ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

BAROPLASTIC BLOCK COPOLYMERS AS A PROCESSING AID

M.Sc. Thesis by
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BAROPLASTİK ÖZELLİK GÖSTEREN BLOK KOPOLİMERLERİN YARDIMCI MADDE OLARAK KULLANILMASI

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FOREWORD

This master study has been carried out at Istanbul Technical University, Institute of Science and Engineering, Polymer Science & Engineering Program.

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Evrim Büyükaslan

Textile Engineer

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ABBREVIATIONS

PS	**:** Polystyrene
PEHA	**:** Poly(ethyl hexyl acrylate)
PBA	**:** Poly(butyl acrylate)
PI	**:** Polyisoprene
PB	**:** Polybutadiene
PBMA	**:** Poly(*n*-butyl methacrylate)
PVME	**:** Poly(vinyl methyl ether)
PMSO	**:** Poly(methyl phenyl siloxane)
PHMA	**:** Poly(hexyl methacrylate)
PPMA	**:** Poly (pentyl methacrylate)
PEP	**:** Poly(ethylene propylene)
PEE	**:** Poly(ethyl methylene)
SANS	**:** Small angle neutron scattering
UDOT	**:** Upper disorder-to-order temperature
LDOT	**:** Lower disorder-to-order temperature
CRP	**:** Controlled/'living' radical polymerization
NMP	**:** Nitroxide mediated polymerization
RP	**:** Radical polymerization
ATRP	**:** Atom transfer radical polymerization
AGET ATRP	**:** Activators generated by electron transfer ATRP
PDI	**:** Polydispersity
TEM	**:** Transmission electron microscopy
AFM	**:** Atomic force microscopy
DSC	**:** Differential scanning calorimeter
UCST	**:** Upper-critical solution temperature
CuCl	**:** Copper (I) chloride
CuBr	**:** Copper (I) bromide
EBP	**:** Ethyl-2-bromo propionate
THF	**:** Tetrahydrofuran
PMDETA	**:** *N, N, N′, N″, N″*-pentamethyldiethylenetriamine
Bipyr	**:** 2,2′-bipyridine
$CDCl_3$	**:** Deuterated chloroform
NMR	**:** Nuclear magnetic resonance
GPC	**:** Gel permeation chromatography
GC	**:** Gas chromatography

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SUMMARY

Thermal processes such as extrusion, injection molding and blow molding have been used over decades for shaping thermoplastics. However these processing methods have several disadvantages such as energy costs, degradation, discoloration, poor properties of final product and recyclability. Polymers are compounded with additives, fillers and reinforcements to improve mechanical strength, reduce the costs and increase the processability. Eventhough compounding facilitates the processing and improves final properties, recyclability remains as a distinct problem for the thermal processes.

Considering the mentioned difficulties of thermal processes, thermodynamic pressure is though as a correspondent of heat in thermal processes. Miscibility is an important parameter for the processing of blend polymers and thermoplastic elastomers since an increase in miscibility results with an improvement of processing due to the eased flow. Thermodynamic pressure is recorded as a factor for increasing the miscibility of the phase seperated block copolymers which show an upper disorder-order transition, UDOT, and the processability under pressure at low temperatures is named as "baroplastic" property. In this study, originating from the miscibility inducing effect of pressure, homopolystyrene is blended with baroplastic polystyrene-*b*-poly(ethyl-2-hexyl acrylate), PS-*b*-PEHA, diblock copolymers and PEHA-*b*-PS-*b*-PEHA, PS-*b*-PEHA-*b*-PS triblock copolymers. Their processability is evaluated under pressure at room temperature. While homopolystyrene is a powder like polymer that could not normally be processed under pressure at room temperature, it is quest for if the baroplastic addition assists processability under given conditions. To be able to understand the effect of topology and molecular weight on processability variable PS-*b*-PEHA diblock copolymers and PEHA-*b*-PS-*b*-PEHA, PS-*b*-PEHA-*b*-PS triblock copolymers were synthesized with different compositions and molecular weights. In the industry, homopolystyrenes have different molecular weights according to the desired properties and end users. Accordingly variable polystyrenes are synthesized with different molecular weights in order to blend with baroplastic block copolymers and their processability differences are examined.

BAROPLASTİK ÖZELLİK GÖSTEREN BLOK KOPOLİMERLERİN YARDIMCI MADDE OLARAK KULLANILMASI

ÖZET

Ekstrüzyon, plastik enjeksiyon ve şişirme kalıp sistemleri termoplastik imalatında yaygın olarak kullanılan ısıl işlemlerdendir. Ancak ısıl işlemlerin yüksek enerji sarfiyatının yanı sıra elde edilen ürünün istenilen niteliklerde olmaması, degredasyon ve geri dönüşüm gibi problemleri mevcuttur. Polimerler mekanik özellikleri iyileştirmek, maliyetleri düşürmek ve işlenebilirliği kolaylaştırmak amacıyla katkı maddeleri, dolgular veya kuvvetlendiricilerle karıştırılırlar. Bu karıştırma işlemi polimer işlenilebilirliği ve son ürün özellikleri üzerinde iyileştirici etkiye sahip olsa da geri dönüşüm, ısıl işlemler için önemli bir problem olmaya devam eder.

Isıl işlemlerdeki bu zorluklar göz önünde bulundurularak, termodinamik basıncın ısıl işlemlerdeki sıcaklığın yerini tutacak bir etki yaratabilme ihtimali üzerinde durulmuştur. Karışımlarda ve termoplastik elastromerlerde "karışabilirlik" akışı kolaylaştırıcı etkiye sahip olmasından ötürü proses açısından önemli bir parametredir.

Termodinamik basıncın "üst düzensiz-düzenli geçiş" gösteren blok kopolimerler üzerinde karışabilirliği artırıcı etkisi olduğu saptanmıştır ve bu duruma bağlı olarak malzemede ortaya çıkan proses edilebilme özelliğini "baroplastik özellik" olarak isimlendirilmiştir. Bu çalışmada basıncın karışabilirliği artırıcı etkisine dayanarak, polistiren, baroplastik poli(stiren-*b*-2-etil hegzil akrilat), PS-*b*-PEHA, diblok kopolimer veya PEHA-*b*-PS-*b*-PEHA, PS-*b*-PEHA-*b*-PS tri-blok kopolimerler ile karıştırılmış ve ortaya çıkan karışımın oda sıcaklığında basınç altında işlenebilirliği incelenmiştir. Toz yapıdaki polistiren, normal koşullarda oda sıcaklığında basınç altında şekil alma özelliğine sahip değildir. Bu çalışmada polistirene baroplastik özellik gösteren blok kopolimer takviyesi yapılmasının oda sıcaklığında basınç altında işlenebilirliğe yardımcı olup olmadığı sorgulanmıştır. Topolojinin ve molekül ağırlığının işlenebilirlik üzerinde etkilerini inceleyebilmek amacıyla farklı kompozisyon ve molekül ağırlıklarında PS-*b*-PEHA diblok ve PEHA-*b*-PS-*b*-PEHA, PS-*b*-PEHA-*b*-PS triblok kopolimerleri sentezlenmiştir. Sanayide kullanılan polistirenler istenilen özelliklere ve son kullanım yerlerine bağlı olarak değişen molekül ağırlıklarındadırlar. Dolayısıyla baroplastik blok kopolimerlerle karıştırılmak üzere farklı molekül ağırlıklarında polistirenler sentezlenmiş ve homopolistiren molekül ağırlıklarının işlenebilirlik üzerinde oluşturduğu farklılıklar ayrıca araştırılmıştır.

1. INTRODUCTION

From the beginning of the 20th century polymers became an indispensable raw material for the construction of many articles such as pipes, rods, films or molded parts. As a material, polymers mostly meet the desired properties of end products therefore they are frequently employed in many industries. As it is possible to achieve good mechanical properties, chemical/thermal stability, isolation/ conductivity and many other features by using polymers as a material, polymers rapidly took place in the market and polymeric products gradually substituted the metal, porcelain and glass made products. However it is not common to use a neat polymer during processing since it is mostly desirable to provide additional properties to the final product besides its handling and processing problems with the known processing techniques. Due to these facts, polymers are compounded with additives, fillers or reinforcements. Most commonly used additives are pigments, processing aids, antidegredants, stabilizers and retarders. In general, additives improve mechanical strength of final product, ease the processibility and reduce costs.

In terms of processing, polymeric materials can be classified as thermoplastic and thermosets. Thermoset materials cannot be remelted so that their transformation is permanent. They are usually resistant to high temperatures and they have a hard surface with rigid structure while thermoplastics are considerably flexible. Commodity polymers and engineering polymers are classes of thermoplastic polymers which constitute most of the polymeric product applications. Films, sheets, tubes, bottles and packages are well-known application fields of commodity plastics. In comparison to commodity plastics, engineering plastics are capable of bearing higher loads for long terms, besides they have better stability against high temperatures. Injection molding, extrusion and blow molding are the most common processing techniques that are employed for shaping thermoplastics.

Injection molding is the processing technique where the melt of thermoplastic pellets is injected into a mold by high pressure effect. The molten polymer spreads out over

the walls of mold and part is ejected from the mold right after its solidification. Cycle time (per-part processing time) depends on the solidification time of thermoplastic polymers which vary between 15 seconds to 60 seconds. This issue can be considered as a limitation for production efficiency of injection molding. Moreover it is necessary to reach high temperatures for the flowability of polymeric material. The compulsory high temperatures are disadvantageous for energy consumption next to the possible degradation problems, besides some of the compounded additives are instable to high temperatures. Another well-known processing method is extrusion, which is used to process objects with uniform cross section or continuous structure such as tubes, rods or sheets. Similar to injection molding, thermoplastic pellets are melted inside extruder. Rotating screw of extruder carries the pellets to the heated zone where melting and uniform mixing is achieved. Afterwards, molten polymer is forced through the die hole of the extruder to form the required shape. Hollow thermoplastic objects such as bottles and containers are formed by the extrusion blow molding method. In this method a miniature bottle like polymeric form, namely parison, is extruded through an extruder. This thin-walled tube is located between two halves of a larger diameter mold, and then pressurized air is blowed inside the tube causing an expansion. Expanded tube takes the shape of the inner mold and finally the product is ejected by splitting of the mold halves [1].

As one may notice, in all processing techniques it is mentioned that the thermoplastic materials are transformed to the molten state to be able to give a desired shape. Most of the polymers have high melt temperatures, for instance polystyrene, high density polyethylene, nylon 6.6, polypropylene are commodity plastics which have considerably high melting temperatures around 200, 260, 280 respectively [2]. As expected temperature application results with an increase in energy consumption which is strongly avoided due to costs and environmental reasons. Moreover the high temperature necessities cause a reduction in apparel properties of final product mainly due to local degradations resulting in coloration problems.

Recyclability is another important meter for thermoplastics as thermoplastic usage is increasing rapidly. Just in UK, the consumption of polymeric products by 2001 was 4.7 million tones and 64 % of this consumption was recorded as waste. According to data's of Environment Agency only 7 % of polymeric wastes are recycled and the rest is incinerated or sent to landfill [3].

Recyclability is challenging since polymeric wastes reveal a wide range of variety and inhomogenity. Recycling technologies can be classified basically in 4 groups: primary, secondary, tertiary and quaternary recycling. To be able to carry out a primary recycling, the polymeric waste must be uniform and uncontaminated and this requirement is mostly challenging to achieve. Even if primary recycling is done, certain amount of recycled polymer is compounded with raw polymer and other additives during processing. Only thermoplastics can undergo primary recycling and high temperatures are one more time an obligation to be able to implement recycling. The major problem of primary recycling is degradation that results a loss of properties such as mechanical strength, appearance, chemical resistance and processability [4].

To summarize; energy costs, degradation, discoloration, poor properties of final product and recyclability is the major problems of thermal processes. Flow is very important for the processing of thermoplastics and the flowability is achieved by temperature or solvent supported systems which have disadvantages as explained earlier.

As mentioned initially, immisibility of polymeric blends causes processing difficulties as they undergo phase seperation. In thermal processes, to overcome the immisibility problem of block copolymers and polymeric blends, additives and compatibilizers are added during compounding. To decrease the immisibility alternative processing techniques came into question. Pressure is thought as one of the alternatives which can attribute to the processing of immisible polymeric blends and block copolymers. It is desired to shape the polymers by the pressure effect at considerably low temperatures as low as room temperature. Pressure is an important thermodynamic parameter which is effective on the processability of thermoplastics so that it has been drawing a great interest over past. Jansenn *et. al.* studied compressibility of blends by small angle neutron scattering, SANS [5, 6]. Jansenn's studies consecutively followed by many research groups that studied pressure effect of blends and block copolymers. Hammouda and Bauer investigated miscibility effects in polystyrene/poly(vinyl methyl ether), PS/PVME, and in polystyrene/ poly(buty methacrylate), PS/PBMA blends [7]. Hajduk *et. al.* reported a decrease in segregation of block copolymers due to increasing pressure values [8]. Steinhoff and his collegues reported the pressure effect on order to disorder transition in

polystyrene-*b*-polyisoprene, PS-*b*-PI, and polystyene-*b*-poly(methylphenylsiloxane), PS-*b*-PMSO, diblock copolymers and they have recorded a decrease in order-to-disorder transition temperature by an application of small pressures and controversially an increase in higher pressure values [9].

Ruzette *et. al.* pioneered the studies of using pressure as a main driving force for the processing. They studied polystyrene-*b*-poly(hexyl methacrylate), PS-*b*-PHMA, and they reported upper disorder-order transition, UDOT, exhibiting block copolymers reveal a high pressure coefficient which can attribute to the segmental miscibility and cause a flow like effect during processing, and in this study they named this flow like behavior as "baroplastic behavior" and the materials as "baroplastic materials" [10]. Moreover Ruzette and Mayes proved the pressure-induced miscibility of polystyrene-*b*-poly(*n*-butyl methacrylate), PS-*b*-PBMA, and polystyrene-*b*-poly(hexyl methacrylate), PS-*b*-PHMA. They reported that PS-*b*-PBMA exhibit ordering upon heating through a lower disorder-order transition, LDOT, while PS-*b*-PHMA reveals UDOT [11]. In 2003, two new baroplastic candidates, polytyrene-*b*-poly(*n*-butyl acrylate), PS-*b*-PBA, and polystyrene-*b*-poly(2-ethyl hexyl acrylate), PS-*b*-PEHA, block copolymers and PEHA/PS, PBA/ PS-d_8 core-shell nanoparticles were investigated for processibility at room temperature. They demonstrated molding of baroplastic block copolymers and core–shell nanoparticles comprising one glassy and one rubbery component, solely by applying pressure [12].

In this study, we aimed to blend a homopolymer with a block copolymer which can transit from order state to disorder state by pressure effect. As mentioned before, PS-*b*-PEHA block copolymers with similar PEHA/PS content are processed under pressure at room temperature [12]. Based on this fact, in this study we investigated the processability of blends that constituted homopolystyrene and varied compositions of PS-*b*-PEHA and PEHA-*b*-PS-*b*-PEHA, PS-*b*-PEHA-*b*-PS block copolymers. From an industrial point of view, processing of a homopolymer under pressure at low temperatures would be desirable due to the previously mentioned problems of thermal processes. It should be considered that homopolystyrene is a powder like structure which normally cannot be shaped under pressure at room temperature. However, a baroplastic supported system may contribute to achieve processability of homopolystyrene at mentioned conditions.

In this study, baroplastic block copolymers and homopolymers are synthesized by atom transfer radical polymerization, ATRP, and activators generated by electron transfer ATRP, AGET-ATRP. PS-*b*-PEHA , PEHA-*b*-PS-*b*-PEHA and PS-*b*-PEHA-*b*-PS baroplastic block copolymers were synthesized by using PS or PEHA as a macro-initiator. Polystyrene is chosen as macro initiator since handling of poly(2-ethyl hexyl acrylate) is difficult due to its softness and adherence. Blending of baroplastic block copolymers and homopolystyrene is done physically and their processability is investigated as a function of time and pressure.

