- PI_{39} matrix exhibits a total domain periodicity of ~43 nm whereas the crucial width of PS domain is appeared to be equal with ~ 14 nm. Here, as it has been demonstrated from the literature, microphase separation exhibits with the adopted morphology being the 3-phase 4-layer lamellae, while PS domain is displayed as undivided domain (end block) whereas the PB domains are symmetrically divided in two thin smaller layers besides of PS and PI domains. By altering the block sequence from PS-*b*-PB-*b*-PI to PB_{38} -*b*- PS_{24} -*b*- PI_{36} , the resulted domain periodicity of this

matrix is calculated approximately equal to 38 nm. Except from the smaller PS domain width, the specific domain is divided as middle block into two symmetric thinner layers (**Figure 4.32 a**) and therefore the ratio of particle size/microdomain dimension is not the same. Thus, even for almost the same total molecular weight of BCP host and same incorporated particle batch and particles load (4 % wt.), dramatic difference in particles distribution is observed (**Figure 4.32**). In this case, more homogeneous dispersion is evident (**Fig. 4.32 c**). In general, due to the smaller PS domain compared with PS-*b*-PB-*b*-PI sequence, there is not enough width for PS to sequester the NPs (compare **Figure 4.30** with **Figure 4.32 b** in which the schematic illustrations are shown and the difference in space width is evident). Interestingly enough, the nanoparticles placement is confined over an undefined and maybe disorder matrix.



Figure 4.32: Cross sectional TEM image (a) for PB_{38} -b- PS_{24} -b- PI_{36} in a pure state, cartoon (b) of composite PB_{38} -b- PS_{24} -b- $PI_{36}/PS_{grafted}$ Ag NPs and c) generated film after incorporation of 4% wt. particles load.

Chapter 5: Conclusions

The research work involved in this dissertation investigated the selective incorporation of nanoparticles within diblock copolymer and triblock terpolymer matrices by exploiting two different functionalization pathways in order to selectively distribute the NPs in specific domains. In the diblock copolymer composite materials (diBCP/NPs), the manipulation of polymer grafted_NPs through chemical affinity and self-assembly process was a good evaluation in order to have a mechanism which was applied to the highly organized triBCP/NPs nanocomposites. To generate such composite nanomaterials, different approaches were involved to prompt nanoparticles into particular blocks in terms of thermodynamically driven processes. Two series of iron oxide and noble metal functionalized NPs were embedded both in diblock and triblock matrices to study their behavior into hybrid thin and bulk films. All the experiments were categorized in two different tasks.

In the first task, high vacuum technique standards and anionic polymerization were used in order to synthesize a set of thermoplastic elastomer triblock terpolymer hosts consisting from poly(styrene), poly(butadiene) and poly(isoprene) segments of various molecular weight and compositions. It should be mentioned that in the case of the PI and PB the type of microstructure involved in the each block played a significant role and the choice was PB with high -1,4 content (~92%) and PI with high -3,4 content (~60%) in order for these two blocks to microphase separate. In terms of block sequence, it was also really helpful to include the synthesis of several diBCP samples (PS-*b*-PB, PS-*b*-PI, PB-*b*-PI) so as to investigate the control of interactions between inorganic particles and polymer blocks. Afterwards, presynthesized nanoparticles were functionalized by homopolymer chains (PS or PI) by adopting two different surface modification methods: chlorosilane chemistry an thiol terminated tethering from iron oxide (γ -Fe₂O₃, FeO₄) and noble metals (Ag, Au) respectively.

The second task involved the preparation of mixtures of several combinations of BCP host and functionalized particles at specific particles load (% wt) in order to fabricate particles arrangement by the structural guidance of self-organized BCP scaffolds. This study was proven to be really important, since these interfacial interactions govern the spatial distribution and the influence of BCP underlying structure. During solvent vapor annealing (SVA) within an autoclaved chamber the composite structure was developed and its periodic fluctuations were captured mainly through atomic force microscopy (AFM). As a complementary characterization technique, transmission electron microscopy (TEM) measurements revealed the morphology confirming the compatibility of chemically mutual grafted particles with the corresponding blocks. It should be mentioned that different protocols for film preparation and successive treatment were conducted at either bulk or thin film state.