To compare many variables in terms of baroplastic block copolymer contribution to processability is another goal of this work. For this purpose, baroplastic block copolymers are synthesized at different topologies, compositions and molecular weights.

Since industrial homopolymers exhibit a wide range of molecular weights, homopolystyrenes are synthesized at varying molecular weights in order to blend with baroplastic block copolymers.

2. THEORETICAL PART

2.1 Melt Processing Methods

Thermoplastic polymers are transformed into desired shapes by applying a melt processing. There are several melt processing methods and the preferred method depends on the final product properties as well as the processed polymer itself. Flow and thermal properties of polymers are significantly important for processing as well as the shrinkage and warping properties. Since thermoplastics do not reveal a newtonian flow, it is complex to understand the flow properties which are dependent on temperature and shear rate. Thermoplastic polymers also do have high viscosities so that it is necessary to force the molten polymer through the die or into a mold with high pressure. In this case, the mold should be rebust and high costs of molds can be subjected to this matter.

Extrusion, injection molding and blow molding are the widely used melt processing methods.

Extrusion process is especially preferred for forming sheets, wraps or long continuous parts such as pipes, rods etc. There are several devices driven by pressure or plunger to carry out the extrusion but screw extruder is the universally used one. There might me multiple screws in an extruder system, however the simple systems mostly constitute of single screw with helices rotating inside a barrel. Polymer, mostly in pellet forms, are placed in the hoppers and fed through the channel formed between the screw and barrel. By the rotation of the screw, the polymer is conveyed to the foresides of the extruder. Extruder is mostly divided into 3 zones according to the functionality of the zone such as feeding, transition and melting. The extruder is surrounded by electrical heaters which initiate the melting. The melting is propagated by friction between screw and polymer caused by the rotation of the screw. Molten polymer is finally forced through a die and cooled below its glass transition temperature, T_g, after attaining its desired shape [13]. The final shape of objects

carried out by extrusion can be modified by passing them through rollers, blades in other words by applying a pre-processing.

Injection molding is generally used for manufacturing more complex parts. It is a processing technique similar to extrusion, the molten polymer is injected into a mold instead of forcing through a die as in extrusion. The high costs of equipments are a result of high pressure application that is necessary for shaping the thermoplastics in injection molding technique. Injection molding is theoretically a simple technique, however practically it is not that easy due to viscosity of polymer and pressure application [2]. Polymer pellets are melted similar to extrusion, molten polymer is injected inside the mold under high pressure values (approximately 10000 psi) and it takes the inner shape of the mold. Before the part is ejected, it is waited for the molten polymer to cool, solidify and shrink. Consequently an ejection unit is desired to be able to take the part out of the system. Basically injection machine can be divided into 6 systems; injection unit, clamping unit, mold, runner system, control system and tempering devices. As its name indicates injection unit is responsible of injection and plasticization of molten polymer while clamping unit is in charge of holding the clamp. Runners and sprues carry the melt inside the mold [1].

Finally, blow molding is used to shape hollow objects such as bottles and containers. The mold itself defines only the external shape of the hollow object, meanwhile the pressure applied to the inner side attains the required inner shape. A miniature tube, mostly referred as “parison” is produced by melt processing, later the parison is clamped between the halves of the mold. An air channel is also placed in one of the parison edges so that a pressurized air can flow inside the parison enabling a balloon like expanding of the parison. As the molten polymer touches the walls of the cold mold, solidification starts and it is followed by the ejection of the blow molded part [2]. Blow molding is divided into many branches according to the processing methods. Extrusion blow molding and injection blow molding are process types applied often.

2.2 Compounding

Several ingredients are mixed with the thermoplastics in order to attain some additional mechanical or physical properties or to attain specific processing characteristics. This mixing or blending is referred as “compounding” and used almost in every melt processing. It is important to achieve a uniform mixture since better final product properties are also dependent on uniformity. Uniformity during compounding is achieved by propellers, screws, peddles or ribbons based on the phase of the components.

Before the polymer is transformed to the molten stage, compounding is done by additives such as powders, waxes, resins, pigments, reinforcements, liquid or solid plasticizers, antidegredants, colorants or other specialty chemicals.

During compounding homogeneity of the mixture, uniform and fine dispersion of the additives should be considered. Moreover, miscibility of the ingredients appears as another important parameter [2].

2.3 Polymer Blends

At least two different types of polymers are mixed in order to attain individual properties of each polymer to the end product. Statics show that 30 % of polymers are constituted of polymer blends and this rate is continuously increasing. Interfacial tension is significantly important for polymer blends as it influences the compatibility. Polymers totally dissolve in each other as the interfacial tension theoretically approaches to zero. Incompatible and immiscible polymers have high interfacial tension which is related to the polarity discrepancies. As the polarity differs, interfacial tension increases, thus miscibility decrease. Immiscible polymers lead to phase separations during mixing so that “compatibilizers” should be added to mixture for decreasing the phase separation otherwise droplets might form. Co-continuous morphology forms if the relative volume of each polymer increases [14].

2.3.1 Morphology of polymer blends

Polymer blend compositions are effective on the compatibly of the individual polymers as lower concentration of each polymer give rise to single droplet formation while the concentration increasing leads to cylinders and fibers.

Most of the polymer blends exhibit immiscibility. Opacity is a parameter which provides information about the miscibility of blends since refractive index of each polymer in the blend is different. However, opacity is not a certain criteria because the heterogeneity should be larger than 100 nm and refractive index should be greater than 0.01 to be able to observe light scattering. The best detection of miscibility is done by T_g analysis so far. There is a believe that blends that display a single T_g are miscible. However immiscible blends might also exhibit a single T_g when there is finely dispersed phase.

Fox equation is used in order to calculate the T_g of miscible polymer blends.

$$(1/T_{g,mix} = w_1/T_{g,1} + w_2/T_{g,2}) \quad \textbf{(2.1)}$$

Where w_1 and w_2 represent the weight fraction of the component, and T_g, $T_{g,1}$ and $T_{g,2}$ are the T_g's of the blend.

T_g is insensitive when the amount of the second component is less than about 10 wt %. Furthermore, the method should not be used for blends containing polymers whose T_g 's do not differ at least by 10 ^oC from each other [15].

However, in this work not only a single block copolymer is considered but also an addition of a homopolymer is conducted. Thus, it is expected that the morphology of the block copolymer will alter by the addition of homopolymer. The possible blend structures are studied in 1991 by Hashimoto and his co-workers. As shown in Figure 2.1; a) "A" homopolymer and block copolymer may reveal a complete phase separation, b) "A" homopolymer may locally solubilize in the middle of A micro domains or c) "A" homopolymer may uniformly solubilized in "A" micro domains. They concluded that the low molecular weight homopolymers were found to be solubilized, more or less, uniformly into the corresponding micro domain space. Low molecular weight homopolymer "A" is solubilized into "A" micro domain, which generally causes the changes of the molecular conformations of "A" homopolymer chains and "A" block chains, both tending to the stretched normal to the lamellar interface [16]. It can be concluded that the addition of a homopolystyrene impairs the ordered structure of block copolymers by solubilizing into micro domains. So that to observe the mixed phase caused by the effect of pressure in blends of block copolymers and homopolystyrene may not be as easy as in neat block copolymers.

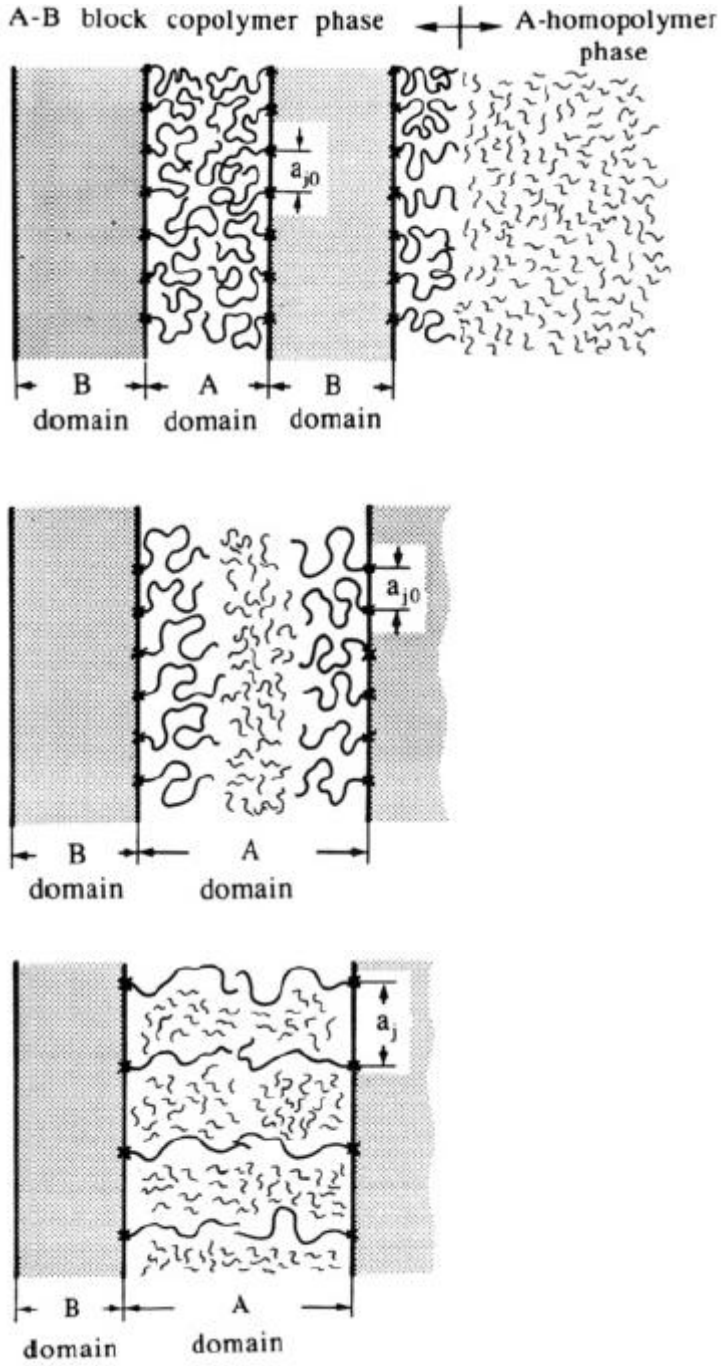


Figure 2.1 : Possible blend structures of diblock copolymers and homopolymers, a) the complete phase seperation into A homopolymer phase and the phase containing the micro domains of the block copolymer, b) the uniform micro domain structure composed of A-B and A in which A homopolymer is locally solubilized in the middle of A micro domains, c) the uniform micro domain structure composed of A-B and A in which A homopolymer is uniformly solubilized in A micro domains.

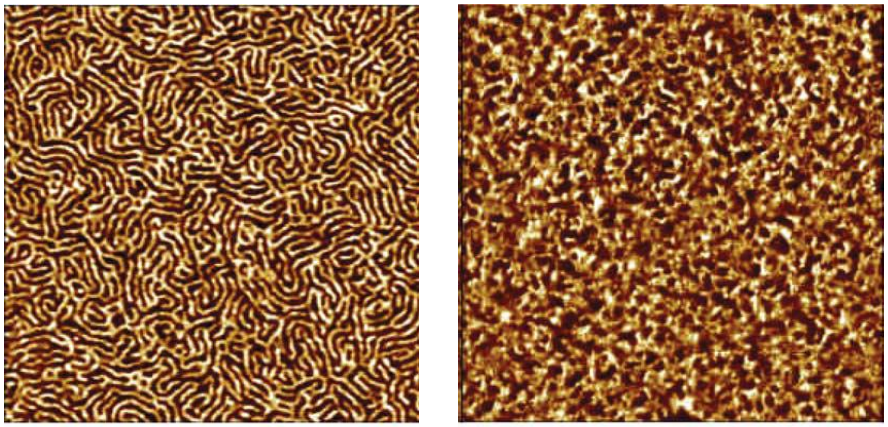
Hashimoto and his co-workers carried on the studies concerning the blends of a block copolymer and homopolymer's morphology. They investigated the micro domain structure of PS-*b*-PI diblock copolymer with homopolystyrene as a function of the homopolymer molecular weight. They found that the blends containting upto 20% homopolystyrene maintane a well-ordered lamaller structure. However the same trend couldn't be catched for the higher moleculer weighted homopolystyrenes. When the amount of homopolymer reached 35%, the lamellar morphology changed to hexagonally packed cylindrical microdomains. They concluded that when the homopolystyrene molecular weight is smaller than the molecular weight of PS in the block, homopolymer chains dissolve in PS domains while longer homopolymer chains, but still having a molecular weight smaller than the PS block in block copolymer, localize in the center of PS domain [17].

Later on similar studies are done for probing the structure of a block copolymer homopolymer blend. The morphological effect of homopolystyrene addition to a block copolymer have been studied for long years by many research groups [18, 19] and it is well summarized in PhD thesis of Romanivna T. K. [20].

The morphology of polymer blends is examined by using microscopic methods or light scattering methods (SANS). Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic fourier microscopy (AFM) are devices which provide a better understanding for polymer blend morphology from a microscopic point of view [15].

Mykhaylyk *et. al*. has studied the morphology of some blends by using AFM. Polystyrene-*b*-polyisoprene-*b*-polystyrene (PS-*b*-PI-*b*-PS) block copolymer was blended with PS and PI homopolymers individually. The molecular weight and polydispersity index (PDI) of PS-*b*-PI-*b*-PS block copolymer was indicated as 128,000 $g.mol^{-1}$ and 1.11 respectively. The PS content in triblock copolymer was 18 wt. % The employed homopolystyrene's molecular weight was relatively small, 1300 $g.mol^{-1}$. The AFM image of mentioned neat block copolymer is given in Figure 2.2. The block copolymer exhibits a finger print phase contrast. In figure 2.3, the block copolymer/PS blends with different blend ratios are shown. As clearly seen from these images the addition of homopolystyrene to the block copolymer impairs the ordered structure of block copolymer and creates a disordered structure [21].

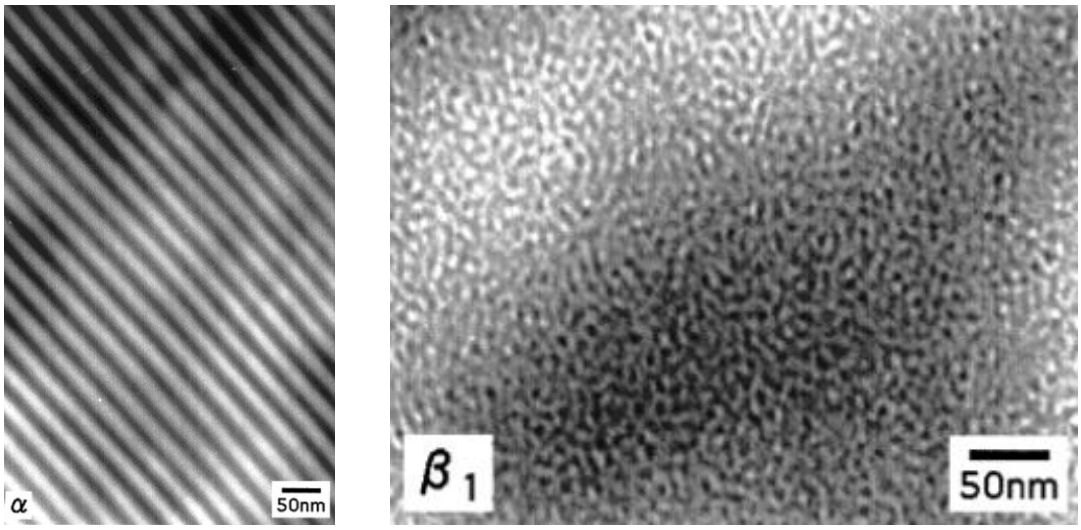
Figure 2.2 : AFM image (phase contrast) of the neat PS-*b*-PI-*b*-PS sample (2 μm scale)



(a) (b)

Figure 2.3 : a) AFM image (phase contrast) of PS-*b*-PI-*b*-PS/homo-PS mixture, 14 wt. % homo-PS added (2 μm scale) , b) AFM image (phase contrast) of PS-*b*-PI-*b*-PS /homo-PS mixture, 27% wt. homo-PS added (2 μm scale)

Recently, Yamaguchi and Hashimoto studied the miscibility of nearly symmetric two block copolymers, PS-*b*-PI, with variable blend ratios and molecular weights. They observed that molecular weight of block copolymers and their blend ratios are important on macro phase separation occurrence. They have employed a higher molecular weight block copolymer (α, M_n: 1 x 10^5) and lower moleculer weight block copolymers (β_1- β_4, M_n: 1,21 x 10^4-2,1 x 10^4). They indicated that the macro phase separation is induced by the micro phase separation, since the solubilization of equilibrium amount of β into lamellar phase of α is limited as α starts to order into lamella. TEM micrographs of blend sample clearly proved the influence of blend ratio and molecular weight of blend components on the phase seperation (Figure 2.4-2.5) [22].



a b

Figure 2.4 : TEM micrographs of a) α (PS-*b*-PI, M_n: 1 x 10^5) b) β_1 (PS-b-PI, M_n:1,21 x 10^5)

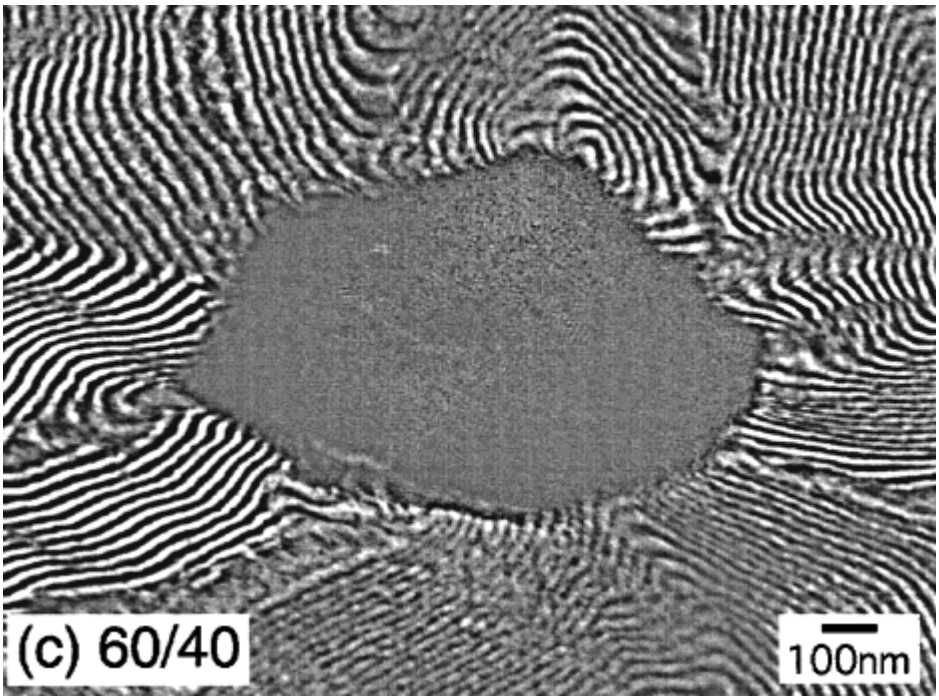


Figure 2.5 : TEM micrographs of α/ β_1 (60/40 wt. %)

2.3.2 Pressure-induced miscibility of block copolymers and blends

As it is explained before, flow is an important parameter for the processing of polymers. Temperature activates the flow of polymer in thermal processes. Pressure is also reported as a parameter which influences the miscibility, indirectly flowability, thus many studies over last 15 years were done about the pressure effect

on morphology of blends and block copolymers. Pressure can induce melt-like behavior in block copolymers and these kinds of block copolymers were named as "baroplastics".

Hydrostatic pressure has been shown to be very effective by means of driving the system from the ordered to the disordered state. In terms of the rheological properties, pressure at constant temperature can be used to force the material from a solid state where micro phase separation impedes flow of the polymer chains to a melt state where the copolymer segments are mixed. If one considers standard processing conditions for polymers, such "baroplastic" behavior could be highly advantageous [23].

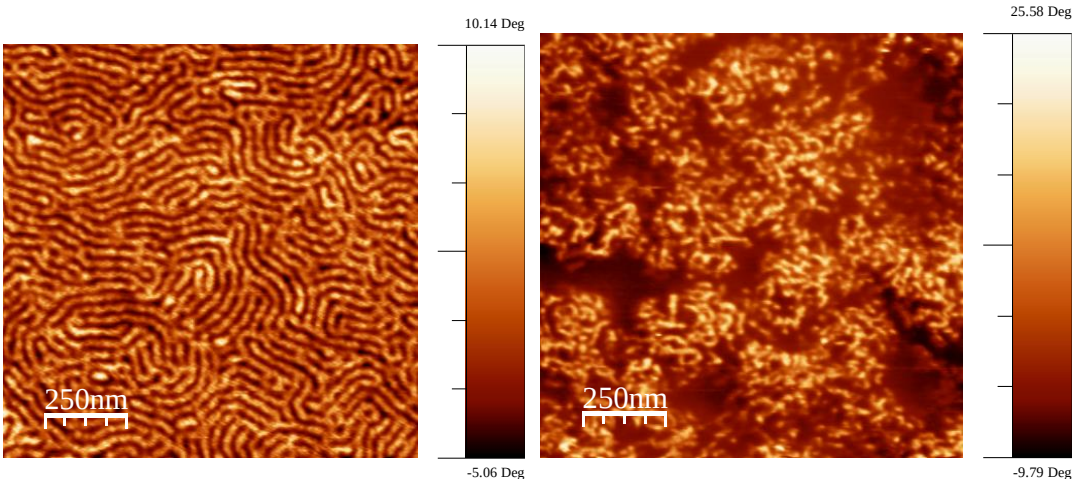
Lately it has been reported that PS-*b*-PBMA, PS-*b*-PHMA, polystyrene-*b*-poly (pentyl methacrylate) (PS-*b*-PPMA), polybutadiene-*b*-polyisoprene (PB-*b*-PI) and poly(ethylene propylene)-*b*-poly(ethyl methylene) (PEP-*b*-PEE) block copolymers exhibit pressure-induced miscibility while PS-*b*-PI and PS-*b*-PB exhibit opposite behavior [10-11, 23]

Another study was done by Kim *et. al.*.They have examined the influence of hydrostatic pressure on closed-loop phase behavior of deuterated polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymers, dPS-PnPMA [24].

The order-to-disorder transition temperature in previous studies has been reported higher than the T_g of both components in block copolymers. However In 2003, baroplastic systems with a high T_g and low T_g has been investigated in terms of processing at ambient temperatures. It has been revealed that, this kind of baroplastic systems may flow due to a semi-solid partial mixing mechanism caused by the pressure. After all high T_g phase is substantially preserved [12].

Recently the pressure-induced miscibility of a block copolymer is studied by AFM and clearly explained in PhD thesis of Sebnem İnceoglu [25]. The images were quite impressive since it provides a clear view of the miscibility of block copolymer domains by the effect of pressure. PEHA-*b*-PS-*b*-PEHA triblock copolymer (52% PEHA) reveals a lamellar structure initially. After processing (300 $kg.cm^{-2}$, 5 min) at room temperature, the lamellar structure is impaired and the initially observed phase seperation became less identified. The mentioned effect of pressure is also reported for $(PS\text{-}b\text{-}PEHA)^{4*}$, 4-arm star-block copolymers and $(PEHA\text{-}b\text{-}PS)^{4*}$, 4-arm star-

block copolymers as well. In Figure 2.6, PEHA-*b*-PS-*b*-PEHA triblock copolymer (52% PEHA) AFM images before, (a), and after, (b), processing are given as a representative example to exhibit the pressure-induced miscibility of block copolymers.



a b

Figure 2.6 : AFM images of PEHA-*b*-PS-*b*-PEHA triblock copolymer (52% PEHA) films a) before, and b) after processing (300 kg.cm^{-2} , 5 min)

As mentioned before baroplastic materials reveal a melt-like behaviour by the effect of pressure. The advantages of baroplastics are well defined by Mayes group and expressed clearly as low-temperature formability, lower energy consumption in manufacture and processing, reduced use of additives, faster production and improved recyclability and potential alternatives to current thermoplastic elastomers, rubber-modified plastics, and semi-crystalline polymers systems [12].

As studies focused on pressure processing of several block copolymers, the topologies altered and variable topologies of different baroplastics are well reported by Inceoglu and Acar [26].

In this study we have studied pressure induced processibility of homopolystyrene blended with PS-*b*-PEHA, PEHA-*b*-PS-*b*-PEHA and PS-*b*-PEHA-*b*-PS block copolymers since a baroplastic property is observed for PS-*b*-PEHA (52 wt. % PEHA) recently [12]. Besides polystyrene is a commodity plastic which is used in every part of daily life and many other applications. ATRP and AGET ATRP methods are used to synthesize mentioned polymer mentioned polymerization

techniques are controlled polymerization techniques that enable synthesis of polymers with desired molecular weights/compositions and low dispersities.

2.4 Controlled/Living Radical Polymerizations

Most of the synthetic polymers are synthesized by free radical polymerization since the production conditions are simple to achieve and many vinyl monomers can undergo a homopolymerization and copolymerization. A deoxygeniazied system with modarate temperature is satisfactory for free radical polymerization and the system has tolerance for moisture and impurities. Eventhough the free radical polymerization have advantages in terms of production, it is not possible to synthesize well-defined polymers.

Controlled/living radical polymerization is actually a similar approach to free radical polymerization, the main difference between two polymerization technique is the way how the radicals are generated. The generation of radicals in conventional radical polymerization is quite slow and irreversible, though the propagation is as fast as monomer addition in every 1 ms. Termination is emerged by combination or disproportionation. As the propagation is this fast it is not possible to control the molecular weight or adding another monomer etc.

In controlled/living radical polymerization the radical formation is reversible, the radicals are generated and consumed rapidly in the initiation stage but the propagation happens slowly enabling the controlled growing of the chains. Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and degenerative transfer processes such as reversible addition-fragmentation chain transfer (RAFT) [27].

ATRP has been one of the controlled/living radical polymerization that has been investigated last 15 years. ATRP enables the synthesis of special block copolymers. In this study we employed ATRP and AGET ATRP for synthesizing block copolymers and homopolymers.

2.4.1 Atom transfer radical polymerization (ATRP)

Fast initiation, slow propagation, predicted polymerization degree, preventing chain transfers and terminations by lowering the energy and equilibrium between growing

radicals and dormant chains should be establish for controlled/living radical polymerizations. Accordingly an ATRP has features of consuming of initiator at the early stages of reaction. The polymerization degree is predicted by Δ[M]/[I]. The propagation is slow in comparison to initiation step, the added number of monomer to active chain is small during one activation step so that the syntesized polymer has a low polydispersity. Most important feature of polymers synthesized by ATRP for our study is the preserved end functionality of chains allowing us to build block copolymers.

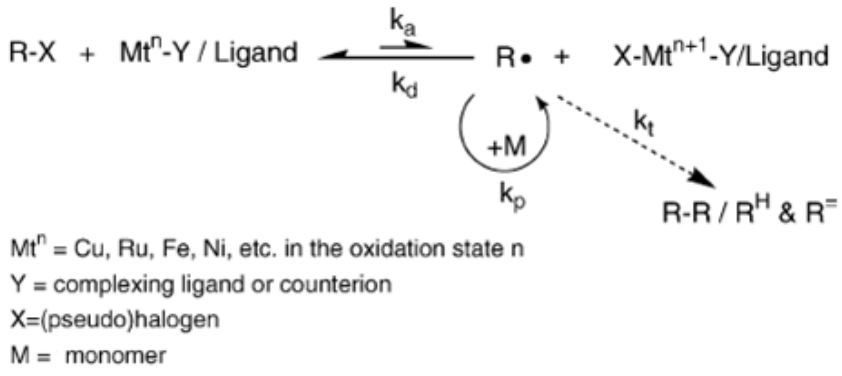


Figure 2.7 : Mechanism for ATRP.

A general mechanism for ATRP is represented in Figure 2.7 [28]. The radicals or the active species, are generated through a reversible redox process catalyzed by a transition metal complex (M_t^n-Y/Ligand, where Y may be another ligand or the counterion) which undergoes an electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, R-X. This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Irreversible termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, X-M_t^{n+1}, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination. A successful

ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation [29].

2.4.1.1 Kinetics and mechanism of ATRP

First-order kinetics behavior, i.e. the polymerization rate (R_p) with respect to the monomer concentration ([M]) is a linear function of time (2.2 and 2.3). This is due to the lack of termination, so that the concentration of the active propagating species ([P*]) is constant (k_p is the propagation constant).

$$R_p = \frac{-d[M]}{dt} = k_p[P^*][M] \qquad \textbf{(2.2)}$$

$$\ln \frac{[M]_0}{[M]} = k_p[P^*]t = k_p^{app} t \qquad \textbf{(2.3)}$$

The consequence of equation 2.2 and the effect of changes in P* are illustrated in Figure 2.8. It shows that a typical linear variation of conversion with time in semilogarithmic coordinates. Such linear behavior indicates that there is a constant concentration of active species [P*] in the polymerization [29].

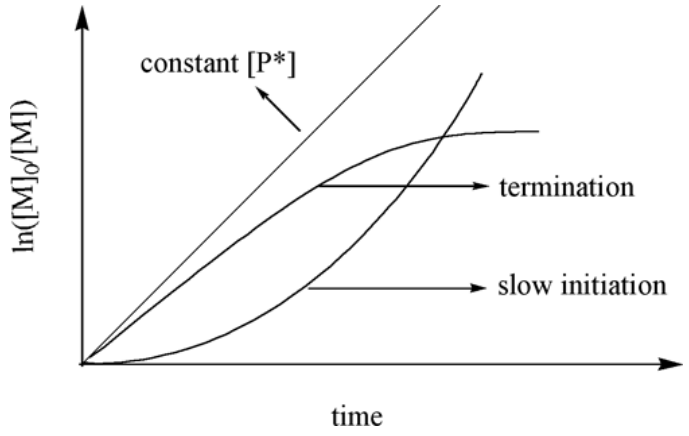


Figure 2.8 : Illustration of the dependence of $\ln([M]_o/[M])$ on time.

This semilogarithmic plot is very sensitive to any change of the concentration of the active propagating species. An upward curvature indicates an increase in [P*], which occurs in case of slow initiation. On the other hand, a downward curvature suggests a decrease in [P*], which may result from termination reactions increasing the concentration of the persistent radical, or some other side reactions such as the

catalytic system being poisoned or redox processes on the radical. It should also be noted that the semilogarithmic plot is not sensitive to chain transfer processes or slow exchange between different active species, since they do not affect the number of the active propagating species.

Predeterminable degree of polymerization (X_n), i.e. the number average molecular weight (M_n) is a linear function of monomer conversion.

$$X_n = \frac{M_n}{M_0} = \frac{\Delta[M]}{[I]_0} = \frac{[M]_0}{[I]_0}(conversion) \qquad \textbf{(2.4)}$$

This result comes from a constant number of chains throughout the polymerization, which requires the following two conditions: that initiation should be sufficiently fast so that nearly all chains start to grow simultaneously; no irreversible chain transfer occurs that increases the total number of chains. The following Figure 2.9 shows that the ideal growth of molecular weights with conversion, as well as the effects of slow initiation and chain transfer on the molecular weight evolution.