To briefly summarize, at the first task of Chapter 4, morphological results of pure diBCP and diBCP/NPs after attentive investigation of SVA the induced structure was formed. For diBCP/NPs fabrication, two symmetric polystyrene-*b*-poly(butadiene) (80 kg/mol and 100 kg/mol or PS_{50} -*b*-PB₅₀ and PS_{40} -*b*-PB₄₀ respectively) and a poly(butadiene)-*b*-poly(isoprene) sample (60 kg/mol) were synthesized. All these hosts were utilized as directing self assembled patterns in order to incorporate nanoparticles.

Spin-coated films of several film thicknesses ranging from 35 to 42 nm contribute in a variety of surface morphologies. Upon PS grafted_7-Fe₂O₃ incorporation, it was deemed that due to the higher molecular weight of PS₅₀-*b*-PB₅₀ when compared with PS₄₀-*b*-PB₄₀, larger domain periodicity (L_0) favored the more successful NPs sequestration while the underlying structure was less influenced. For both combinations of diBCP composites and through AFM imaging, preferential affinity of PS_covered nanoparticles (bright spots) within PS domains (bright regions) is evident for all the aforementioned samples. Basic requirement in order to achieve this affinity is regulated from the attachment of polymer chains onto the NPs periphery. Chlorosilane chemistry via anionic polymerization synthesis succeeded on generating low molar mass grafted chains (6.5 kg/mol) resulting on different areal grafting density for each particle batch. To investigate the same composite in bulk state films, TEM images were also taken and analyzed. Here, in order to achieve the desired orientation, the chain mobility of diBCP/IONPs was investigated with thermal annealing (TA) process. The TEM micrographs from the bulk films revealed no evidence of spatial selectivity of PS_grafted particles within the PS phase. On the contrary, same images pointed out NPs being equally accommodated in both phases perhaps with a slight preference with the PB domain.

Similarly with iron oxide particles, PS_grafted silver $(13\pm3 \text{ nm})$ NPs were incorporated within the PS domain for a given PS₄₀-*b*-PB₄₀ matrix. The selective localization of Ag particles inside PS phase is also confirmed. Several fluctuations of surface formation were found to be solvent annealing time dependent as it has been suggested for diBCP/IONPs. While presynthesized silver and gold particles are capped with oleylamine layer, PS either PI thiol terminated molecules are proven to be beneficial in replacing that surfactant layer with homopolymer brushes respectively. Prior to mixing of the NPs in the BCP solution, TGA analysis validated the degree of functionalization for each NPs batch separately.

In the last case of diBCP composite film, poly(butadiene)-*b*-poly(isoprene) plays the role of highly self-organized fully polydiene scaffold. Interestingly, the spatial distribution of PI_grafted gold particles (12 nm) along invisible (due to common elastic properties with PB domain) stripes of PI domain renders the phase contrast of polydiene blocks clearly distinct.

The second and main task of the present work is devoted on the morphological study of triBCP/IONPs. Symmetric lamellae structure of three phase four layers is adopted by the PS-*b*-PB-*b*-PI material. Although the aroused complexity of the system by the addition of one extra block on the block sequence, the ability of PS_grafted particles being embedded along the edges of PS domain was effectively observed. It was found that Fe_3O_4 were successfully incorporated within the PS phase only by the utilization of a specific triblock terpolymer of the PS₄₅-*b*-PB₃₄-*b*-PI₇₄ type as the host displaying a highly organized template. This was achieved due to microphase separated generated structure of long range order and due to selective segregation of PS_grafted magnetite NPs in the PS domain.

In contrast, upon incorporating the same load of NPs (%10 wt) of the same batch within PS_{26} -*b*- PB_{23} -*b*- PI_{12} host led to not apparent microphase separated morphology. The significantly lower molecular weight led to lower dimensions of the domain periodicity (L_0) and length of the PS domain stripes. Despite the fact that PS_grafted particles appeared to segregate within bright stripes, by the increase of annealing time the whole structure displayed a tendency to form two levels of structures. The below level displays an underlying structure of two phases (polydiene segments separation is not visible via AFM imaging) while the topmost surface layer is composed of well arranged NPs. In bulk film state, microphase segregation of particles was only confirmed for lower particles loading (<4% wt). The accommodation of particles inside the PS domain took place sporadically since for these NPs placement emphatic distortions of the three phase lamellae layer were obvious.

Abstract

The current tendency of exploiting BCP matrix for large area periodic structures has attracted significant academic and commercial interest due to the simplicity of processing. The concept of fabricating novel functional materials through selective incorporation of various nanofillers (such as nanoparticles in this thesis) within one polymer domain belonging to diBCP either triBCPs, makes them excellent candidates for the generation of highly organized hybrid materials.