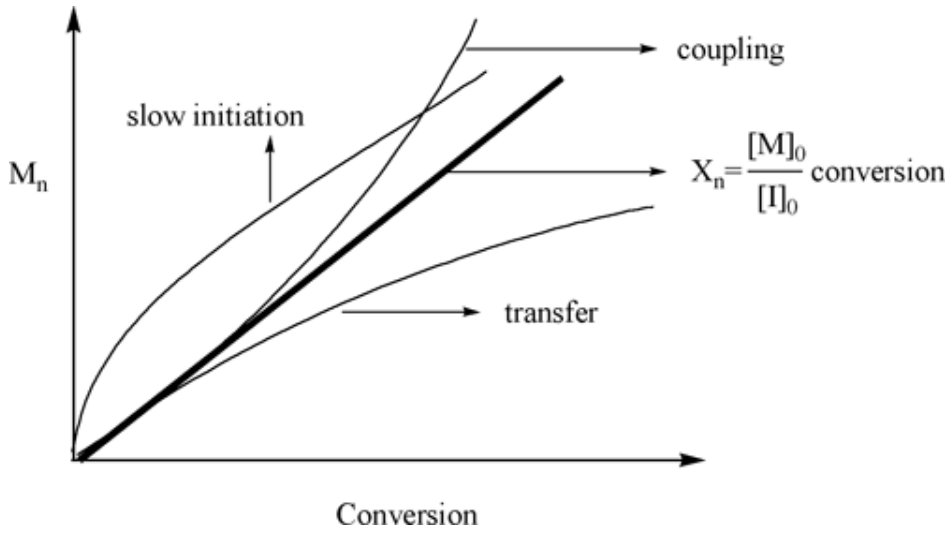


Figure 2.9 : The dependency of molecular weight on conversion.

It is important to recognize that the evolution of molecular weight is not very sensitive to irreversible chain termination, since the number of chains remains unchanged. The effect of termination is only observable on the plot when coupling reactions for polymers with very high molecular weights start to play a significant role. *Narrow molecular weight distribution (polydispersity)*, although this feature is very desirable, it is not necessarily the result of a controlled polymerization, which

only requires the absence of irreversible chain transfer and irreversible termination, but ignores the effect of rate of initiation, exchange and depropagation. Substantial studies [30-32] indicate that in order to obtain a polymer with a narrow molecular weight distribution, each of the following five requirements should be fulfilled.

1. The rate of initiation is competitive with the rate of propagation. This condition allows the simultaneous growth of all the polymer chain.
2. The exchange between species of different reactivity is faster than propagation. This condition ensures that all the active chain termini are equally susceptible to reaction with monomer for a uniform growth.
3. There must be negligible irreversible chain transfer or irreversible termination.
4. The rate of depropagation is substantially lower than propagation. This guarantees that the polymerization is irreversible.
5. The system is homogenous and mixing is sufficiently fast. Therefore all active centers are introduced at the onset of the polymerization.

This should yield a Poison distribution, as quantified in equation 2.5.

$$\frac{X_w}{X_n} = \frac{M_w}{M_n} = 1 + \frac{X_n}{(X_n + 1)^2} \cong 1 + \frac{1}{X_n} \qquad \textbf{(2.5)}$$

According to equation 2.5, polydispersity (M_w/M_n, PDI) decreases with increasing molecular weight. Systems with slow exchange do not follow this perfect distribution but PDI's are defined by the following equation.

$$PDI = \frac{M_w}{M_n} = 1 + \left(\frac{k_p [RX]_o}{k_{deact} [Cu^{II} LnX]} \right) \left(\frac{2}{Conv.} - 1 \right) \qquad \textbf{(2.6)}$$

Equation 2.6 explains how the polydispersities in polymerization systems with relatively fast exchange decrease with conversion, $[R\text{-}X]_o$ corresponds to the concentration of dormant polymer chains and $[Cu^{II}\ LnX]$ is the concentration of deactivator. Polydispersities are higher for low conversion stages due to the fact that, X_n ratio of long chains to short chains (i.e. difference of chain length) is bigger than high conversion stages. Second, the final polydispersities should be higher for higher

values of the ratio, k_p/k_{deact}. Thus, under similar condition, the polymerization of acrylates yields higher polydispersities than that of styrene, because k_p for acrylates is much larger than for styrene [33]. A polymerization that satisfies all five prerequisites listed above is expected to form a final polymer with a polydispersity less than 1.1 for X_n greater than 10.

2.4.2 Components of ATRP

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

2.4.2.1 Monomers

In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. However, even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species [34].

Each monomer possesses an intrinsic radical propagation rate, so the concentration of propagating radicals and the rate of radical deactivation may need to be adjusted to maintain polymerization control. For the polymerization of each monomer, the corresponding alkyl halide end group will possess its own unique redox potential. Therefore, in combination with the same metal catalyst, each end group will exhibit a different atom transfer equilibrium constant, deactivation rate constant, and corresponding concentration of propagating radicals [33].

2.4.2.2 Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

A variety of halogenated initiators and macro initiators activated by various types of aryl, sulfonyl and carbonyl groups can be used in ATRP systems. In ATRP, alkyl halides (R-X) are typically used as initiator. The (pseudo) halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex [35].

2.4.2.3 Catalyst and transition metals

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. The metal center must have at least two readily accessible oxidation states separated by one electron. The metal center should have reasonable affinity toward a halogen. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo) halogen. The ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species. A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe, Ni, Ru, etc. have been used to some extent [29, 36]

2.4.2.4 Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions. [35]. In this study, *'N,N,N,N,N*-Pentamethyl diethylene triamine (PMDETA) and Tris(2-(dimethylamino)ethyl)amine(Me_6TREN), bipyrdine are used as ligands for solubilizing the metal complex.

2.4.2.5 Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers.

2.4.2.6 Temperature and reaction time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures. The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight. Therefore, for successful ATRP, optimum temperature should be found depending on the monomer, catalyst and the other components of ATRP [29].

2.4.3 Activators generated by electron transfer (AGET) ATRP

Classic ATRP method is a controlled polymerization method which enables the synhesis of homopolymers, copolymers, branched, star and grafted polymers etc. with lower PDI. However transition metal compounds might oxidize thus special care should be taken. To overcome mentioned problem of ATRP, reverse ATRP and AGET ATRP methods are developed. Reverse ATRP method has some limitations as well. The transferable atom (X) is added to the reaction thus the generated higly active catalyst complex restricts the formation of block copolymers. To overcome the mentioned problems of ATRP and reverse ATRP, a new method was developed by Jakubowski and Matyjaszewski. They reported that: "The procedure used to generate activator relies on electron transfer rather than reduction by organic radicals; therefore, this method is called AGET ATRP. This novel procedure has all the benefits of a normal ATRP process combined with the additional benefit of adding the catalyst complex to the reaction mixture in its more stable higher oxidation state" [37].

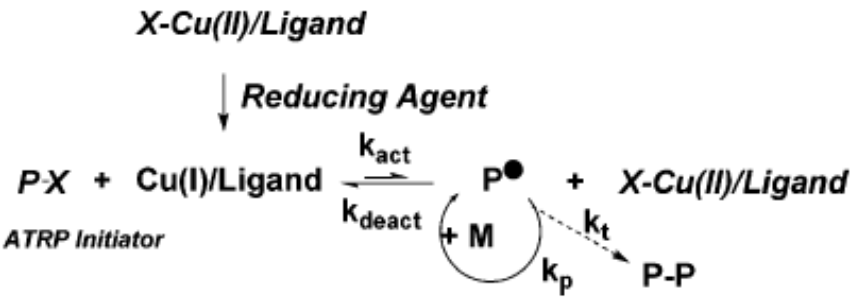


Figure 2.10 : Mechanism for AGET ATRP

3. EXPERIMENTAL PART

3.1 Chemicals

Styrene (S, 99 %, extra pure), 2-ethyl hexyl acrylate (EHA, 99 %, stabilized), copper (I) chloride (CuCl), copper (I) bromide (CuBr, 98 %), copper (II) bromide ($CuBr_2$, 98 %), ethyl-2-bromo propionate (EBP, 99 %), bipyridine *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99 %), ethylene glycol (99+ %), ascorbic acid (AA) were purchased from Acros. 2-Bromopropionylbromide (BPB, 97 %) were purchased from Aldrich. Sodium sulphate, anhydrous (Na_2SO_4, 99 %), tetrahydrofuran (THF), methanol (MeOH), and dichloromethane (CH_2Cl_2) were purchased from J.T. Baker. Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized as described in litrature [38-40].

3.2 Synthesis of Di-functional ATRP Initiator

Ethylene glycol (7.28 mL, 130 mmol) and triethylamine (39.87 mL, 286 mmol) were placed into a 500 mL round-bottom flask with 50 mL of CH_2Cl_2 (anhydrous). The reactor was cooled to 0 °C in an ice/water bath, and a solution of BPB (29.96 mL, 286 mmol) and 70 mL of CH_2Cl_2 was added dropwise with stirring over a period of 1 hour. After complete the adding solution, the reactor was kept at 0 ^oC for 3 hours while stirring. A white precipitate of triethylammonium bromide formed upon addition of the acid bromide.

The reaction was left to react for 2 days and allowed to warm to room temperature of its own accord. Upon completion the ammonium salt removed by filtration and the mixture was transferred to a separatory funnel with 300 mL of CH_2Cl_2 and extracted consecutively with 200 mL of distilled water, 200 mL of $NaHCO_3$(aq), and 200 mL of distilled water. The organic phase was dried over Na_2SO_4 (anhydrous) and filtered and the solvent removed by rotary evaporation and then by under reduced pressure.

The product was distilled under vacuum (bp: 140 ^{o}C, 4 mbar) to give colourless oil. (2-Br*, 330 g/mol, ethylene glycol bis(2-bromopropionate), yield: 24.25 g, 63.5%)

^{1}H NMR ($CDCl_3$), δ: 4.37-4.29 (m, 6H, C-$\underline{CH_2}$-O-C(O)-$\underline{CH}$-(CH_3)Br), 1.78-1.75 (d, 6H, CH(Br)-$\underline{CH_3}$) ppm.

3.3 Synthesis of Linear Polystyrenes

A typical ATRP or AGET-ATRP procedure was performed for synthesis of polystyrenes. For ATRP, the catalyst (CuBr or CuCl) was placed in a flask which was sealed with a Teflon stopper and contained a side arm with a Teflon valve (Chemglass). The flask was deoxygenated by vacuum-thaw-nitrogen cycles. Styrene (S) as monomer, PMDETA as ligand, toluene as solvent and finally ethyl-2-bromo propionate (EBP) were added as initiator. All liquid components were sparged with nitrogen prior to transferring them into the flask. The mixture was sparged with nitrogen for 10 min prior to placing it in a thermostatically controlled oil bath at 110 ^{o}C and 400 rpm stirring rate.

After the required time, the polymerization was terminated with methanol and diluted with CH_2Cl_2, then passed through neutral alumina to remove the catalyst and precipitated into methanol. The product was dried in vacuum. Conversion was calculated gravimetrically.

3.4 Synthesis of Linear Macro-initiators

Polystyrene (PS) and poly(2-ethyl hexyl acrylate) (PEHA) macro-initiators were prepared by ATRP of styrene and 2-ethyl hexyl acrylate. Also AGET-ATRP is used in order to synthesize one of the PS macroinitiators.

A typical ATRP procedure was performed as follows; the catalyst, CuBr or CuCl was placed in a flask which was sealed with a Teflon stopper and contained a side arm with a Teflon valve (Chemglass).

The flask was deoxygenated by vacuum-thaw-nitrogen cycles for three times. S or EHA as a monomer, bipyr, Me_6TREN or PMDETA as a proper ligand and toluene as solvent and finally, an EBP or di-functional ATRP initiator were added. All liquid components were sparged with nitrogen prior to transferring them into the flask. The

mixture was sparged with nitrogen for 10 min prior to placing it in a thermostatically controlled oil bath at required temperature and 400 rpm stirring rate.

After the required time, the polymerization was terminated with methanol and diluted with THF, then passed through neutral alumina to remove the catalyst and precipitated into methanol. The product was dried in vacuum.

For AGET-ATRP, the catalyst, $CuBr_2$ and ascorbic acid as reducing agent were placed S as monomer, PMDETA as ligand, toluene as solvent and finally EBP as initiator were added. All liquid components were sparged with nitrogen prior to transferring them into the flask. The mixture was sparged with nitrogen for 10 min prior to placing it in a thermostatically controlled oil bath at 70 ^{o}C and 400 rpm stirring rate.

3.5 Synthesis of Block Copolymers

Block copolymers were synthesized according to one-pot or two-pot method. A typical ATRP procedure was performed. For two-pot method firstly, PS or PEHA were synthesized as described in **3.4** and then one of these homopolymer as a macro-initiator and CuBr or CuCl as a catalyst were placed in a flask which was sealed with a Teflon stopper and contained a side arm with a Teflon valve (Chemglass). The flask was deoxygenated by vacuum-thaw-nitrogen cycles for three times., EHA or S as a monomer, PMDETA as a ligand, toluene as solvent were added to the flask. All liquid components were sparged with nitrogen prior to transferring them into the flask. The mixture was sparged with nitrogen for 10 min prior to placing it in a thermostatically controlled oil bath at required temperature and 400 rpm stirring rate. To be able to control the molecular weight of polymer, periodically taken samples were injected to gel permeation chromatography (GPC). Conversion was calculated gravimetrically. For one-pot method, once first monomer polymerized to complete conversion, the second monomer was added to the flask under nitrogen atmosphere to obtain the block copolymers. In this cases, the samples were taken periodically via a syringe to follow the molecular weight of the polymer by GPC and the conversion of polymerization by gas chromatography (GC) measurements.

3.6 Processing of Baroplastic Block Copolymer/Homopolystyrene Blends

Baroplastic materials reveal a pressure-induced miscibility at ambient temperatures. In order to observe the processibility properties of the synthesized baroplastics with homopolymers, variable blends are prepared. Prepared blends are processed with compression and some of the blends with extrusion molding.

blends in powder forms were introduced into the compression mold (IR pellet mold), which then was closed carefully, placed in the center region of the press and pressed at room temperature.

For compression molding 0.1 g of block copolymers/homopolymer blend in powder form was placed into the compression mold (IR pellet mold), which then was closed carefully, placed in the center region of the press and pressed at room temperature (6 ton, 300 $kg.cm^{-2}$). The amount of polymer was set according to the previously done studies of the effect of sample weight on processibility. For extrusion molding 0.7 g blend was takento produce 3-5 cm tape..

3.7 Recycling of Baroplastic Block Copolymer/Homopolystyrene Blends

To observe the recycling abilities of baroplastic/homopolystyrene blends, extruded blend samples were chopped into little pieces mechanically by a razor. The chopped samples were fed to the extrusion mold and the mold was placed under manual press and processed at room temperature under pressure (approx. 100 $kg.cm^{-2}$, piston diameter: 12 mm). Re-extursion of the samples is repeated for 15 times and each time is referred as “1 processing cycle”.

3.8 Measurements and Characterization

3.8.1 Nuclear magnetic resonans spectroscopy (NMR)

To identify the character of initiators and the compositions of block copolymers, they were dissolved in deuterated chloroform ($CDCl_3$), and the ^1H NMR spectra were measured on a Bruker AC250 (250 MHz) NMR spectrometer with the internal reference.

3.8.2 Gel permeation chromatography (GPC)

The molecular weights and polydispersities of polymers were measured by a gel permeation chromatography (GPC) system consisting of an Agilent 1200 series pump, three Waters Styragel HR columns (guard, 4, 3) and an Agilent 1100 series RI detector with a THF flow rate of 1 mL/min, poly(methyl methacrylate) or polystyrene were used as calibration standards.

3.8.3 Atomic force microscopy (AFM)

Atomic force microscopy characterization was performed at 25 ^{o}C in air. The morphological observation of the samples was conducted on a Nanoscope IIIa scanning probe microscope (Veeco, Digital Instruments, Multimode Model, High Resolution Scanner Serial No: 4683ev, Santa Barbara, CA) in a tapping mode. A silicon tip (Olympus) with spring constant 28.81 N/m and resonans frequency of 281.4 kHz were used. Tapping mode in 2-3 Hz scanning rate was used for measurements. WSxM software was used to process data [41].

3.8.4 Differential scanning calorimeter (DSC)

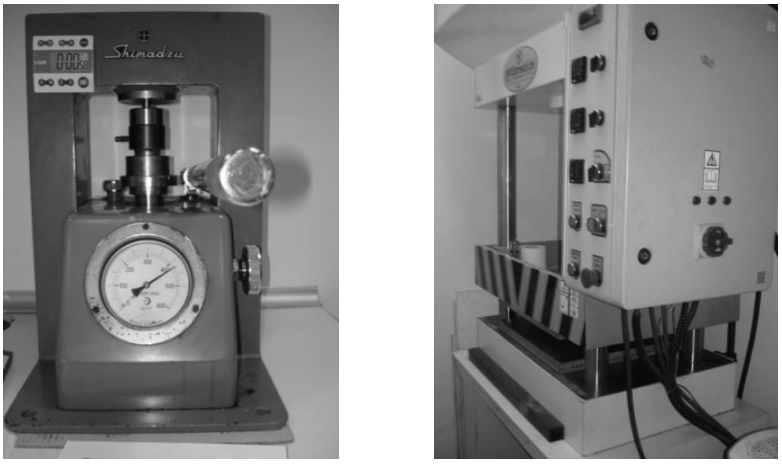
Differential scanning calorimetry (DSC) measurements using Q1000 (TA Instruments) were evaluated from the second heating run from -90 ^{o}C to 200 ^{o}C with a ramp rate of 10 ^{o}C/min for both heating and cooling.

3.8.5 Gas chromatography (GC)

Monomer conversions were determined using a Perkin Elmer AutoSystem XL gas chromatography (GC) equipped with an FID dedector using a SGE-G4 capillary column (30 m lenght, 0.25 mm ID, 0.25 μm film thickness). Injector and dedector were kept constant at 280 and 285 ^{o}C, respectively. Analysis was carried out isothermally starting from 40 ^{o}C holding for 1 min followed by an increased temperature to 200 ^{o}C at a heating rate of 40 ^{o}C/min and holding at 200 ^{o}C for 1 min. Conversions were calculated by dedecting the decrease of the monomer peak areas (monomer consumption) relative to the peak areas of toluene as an internal standard.

3.8.6 Manuel and hydraulic presses

For compression molding, a Shimadzu manual press (Figure 3.1-a) having up to 10 ton at 600 $kg.cm^{-2}$ capacity was utilized and a special ordered, heat and pressure controlled Hursan hydraulic press (Figure 3.2-b) having up to 40 ton at 250 $kg.cm^{-2}$ capacity was used.



a b

Figure 3.1 : a) Manuel press (Shimadzu), b) Hydrolic press (Hursan)

3.8.7 Compression and extrusion molds

The processing of baroplastic materials is similar to the processing of industrial plastics but high temperatures are required for shaping commodity plastics whereas baroplastic materials can be shaped at room temperature. The extrusion molds used for baroplastics are in similar design with the molds used for industrial plastics. By the molds that are used in this study, strips of 8 mm x 1 mm are formed.

The employed mold consist of two seperable main parts, surrounded by a steel outer ring which enables the assembly of two main parts even under pressure. The outer ring squezes tightly the two main parts during processing so that polymer do not escape into the cavities of the mold, on the other hand it can be opened when the ejection of the sample is desired.

a b

Figure 3.2 : a) Tape process mold with two body parts, b) A strip mold body and the body of the circle clamp

4. RESULTS AND DISCUSSION

The aim of this thesis is to observe processibility of baroplastic with homopolystyrene blends. In this section, the synthesis and characterization of mentioned baroplastics and homopolystyrenes will be demonstrated and related discussions will be done in detail.

4.1 Synthesis of Homopolystyrenes

Homopolystyrenes was synthesized as macro-initiator for di-block or tri-block copolymer synthesis and/or a component for baroplastic homopolystyrene blend. The polystyrenes have different molecular weights for observing the molecular weight effect of homopolymer in a baroplastic blend system. In addition, for achieving different topologies and variable molecular weight di-block, tri-block copolymers, homopolystyrenes was synthesized with different molecular weights.

Mono-functional polystyrenes (PS-X) were synthesized by ATRP or AGET-ATRP and di-functional (X-PS-X) were synthesized via ATRP using 2,2′-bipyridine and PMDETA as the ligand for complexation with CuX halide salts. Ethyl-2-bromo propionate was used as ATRP or AGET-ATRP initiator for synthesis of PS-X while synthesized di-functional ATRP initiator was used for X-PS-X. Ascorbic acid (AA) was used as reducing agent for polymers synthesized via AGET-ATRP. The characteristics of homopolystyrenes are given in Table 4.1.

Table 4.1 : Characteristics of PS-X and X-PS-X homopolystyrenes.

Run	$[M]_o$ (mol L^{-1})	$[M]_o$:$[I]_o$	Time (h)	Conv. (%)	$M_{n,GPC}$ [f]	M_w/M_n [f]
PS1[a]	4.65	400	140.00	71.7	12600	1.17
PS2[b]	5.24	192	19.00	72.2	17500	1.07
PS3[c]	7.91	100	26.50	94.0	20000	1.17
PS4[d]	8.72	300	22.00	46.0	24900	1.15
PS5	6.00	200	17.30	92.0	31800	1.12
PS6[c]	8.72	400	27.50	78.0	40400	1.16
PS7[e]	8.72	609	18.00	89.5	52200	1.22
PS8[c]	7.91	400	26.50	90.0	52400	1.12

[a] T: 70 °C, $[EBP]_o$:$[CuBr_2]_o$:$[PMDETA]_o$:[AA] = 1 : 0.2 : 2 : 2
[b] T: 100 °C
[c] T: 110 °C, $[EBP]_o$:$[CuBr]_o$:$[PMDETA]_o$= 1:1:1,
[d] T: 100 °C, $[2\text{-}Br^*]_o$:$[CuBr]_o$:$[Bipyr]_o$= 1:2:2
[e] T:110 °C$[EBP]_o$:$[CuCl]_o$:$[PMDETA]_o$= 1:1:1.
[f] Calculated from GPC calibrated with linear polystyrene standards

4.2 Synthesis of PS-*b*-PEHA by ATRP

There are two different methods for block copolymer synthesis by ATRP method: one pot and two-pots. In this thesis two-pots method was employed for synthesis of di-block copolymers where firstly one monomer was polymerized in first batch and after several purification, first polymer was used as macro-initiator for the second monomer [42]. $[M]_o/[I]_o$ ratios are setted in changing values to be able to have different molecular weights and compositions of diblock copolymers. The molar analysis of block copolymers was calculated by ^1H NMR, as related peaks integration give molar ratios of di-block copolymer components.

PS-*b*-PEHA diblock copolymers are synthesized by using previously synthesized polystyrenes as macro-initiator, CuBr as catalyst, PMDETA as ligand and finally toluene as solvent. The characteristics of di-block copolymers are given in Table 4.2.

Table 4.2 : Characteristics of the PS-*b*-PEHA di-block copolymers[a]

Run	$[M]_o$ mol L^{-1}	$[M]_o$:$[I]_o$	Macro initiator	$M_{n,GPC}$ (MI)	Time (h)	Conv. (%)	$M_{n,GPC}$[b]	M_w/M_n[b]	Comp.[c] (PEHA, %)
BP1[d]	1.62	200	PS2	17500	17	56	25600	1,51	49
BP2[e]	2.68	500	PS1	12600	18	29	33000	1.46	55
BP3[f]	2.67	600	PS6	40400	19	52	60000	1.58	50

[a] T: 90 °C
[b] Calculated from GPC calibrated with linear polystyrene standards
[c] Compositions were calculated by ^{1}H NMR analysis
[d] $[PS\text{-}Br]_o$:$[CuCl]_o$:$[PMDETA]_o$ = 1:2:3
[e] $[PS\text{-}Br]_o$:$[CuBr]_o$:$[PMDETA]_o$ = 1:1:1
[f] $[PS\text{-}Br]_o$:$[CuBr]_o$:$[PMDETA]_o$ = 1:5:5

The molecular weights and polydispersities of di-block copolymers are traced by GPC. The elution time is lowered compared to the homopolystyrene which was used as macro-initiator for di-block copolymer synthesis. The di-block copolymer formation observed for BP1 by GPC is given as an example in Figure 4.1.

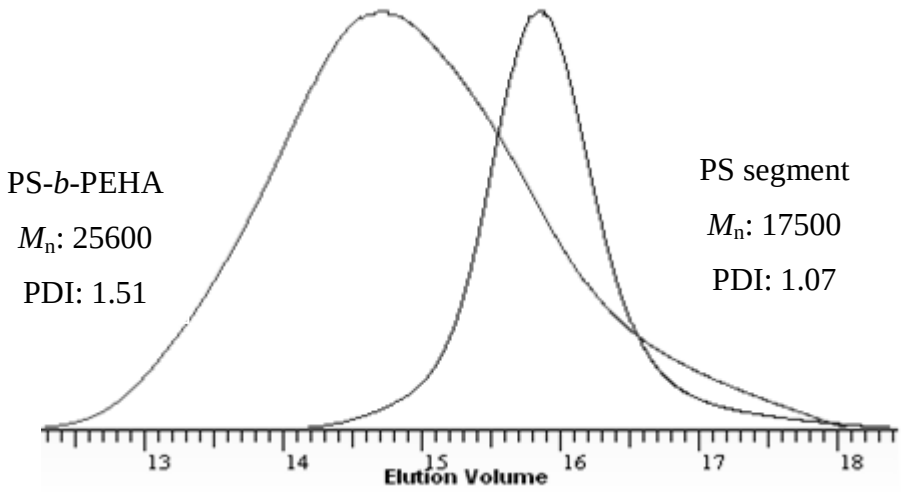


Figure 4.1 : GPC traces of the PS segment (PS2) and PS-*b*-PEHA di-blockcopolymer (49 % PEHA, BP1).

The block copolymer's composition was calculated using ^{1}H NMR measurements by integrating the characteristic peak of the PEHA segment (-C(O)O$\underline{CH_2}$-) at 3.9 ppm versus the aromatic peaks of the PS segment at 6.34-7.06 ppm. ^{1}H NMR spectrum of $PS_{0.49}$-*b*-$PEHA_{0.51}$ diblock copolymer (BP1) in $CDCl_3$ was shown in Figure 4.2.

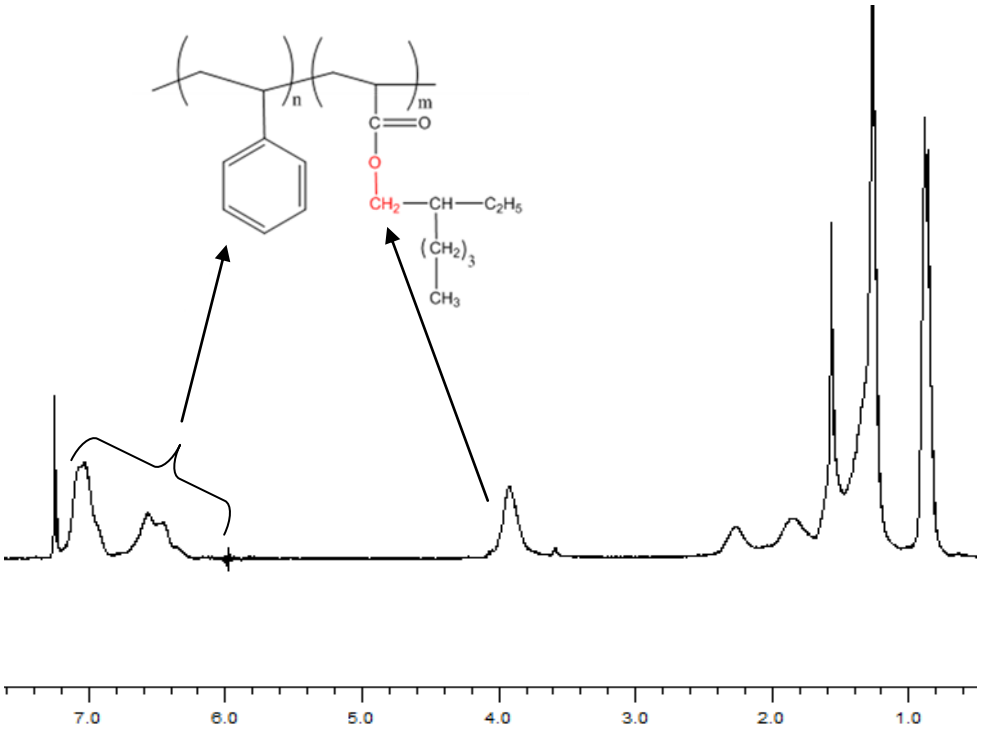


Figure 4.2 : ^{1}H NMR spectrum of $PS_{0.49}$-*b*-$PEHA_{0.51}$ diblock copolymer (BP1) in $CDCl_3$.

4.3 Synthesis of PEHA-*b*-PS-*b*-PEHA by ATRP

Two-pot ATRP method is used to synthesize triblock copolymer similar to di-block copolymer synthesis. However the macro-initiator used (polystyrene) is di-functional (X-PS-X). The molar analysis of block copolymers was done by ^{1}H NMR, as related peaks integration give molar ratios of diblock copolymer components. PEHA-*b*-PS-*b*-PEHA triblock copolymers are synthesized by using previously synthesized polystyrene (PS4) as macroinitiar, CuBr as catalyst, PMDETA as ligand, EHA as monomer and finally toluene as solvent. Characteristics of the PEHA-*b*-PS-*b*-PEHA triblock copolymers is shown in Table 4.3.

Table 4.3 : Characteristics of the PEHA-*b*-PS-*b*-PEHA triblock copolymers[a]

Run	$[M]_o$	$[M]_o$:$[I]_o$	Macro initiat.	$M_{n,GPC}$ (MI)	Time (h)	Conv (%)	$M_{n,GPC}$[b]	M_w/M_n[b]	Comp.[c] (PEHA,%)
BP4	1,67	300	PS7	24900	15	70	62500	1,87	57

[a] T: 100 °C, $[X\text{-}PS\text{-}X]_o$:$[CuBr]_o$:$[PMDETA]_o$ = 1:2:2.
[b] Calculated from GPC calibrated with linear polystyrene standards.
[c] Compositions were calculated by ^1H NMR analysis.

4.4 Synthesis of PS-*b*-PEHA-*b*-PS by ATRP

The PS-*b*-PEHA-*b*-PS tri-block copolymer was synthesized via one-pot synthetic routes as shown in Figure 4.3 and previously synthesized di-functional ATRP initiator is used [ethylene glycol bis(2-bromopropionate)]. The chacteristics of synthesized PS-*b*-PEHA-*b*-PS tri-block copolymer is given in Table 4.4.

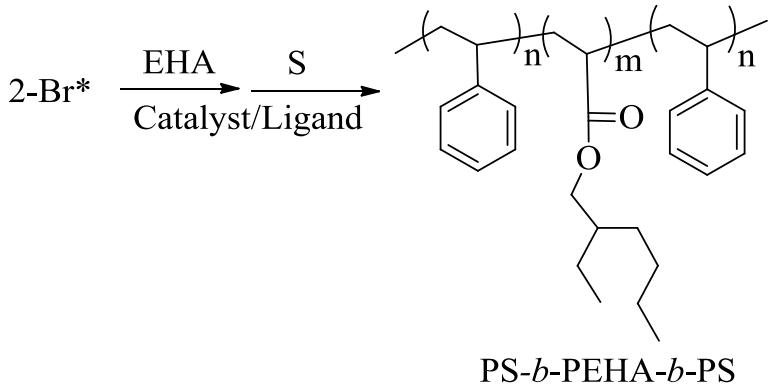


Figure 4.3 : Synthesis of PS-*b*-PEHA-*b*-PS tri-block copolymer.

Table 4.4 : Characteristics of the PS-*b*-PEHA-*b*-PS tri-block copolymer[a]

Run	$[M]_o$	$[M]_o$:$[I]_o$	Macro initiat.	$M_{n,GPC}$ (MI)	Time (h)	Conv (%)	$M_{n,GPC}$[b]	M_w/M_n[b]	Comp.[c] (PEHA,%)
BP5[b]	1,9	98	-	18800	19	70	30200	1,49	50

[a] T: 70 °C, $[2\text{-}Br^*]_o$:$[CuCl]_o$:$[Me_6TREN]_o$= 1:1.5:1.5
[b] Calculated from GPC calibrated with linear polystyrene standards.
[c] Compositions were calculated by ^1H NMR analysis.