Using the "grafting to" method, presynthesized iron oxide and noble metal nanoparticles were modified with surface chemistry approaches in order to attach homopolymer chains onto the particles periphery. As a final goal, these can be directly used as nanosize inorganic inclusions by mixing them with BCP solutions. For this purpose, diblock copolymer and triblock terpolymer systems of thermoplastic elastomers comprising of widely used polymer blocks such as polystyrene, poly(butadiene) and poly(isoprene) were used as the directing self-assembled pattern. All synthetic efforts were conducted via anionic polymerization techniques according to high vacuum standards.

Subsequently, to investigate how the particles incorporation affects the existing morphologies AFM and TEM imaging of the resultant composite films illustrated potential morphological developments. Additionally, TGA, XRD, surface ellipsometry, ¹H-NMR and SEC instrumentation was used for investigating the success of the research work involved in this dissertation. To increase chain mobility and control the evolution of the time dependent phases, thermodynamically driven processes of solvent vapor annealing and thermal annealing were proven to be of extreme importance.

Περίληψη

Η συνεχώς ακμάζουσα επιστημονική αναζήτηση για νανο-υλικά που χαρακτηρίζονται από οργάνωση σε μεγάλες επιφάνειες (DSA) μέσω των υποστρωμάτων από συμπολυμερή κατά συστάδες (BCP) έχει αποκτήσει τα τελευταία χρόνια σημαντικό ακαδημαϊκό ενδιαφέρον εξαιτίας της απλότητας της μεθόδου. Η ιδέα της παρασκευής πρότυπων δραστικών υλικών μέσω της επιλεκτικής ενσωμάτωσης σωματιδίων σε νάνο διαστάσεις καθιστά τα δισυσταδικά και τα τρισυσταδικά συμπολυμερή ως εξίσου σημαντικές πολυμερικές μήτρες που μπορούν να τα φιλοξενήσουν και να οδηγήσουν στην παρασκευή υβριδικών υλικών υψηλής οργάνωσης.

Ακολουθώντας την μέθοδο "εμβολιασμό σε", ήδη συντεθειμένα νανοσωματίδια οξειδίου του σιδήρου (γ-Fe₂O₃, Fe₃O₄) και ευγενών μετάλλων (Au και Ag) υπέστησαν χημική τροποποίηση της επιφάνειας τους με σκοπό να προσδεθούν ομοπολυμερικές αλυσίδες. Τελικός σκοπός αυτών των ανόργανων σωματιδίων είναι να διασπαρθούν μέσω της ανάμιξης τους με διαλύματα συμπολυμερών και τριπολυμερών. Γι' αυτόν το λόγο, για την παρασκευή αυτό-οργανομένων υποστρωμάτων, χρησιμοποιήθηκαν δισυσταδικά συμπολυμερή και τρισυσταδικά τριπολυμερή συνδυάζοντας συστάδες πολυστυρενίου, πολυ(βουταδιενίου) και πολυ(ισοπρενίου). Όλες οι συνθετικές προσπάθειες της παρούσας διδακτορικής διατριβής διεξήχθησαν μέσω της μεθόδου του ανιοντικού πολυμερισμού στα πλαίσια της τεχνικής "υψηλού κενού".

Ακολούθως, προκειμένου να μελετηθούν ο μηχανισμός με τον οποίο ενσωματώνονται τα σωματίδια εντός των μητρών και κατά πόσο επηρεάζουν την μορφολογία των αρχικών μητρών, ο μορφολογικός χαρακτηρισμός με Ατομική Μικροσκοπία Δύναμης (AFM) και Ηλεκτρονική Μικροσκοπία Διέλευσης (TEM) απέφερε σημαντικά αποτελέσματα. Επιπρόσθετες τεχνικές χαρακτηρισμού όπως TGA, XRD, SE, ¹H-NMR and SEC αποδείχθηκαν ιδιαίτερα χρήσιμες για την επιτυχή ανάλυση και περιγραφή των αποτελεσμάτων της διατριβής.

Κλείνοντας, με γνώμονα την αύξηση της "κινητικότητας" των πολυμερικών αλυσίδων αλλά και τον έλεγχο της εκάστοτε προκύπτουσας μορφολογίας, ιδιαίτερα σημαντική αποδείχθηκε η θερμική ανόπτηση (TA) αλλά και η ανόπτηση μέσω ατμών διαλύτη (SVA) καθώς και ο χρόνος εφαρμογής της.

[126]

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