4.5 Blending Baroplastic Block Copolymers with Homopolystyrenes

To obtain a homogenous blend, a physical mixing was performed to the components of the blend, in this case baroplastic materials and homopolystyrenes. According to the desired blending ratios, baroplastic materials and homopolystyrenes were weighed and dissolved in CH_2Cl_2, finally obtained blend solution was precipititated in MeOH. The blend solution was stirred for one night and a slow evoporation of solvent was carried out. Finally obtained polymer blend was kept in vacuum oven at 55 ^oC. Prepared blends of baroplastic block copolymers and homopolymers are given in Table 4.5.

Table 4.5 : Blends of baroplastic block copolymers and homopolystyrenes

Baroplastic Name	Baroplastic Structure and molecular weight	Blended Homopolystyrene and molecular weight	Weight percent of Baroplastic in the blend (wt.%)
BP1	Di-block copolymer $PS_{0,51}$-*b*-$PEHA_{0,49}$ (26K)	PS3 (20 K)	40
			50
			60
		PS5 (32K)	40
			50
			60
		PS7 (52K)	40
			50
			60
BP2	Di-block copolymer $PS_{0.45}$-*b*-$PEHA_{0.55}$ (33K)	PS5 (32K)	40
			50
			60
BP3	Di-block copolymer $PS_{0.50}$-*b*-$PEHA_{0.50}$ (60K)	PS5 (32K)	40
			50
			60
BP4	Tri-block copolymer $PEHA_{0,28}$-*b*-$PS_{0,43}$-*b*-$PEHA_{0,28}$ (62K)	PS8 (53K)	30
			40
			50
			60
			70
BP5	Tri-block copolymer $PS_{0.25}$-*b*-$PEHA_{0.50}$-*b*-$PS_{0.25}$ (30K)	PS5 (32K)	40
			50
			60

4.6 Extrusion and Compression Molding of Baroplastic Block Copolymer/Homopolystyrene Blends

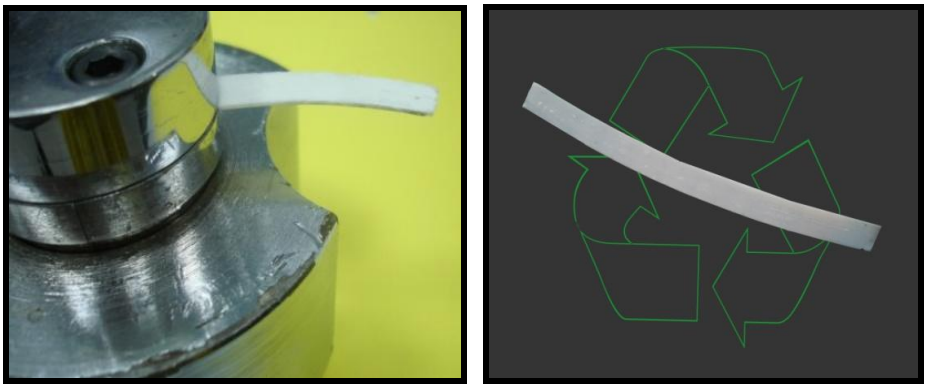
The blends that were prepared according to the mentioned preperation methods were processed under pressure, initially by compression molding. The samples which revealed better processibility properties was extruded by the tape process mold for visually observing the melt-like flow of the blends.

It was previously mentioned in the theoritical part that, the pressure-induced missibility of block copolymers provide a melt-like flow obtaining a processibility for these polymers. A similar approach was observed for the blends of baroplastic block copolymers and homopolystyrenes. It is estimated that the pressure-induced missibility of block copolymers triggers the processibility of homopolystyrene. While a neat homopolystyrene could not be processed under pressure at ambient temperature, baroplastic block copolymer aided homopolystyrenes were processed at mentioned conditions. However not all of the blends were revealed a satisfactory processibility since some of the processed polymers were fallen apart while removing pellets from the mold due to the lack of mechanical strength. As expected, the baroplastic ratio in the blend was significantly important for the processibility of homopolystyrene.

In previous studies of baroplastic materials, it was observed that the baroplastic material processed under pressure becomes transparent [24]. However, blends of baroplastic did not show the same behaviour since the pressure applied blends remains opaque (Figure 4.4). This might be due to the homopolystyrene component in the blend since the neat baroplastic processing leads to transparency.

In this study, the extrusion processibility of some of the blends was investigated, too. Initially the samples were compression processed according to the above mentioned method. The blends that revealed better processibility in compressing processing were tested via extrusion processing as well (Figure 4.5 and 4.6). As mentioned earlier extrusion processing is a technique similar to the industrial extrusion, however the samples are not objected to any temperature and the powder polymer is forced through the extrusion hole just by the pressure effect.

Figure 4.4 : Images of unprocessed and compression molded (100 kg.cm^{-2}, 2 min) samples of BP3/ PS5 blend (40 w% PS5)



a b

Figure 4.5 : Image of extruded tape sample (Piston diameter:12mm, app. 100 kg.cm^{-2}) of a) BP1/PS3 blend (50 w% PS3), b) BP3/PS5 blend (40 w% PS5)

Figure 4.6 : Images of extruded tape sample (Piston diameter:12mm, app. 100 kg.cm^{-2}) of BP1/PS5 (40 w% BPS5)

4.7 Investigation Blend Processibility by DSC Measurements

As mentioned previously, baroplastics consist of two immissible phases. However, these immisible phases become partially miscible by the application of pressure and generate a new mixed phase ($T_{g,mix}$). Thus, after the processing of baroplastics miscible and immiscible phases can be observed within the same structure. There are several methods to identify the mixed phase by DSC.

As explained in theoretical part in details, the addition of homopolymer effects the micro domain structure of block copolymer. In this study homopolymers were blended with block copolymers which reveal baroplastic behaviours caused by the effect of pressure. In blends of block copolymers and homopolystyrene may not be as easy as in neat block copolymers. In Figure 4.7 and Figure 4.8 pressure-induced missibility of a diblock copolymer (BP1) and a triblock copolymer (BP4) are shown respectively by means of DSC thermograms. A mixed phase causes a third T_g value referred as $T_{g,mix}$ which proves that the immisible segments partially becomes miscible.

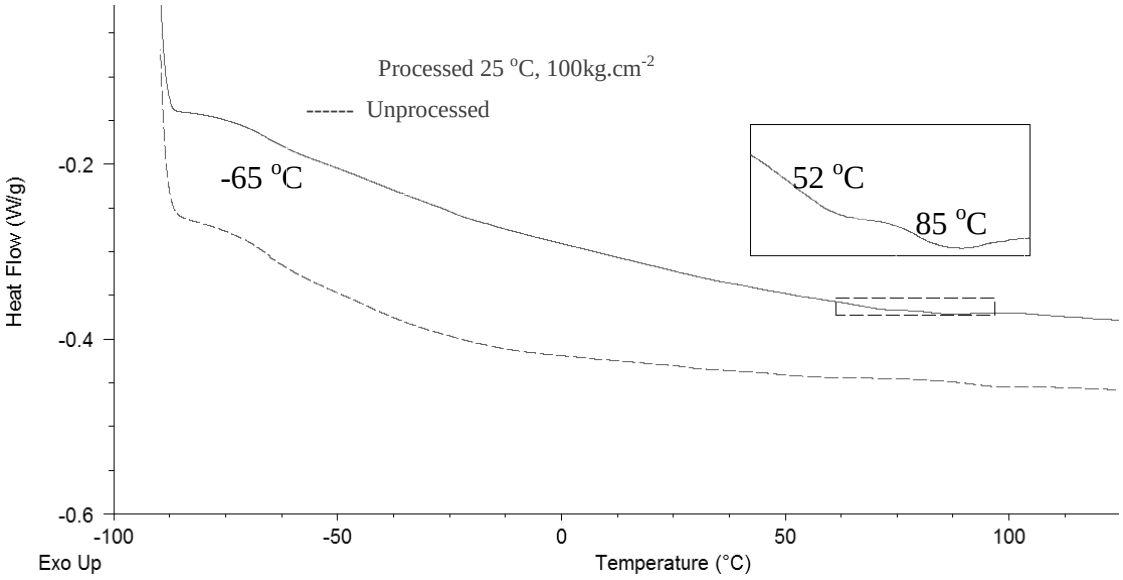
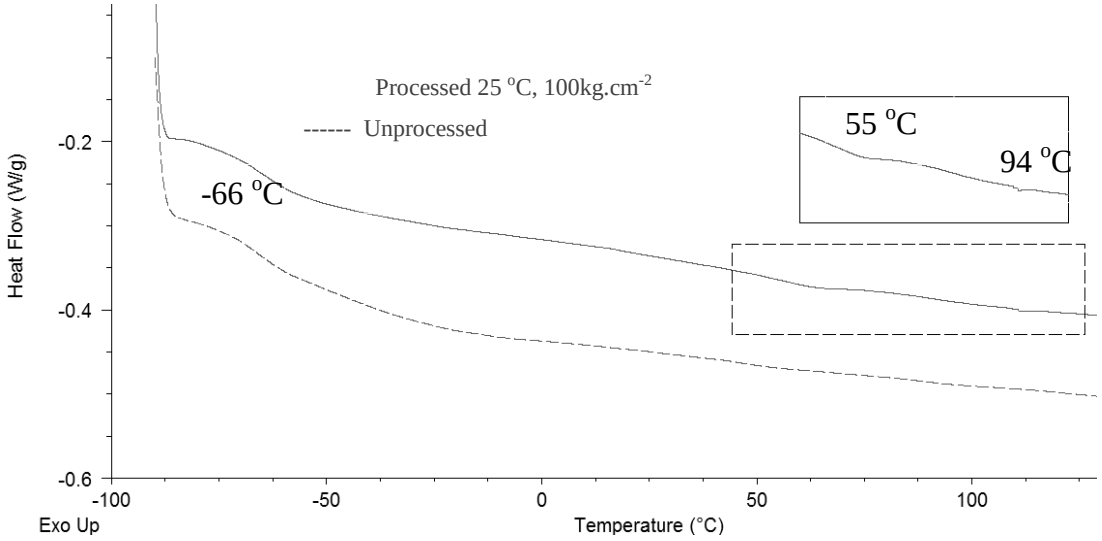


Figure 4.7 : DSC thermogram of PS-*b*-PEHA baroplastic diblock copolymer (49% PEHA, BP1)



DSC thermogram of PEHA-*b*-PS-*b*-PEHA baroplastic triblock copolymer (57% PEHA, BP4) BP1-BP4 baroplastic materials were blended with different homopolystyrenes at variable ratios as mentioned in Table 4.5 and processed by compression molding. After processing a $T_{g,mix}$ was observed as well as a characteristic endotermic peak around 103-105 °C due to the homopolystyrene addition. A representative example of a blend of diblock and triblock baroplastic material and homopolystyrene is given in Figure 4.9 and 4.10. The $T_{g,mix}$ value appeared at similar temperature values in comparison to the neat baroplastic materials.

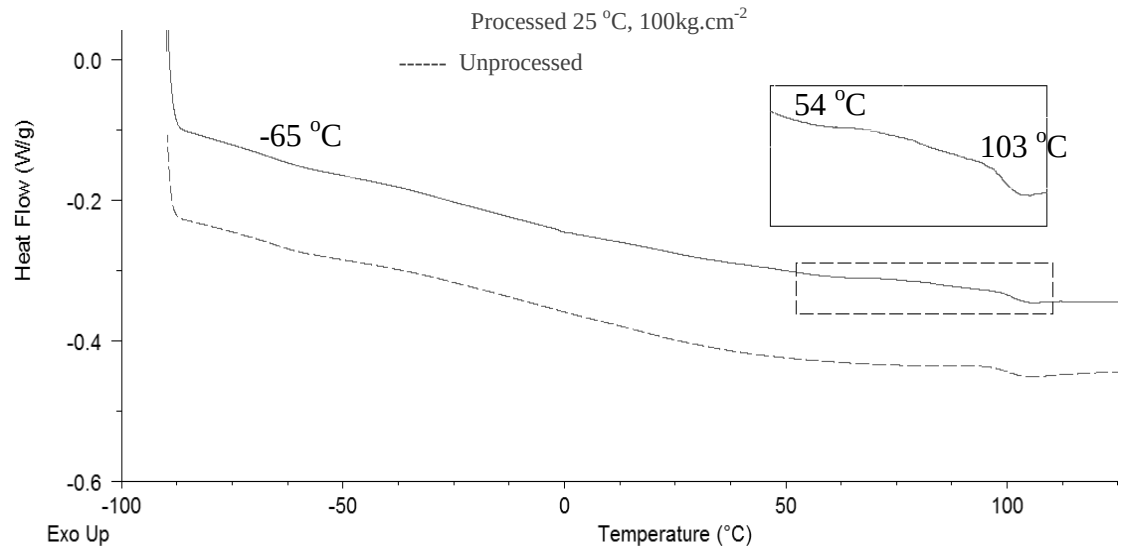


Figure 4.8 : DSC thermogram of baroplastic PS-*b*-PEHA (49 % PEHA, BP1), homopolystyrene (40 w% HP5) blend

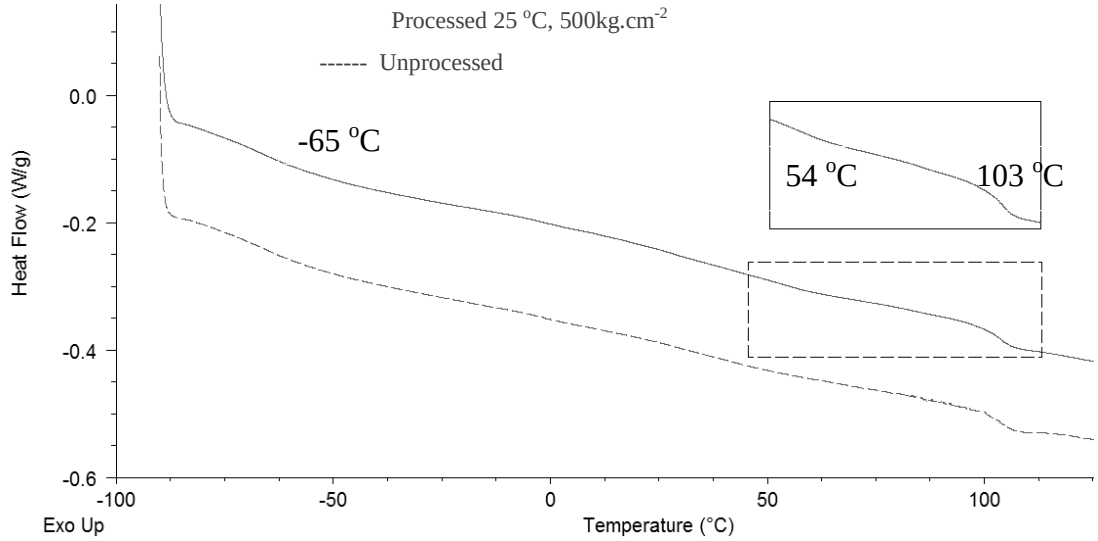
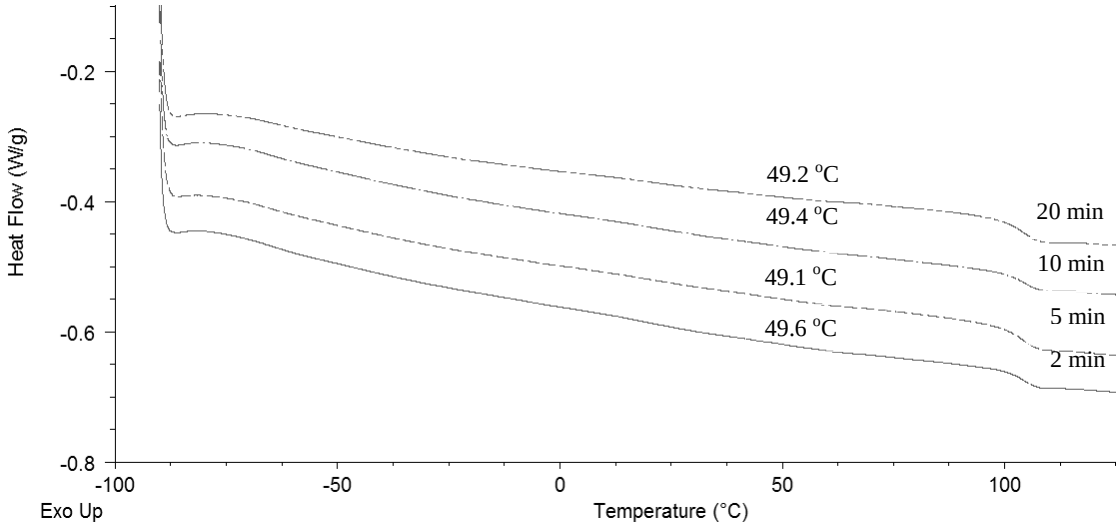


Figure 4.9 : DSC thermogram of baroplastic PEHA-*b*-PS-*b*-PEHA (57% PEHA, BP4), homopolystyrene (40 w% PS8) blend

4.7.1 Time and pressure effect on processibility

In order to optimize the processing conditions, time and pressure effect is studied. Minimizing the time and pressure is essential for production, as shorter time and less pressure bring out significant economic advantages. Thus BP1 was blended with PS3 at a 50 w% ratio and processed under 500 kg.cm^{-2} by compression molding for 2, 5, 10 and 20 minutes. DSC measurements of each sample was showed that the $T_{g,mix}$ value appeared around 49 °C for all individual samples (Figure 4.11) which proves that the mixed phase generation is not time dependent (up to 20 min). Since it is proved that, 2 minute processing time is sufficient for the formation of mixed phase, the processing time has been kept 2 minute for the rest of the study to save time and for faster processibility.



Time effect on processed baroplastic PS-*b*-PEHA, (49 % PEHA, BP1) and homopolystyrene (50 w% PS3) blend, 25 ^{o}C, 500 kg.cm^{-2}.Further on, pressure effect is tested on blends of BP1 and PS5 (50 w%) at varying pressure values: 100, 300 and 500 kg.cm^{-2}. As shown in Figure 4.12, the pressure values between 100 and 500 kg.cm^{-2} do not make any significant difference on $T_{g,mix}$. As $T_{g,mix}$ is attributed to the mixed phase of block copolymer segments, pressure higher than 100 kg.cm^{-2} do not give rise to any further increasing of miscibility. Thus in this study, from now on 100 kg.cm^{-2} is chosen for processing as lower pressure values bring economical advantages.

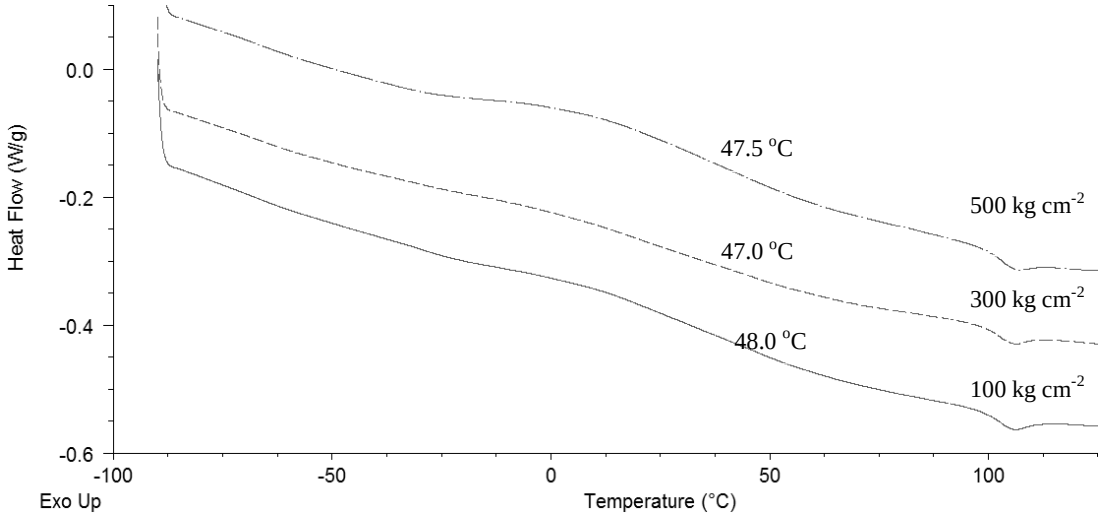


Figure 4.10 : Pressure effect on processed PS-*b*-PEHA diblock copolymer, (49% PEHA, BP1) and homopolystyrene (50 w% PS5) blend, 25 ^{o}C, 2 min.

4.7.2 Molecular weight and blend ratio effect of homopolystyrene on processibility

In industry polystyrenes are used in a wide range of molecular weight. In this study, the influence of molecular weight of the homopolystyrene was investigated. Thus BP1 was blended individually at varying ratios with PS3, PS5 and PS7. The blends are processed at room temperature at 100 kg.cm^{-2}. It is observed that as the homopolystyrene content increases in the blend, the processability becomes difficult which is already expected. The processed samples with 60 wt% homopolystyrene content revealed very low mechanical strength and broken apart while removing from the mold. However all samples with 40 w% homopolystyrene have been

processed easily and the obtained pellets were removed from the mold without encountering any problem.

Considering the processing, there wasn't any significant difference depending on the homopolystyrene molecular weight since samples with same blend ratios revealed similar processing abilities. However, it should be considered that the used homopolystyrenes M_n values are between 20000 to 52000 g.mol^{-1} which is not a very wide range.

Moreover, after DSC measurements it was not so easy to identify the $T_{g,mix}$ values of the samples. As there is a dominant homopolystyrene structure in the blend, the sharp polystyrene peak probably prevent the $T_{g,mix}$ to be easily identified or maybe the T_g values intersect each other as explained in introduction part.

Table 4.6 : Processibility features of baroplastic materials with homopolystyrenes at different molecular weights

Baroplastic (BP1, w%)	Homopolystyrene (w%)	Processibility
BP1(40 wt.%)	PS3(60 wt.%)	⊗
BP1(50 wt.%)	PS3(50 wt.%)	⊕
BP1(60 wt.%)	PS3(40 wt.%)	⊕
BP1(40 wt.%)	PS5(60 wt.%)	◯
BP1(50 wt.%)	PS5(50 wt.%)	⊕
BP1(60 wt.%)	PS5(40 wt.%)	⊕
BP1(40 wt.%)	PS7(60 wt.%)	◯
BP1(50 wt.%)	PS7(50 wt.%)	⊕
BP1(60 wt.%)	PS7(40 wt.%)	⊕

⊗: couldn't be processed ◯: partially processed ⊕ : processed successfully

4.7.3 Molecular weight effect of baroplastic block copolymers on processibility

In this study, investigating the effect of molecular weight of baroplastic material on processibility is another object as the molecular weight of baroplastic materials may be up to 200000 g.mol^{-1} as established by our research group and indicated in Sebnem Inceoglu's PhD thesis [26]. Thus BP1 and BP3 having different molecular weight but same composition have been synthesized in order to observe the molecular weight effect on processibility.

BP1 and BP3 baroplastic materials are individually blended with same homopolystyrene at the same blend ratios and extursion tested. Both samples are easily extruded (Figure 4.5 and 4.6). The extruded samples are measured by DSC for examining the molecular weight effect of baroplastic material on mixed phase which is attributed to the processing of block copolymers at room temperature.

Very clear mixed T_g values are obtained from the extrusion tested tapes, which proves the formation of a mixed phase by the application of pressure (Figure 4.13). Two different blends did not reveal a very significant difference of $T_{g,mix}$. As $T_{g,mix}$ appears after processing due to the mixed phase of block copolymers, it can be concluded that the molecular weight of baroplastic block copolymer up to 60000 g.mol^{-1} is not effective on formation of mixed phase.

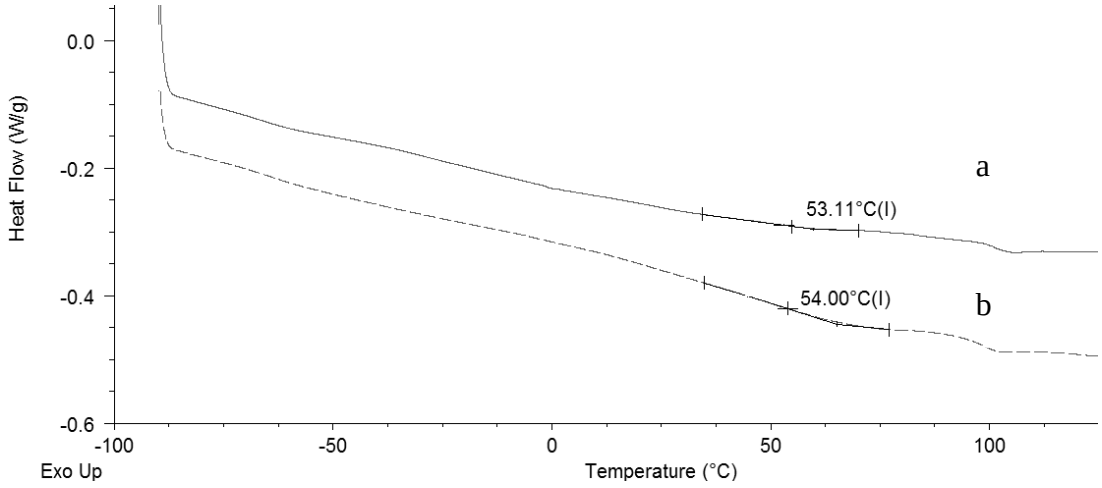


Figure 4.11 : DSC thermograms of homopolystyrene (PS5) blended baroplastic a) PS-*b*-PEHA diblock copolymer (50 % PEHA, BP3), b) PS-*b*-PEHA diblock copolymer (49% PEHA, BP1) blend (60 w%) extruded tapes.

4.7.4 Composition effect of baroplastic block copolymer on processibility

In this research, the effect of block copolymer's PEHA % on processibility of blends was examined. For this purpose BP1 and BP2 diblock copolymers were blended with same homopolystyrene (PS5). BP1 and BP2 has relatively similar molecular weights (26000 and 33000 g.mol^{-1}, respectively) while BP1 has 50 % PEHA content and BP2 55 % PEHA content. During processing it is noticed that BP1/HP5 (40 w% HP5) sample was easily compression molded, BP2/BP5 (40 w% HP5) sample was very soft and sticky for compression mold and sticks on the walls of the mold. However BP2/BP5 (60 wt.% BP5) sample was easily compression molded. Thus it is

possible to say that an increased PEHA content up to 55% of diblock enables an easier processing for the baroplastic/homopolystyrene blend under pressure. It is quite advantagous as the usage of baroplastic block copolymer is lessened by the increased PEHA content. It should be also considered that, this generalization is done for the PS-*b*-PEHA diblock copolymer with relatively low molecular weights.

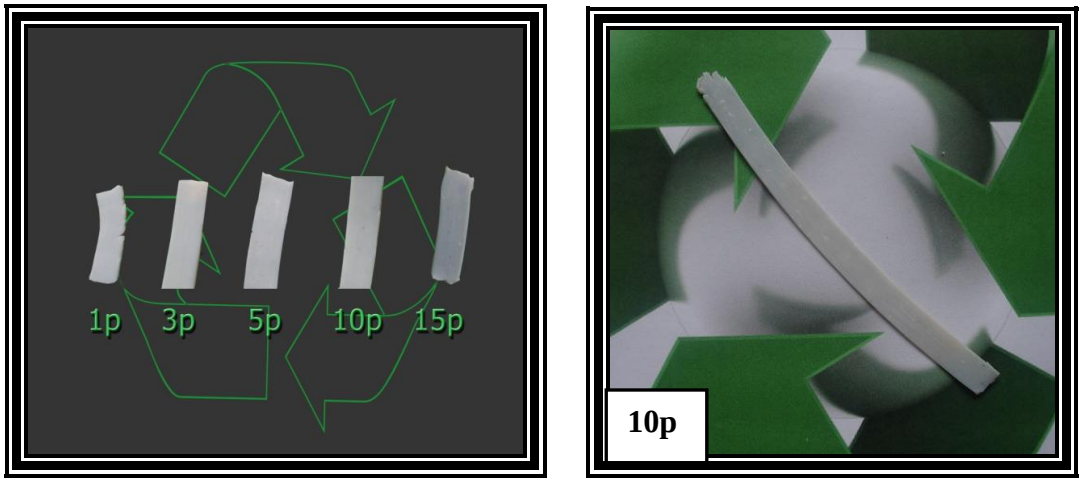
4.7.5 Topology effect on processibility

In this study we used diblock and triblock copolymer in order to see the topology effect. BP1 (PS-*b*-PEHA, 50% PEHA) and BP5 (PS-*b*-PEHA-*b*-PS, 50% PEHA) baroplastic block copolymers are blended with homopolystyrenes in order to see the topology differences. The moleculer weight of baroplastic materials are relatively close to each other (26000 and 30000 $g.mol^{-1}$) and they are blended with PS5 homopolystyrene (32000 $g.mol^{-1}$). However, no significant processing difference were visible between the mentioned blends.

4.8 Recycling of baroplastic block copolymer/homopolystyrene blends

As it was mentioned at introduction part, recycling is one of the major problems of thermal processes. In this study, we investigated the recycibility properties of the baroplastic block copolymer/homopolystyrene blends. The blend samples are initially extruded and afterwards extruded tape samples are chopped mechanically into little pieces. These little pieces are re-fed to the laboratory scale extruder which is maintained under pressure at room temperature and re-extrusion is achieved. This cycle is repeated for 15 times and each cycle is referred as "1 process". 15^{th} processed sample was still processible and durable. In Figure 4.14, the recycled samples of BP1/HP5 (40 w% HP5) and BP3/HP5 (40 w% HP5) are given. While "1p" corresponds to the 1^{st} extruded tape sample of the mentioned blend, "15p" corresponds to the 15 times repeated extrusion cycles. The employed extrusion is the mold that has been explained in 3.8.7. As clearly observed from Figure 4.14-a, there is no visual difference between the extruded samples by the increased number of processing cycles. Moreover in Figure 4.14-b, it is clear to see that a long tape sample is still formable eventhough the processing number is 10. This is very advantagous in comperison to the thermal processing techniques where degredations appear to be one of the main limitations of recycling. In Figure 4.15, it is

demonstrated that there was no degredation between the 1st and 15th processed blend sample. One might expect to see 2 different GPC peaks as a blend sample is in consideration, however diblock copolymer and homopolsytrene has similar molecular weights which results an intersection of the GPC peaks.



a b

Figure 4.12 : Recycled samples a) BP1/HP5 (40 w% HP5), b) BP3/HP5 (40 wt.% HP5)

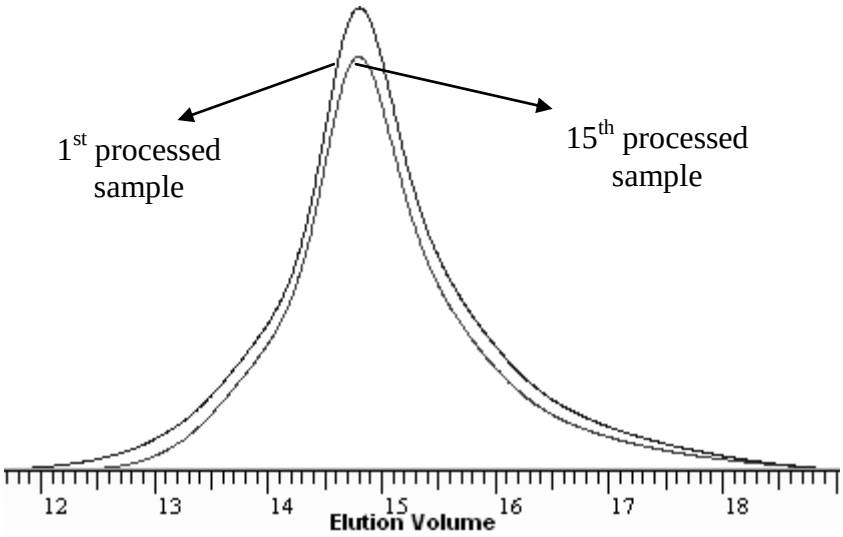


Figure 4.13 : GPC traces of recycled samples of BP1/HP5(40 w%)

A further study has been carried out to probe the differences between thermal behaviours of 1st and 15th processed samples. In previous sections, we mentioned that pressure has a possitive effect on the miscibility of block copolymers. In

addition to the pressure, here we investigated the effect of processing numbers on the miscibility of block copolymers. According to Fox equation (as explained in introduction) the totally miscible blends should give single T_g which is aplicable to our case as well. If homopolystyrene and block copolymer becomes completely miscible after some processing cycles, it is expected that a single T_g might be appearent which is some where between homopolystyrene T_g and PEHA T_g. According to Fox equation; BP1/HP5 (40 w% HP5) blend $T_{g,mix}$ was calculated as 15.77 ^oC, assuming that the system becomes completely miscible after an unknown processing cycles. According to the mentioned assumption, we investigated the $T_{g,mix}$ shift of BP1/HP5 (40 w% HP5) extruded tapes by the increased number of processing. $T_{g,mix}$ values of 1st processed and 15th processed samples were measured 54 and 48 ^oC, respectively (Figure 4.16). After processing the tape for 15 times, the $T_{g,mix}$ values shifted to the lower temperatures. This result was consistent with the Fox equation and thought to be a reason of increased miscibility due to increased processing numbers.

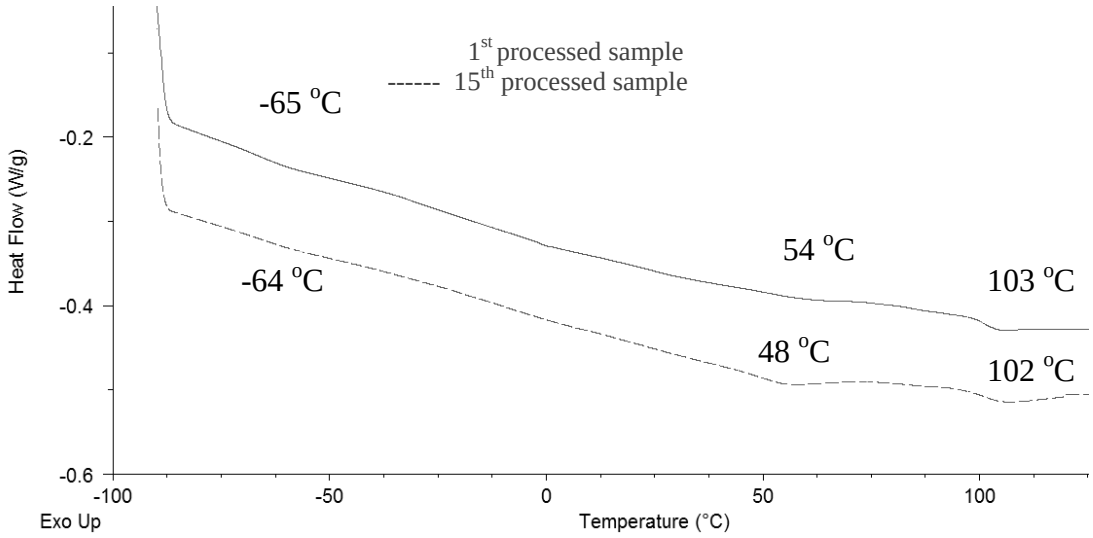


Figure 4.14 : DSC thermograms of extruded BP1/HP5 (40 w% HP5) sample

4.9 Investigation of Morphology of Baroplastic Block Copolymers and Homopolystyrene by AFM Studies

To examine the influence of processing of baroplastic materials and homo polystyrenes in ambient temperatures AFM is used in tapping mode. Here in, for AFM measurements, the block copolymers and their blends were prepared as a film

by solution casting using toluene on mica surface at room temperature. The solution concentration of block copolymer and blends was adjusted around ~ 5% (w/v). To eliminate the thermal history and thus to reach the thermodynamic equilibrium, the films were annealed for 1 hour at 110 °C after solvent casting which is well above the glass transition temperatures of each polymer segment. For observing the pressure effect on phase separation of block copolymer blends, the extrusion processed tapes are probed by AFM. The phase images of annealed films and processed tapes were investigated by Tapping Mode AFM.

As mentioned in theoretical part, the addition of homopolystyrene influences the micro phase structure of block copolymers.

In this study AFM images of two different blends are investigated. For each blend, the same homopolystyrene is employed and the addition of homopolystyrene is kept w40% in order to see the structural differences caused by the block copolymer and homopolymer interaction.

In Figure 4.17, the influence of pressure, in other words processing, can be observed as an increase in disordered state. As mentioned before, it is expected that the addition of homopolystyrene deforms the ordered structure of block copolymer and the solubility of homopolystyrene depends on many parameters such as homopolymer molecular weight, blend ratio, temperature and solvent.

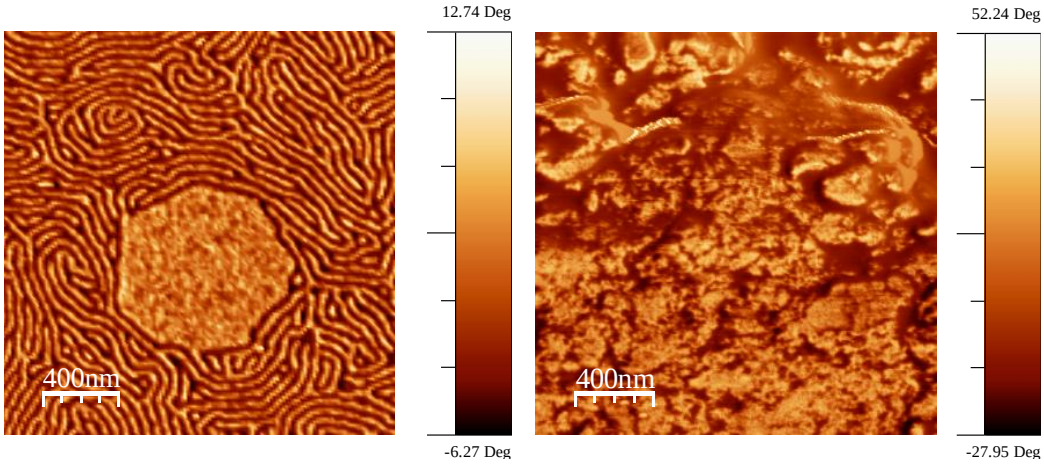
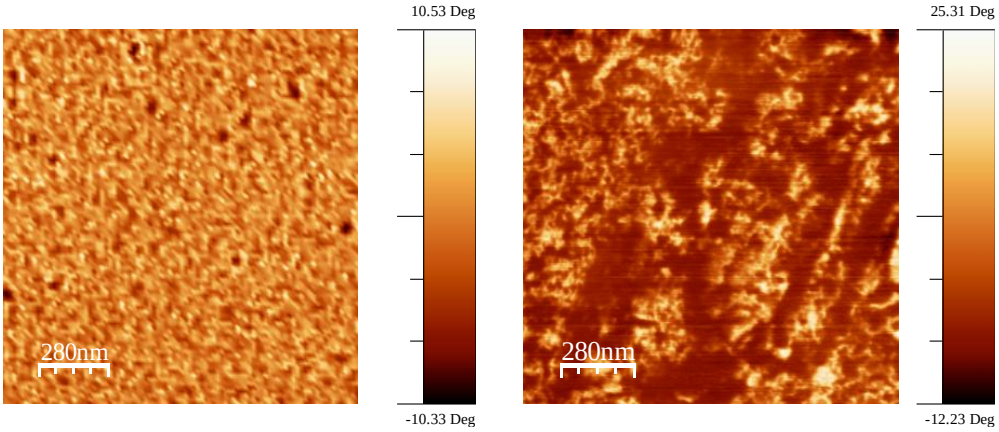


Figure 4.15 : AFM phase images of PS-*b*-PEHA diblock copolymer (49% PEHA, BP1) blended with 40 w% polystyrene (PS5) a) annealed film, b) extuded tapes

The AFM images of PS-*b*-PEHA diblock copolymer (BP1) blended with polystyrene (40 w% PS5) revealed quite interesting results. Most of the diblock copolymers with nearly symetric blocks exhibit a lamellar structure. However, in BP1/PS5 (40 w% PS5) AFM images, a clear macro phase seperation was observed (Figure 4.14-a). The homopolymer PS5 molacular weight (M_n= 32000 g.mol^{-1}) is higher than the molecular weight of PS segment in BP1 diblock copolymer. In introduction part, it was mentioned that if the molecular weight of homopolystyrene is higher than the molecular weight of equivalent segment in diblock copolymer, than a macro phase seperation might appear which is competible with our result. Moreover obtained AFM images were quite similar to the AFM images reported by Yamaguchi and Hashimoto as explained detailed in introduction part which supports the macro phase seperation in our case [22]. In Figure 4.17-b, the extruded tape of the blend sample is given, it is clearly observed that the lamellar structure is not present any more. The morphology has changed from ordered state to the disordered state by the processing. This proves the pressure-induced miscibility of block copolymers.

Moreover BP3/HP5 (40 w%) blend AFM phase images of film and extruded samples are also examined. (Figure 4.18). In BP3/HP5 (40 w%) sample, homopolymer PS5 molacular weight (M_n=32000 g.mol^{-1}) is smaller than the molecular weight of PS segment in BP3 diblock copolymer. . In introduction part, it was mentioned that if the molecular weight of homopolystyrene is relatively smaller than the molecular weight of equivalent segment in diblock copolymer, the homopolymer might solubilize in the domains of block copolymer. In Figure 4.18-a, we see the film sample of BP3/HP5 (40 w%) blend, and it is not a fully ordered structure, even if the lighter PS and darker PEHA segments are quite visible. As it is not a ordered state as in BP1/PS5 (40 w% PS5), it is thought that the homopolystyrene (PS5) is dissolved in diblock copolymer's polystyrene segments. Some black dots are also noticible in AFM image of film sample, these seems to happen due to the evaporation of the solvent or maybe some experimental errors.

The Figure 4.18-b is the AFM image of the extruded sample of BP3/HP5 (40 w%) blend. When compared to the film sample, it is possible to comment that the morphology has became more disordered. This again supports that the pressure processing has increased the miscibility.



a b

Figure 4.16 : AFM phase images of PS-*b*-PEHA diblock copolymer (50% PEHA, BP3) blended with 40% wt. polystyrene (PS5) a) annealed film, b) extruded tapes.

5. CONCLUSION

Pressure-induced miscibility of several block copolymers and blends were revealed in previous studies. It was reported that PS-*b*-PEHA and PEHA-*b*-PS-*b*-PEHA block copolymers with close PS/PEHA compositions reveal a pressure-induced miscibility which makes them baroplastic materials. However, pressure effect on homopolymer/ baroplastic blends was not investigated. In this study, we probe the pressure effect on processability of a homopolystyrene by the addition of variable amounts of baroplastic block copolymers.

While a homopolystyrene cannot be shaped by pressure at room temperature, addition of a baroplastic PS-*b*-PEHA, PEHA-*b*-PS-*b*-PEHA or PS-*b*-PEHA-*b*-PS block copolymer addition elevated the processability of the blend at given conditions. The homopolstyrene/baroplastic block copolymer blends were processed by compression mold and extrusion mold. The decreased amount of baroplastics was reduced the processability of blends. The blends having less than 50 w% baroplastic material could not be processed. The blends with 60 w% baroplastic addition revealed very good processing and the blends are easily extruded.

Two baroplastic PS-b-PEHA block copolymers with similar composition (50 % PEHA and 49 % PEHA) but different molecular weights (26 K and 60 K) were revealed similar processing abilities when they were blended with same homopolystyrene.

Also baroplastic PS-b-PEHA block copolymer (49% PEHA, M_n=26000 g.mol^{-1}) was blended individually with homopolystyrenes which have different molecular weights (M_n=20000, 32000 , 52000 g.mol^{-1}). However, a significant processing difference was not observed for these blends.

In this research, the effect of block copolymer's PEHA % on processibility of blends was examined, too. For this purpose two diblock copolymers with different PEHA contents and similar molecular weights (49 % PEHA, 26000 g.mol^{-1} and 55 % PEHA, 33000 g.mol^{-1}) were blended with same homopolystyrene. During processing it was noticed that homopolystyrene blend which has a higher PEHA containing

block copolymer exhibit and easier processing at lower baroplastic block copolymer addition. 40 w% baroplastic block copolymer was enough and increased baroplastic block copolymer ratio caused a gummy sample which makes the processing difficult as the polymer sticks on the walls of the mold and becomes harsh to remove the sample from the mold. This result seems to happen advantagous as the usage of baroplastic block copolymer was lessened by the increased PEHA content. It should be also considered that, this generalization was done for the PS-*b*-PEHA diblock copolymer with relatively low molecular weights.

Finally, topology differences of the samples were probed. In this study, diblock and triblock copolymer were used in order to see the topology effect. Baroplastic PS-*b*-PEHA, 49 % PEHA diblock copolymers and baroplastic PS-*b*-PEHA-*b*-PS, 50 % PEHA triblock copolymers were blended with homopolystyrenes in order to see the topology differences. The moleculer weight of baroplastic materials are relatively close to each other (26000 and 30000 $g.mol^{-1}$) and were blended with a homopolystyrene (32000 $g.mol^{-1}$). However, no significant processing difference were visible for the mentioned blends samples.

It should be noted that mechanical tests of the samples couldn't be done by dinamic mechanical analyzer or tenstile tester since the samples were being cut by the clamps of the instruments. For further studies, compounding with a plasticizer or a reinforcement filler might increase the mechanical strength as well as reducing the costs. Moreover, it would enable us to tests the samples mechanically.

The miscibility properties of blends after and before pressure were observed by DSC measurements and AFM. Block copolymers with immiscible segments exhibit two different T_g's due to individual T_g of each segment. For blends, similar to the baroplastic materials, a third T_g was observed which refers to the mixed phase caused by the application of pressure.

Time and pressure effect on processibility of mentioned blends were investigated. 2 minutes of pressure application at 100 $kg.cm^{-2}$ was found sufficient for processing since longer processing times and higher pressure values do not give a better processability.

Most of the di-block copolymers with nearly symetric blocks exhibit a lamellar structure. However in $PS_{0.51}$-*b*-$PEHA_{0.49}$/ HomoPS blend (40 w% HomoPS) AFM

images, a clear macro phase seperation was observed. The homoPS molecular weight (M_n= 32000 g.mol^{-1}) is higher than the molecular weight of PS segment in di-block copolymer $PS_{0.51}$-*b*-$PEHA_{0.49}$ and this case probably leads to macro phase seperation which was a competible result with the recently reported blend studies. While the film sample of mentioned blend is in ordered state, after pressure-processing, the phase image of extruded sample exhibits a disordered state. The segment of block copolymer became miscibile and macro phase seperation was no longer visible. This was though to be a reason of pressure-induced miscibility of block copolymers.

Another AFM study is done for PS $_{0.50}$-*b*-PEHA $_{0.50}$/HomoPS sample. However this time the molecular weight of HomoPS is smaller than the correspondent PS block of di-block copolymer. According to the literature, it is expected that this case *generally* should conclude with solubilizing of homoPS in di-block copolymers equivalent domain. The film samples of the mentioned blend gave some phase separation in, however this separation was not recognizable as the previously blend which demonstrated a clear macro phase separation. This might be due to the solubilized homoPS in block copolymer segments. But the increased disordered manner was also observable for this blend sample. The extruded tape sample of the blend was more disordered when compared to the film sample.

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