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Study of the Surface Morphology of Polyisobutylene-based Block Copolymers by Atomic Force Microscopy

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Summary: This paper reports the investigation of the nanostructured surface morphology of linear polystyrene-block-polyisobutylene-block-polystyrene (SIBS) triblock copolymers and novel arborescent SIBS block copolymers by Atomic Force Microscopy (AFM) in the tapping mode. Thin films spin coated from toluene onto silicon wafers were studied. The nanostructured morphology of the block copolymers varied with the hard polystyrene (PS) and soft polyisobutylene (PIB) segment composition, ranging from spherical to lamellar nanometer-sized discreet PS phases dispersed in a continuous PIB matrix. Annealing the samples resulted in well developed/ordered structures. The arborescent blocks had irregularly distributed PS phases in the PIB matrix. Annealing had a dramatic effect on the morphology which still remained irregular. Three-dimensional AFM image and section analysis indicated the presence of a height difference between PIB (high-lying plateaus or hills) and PS (low-lying plateaus or valleys) in the block copolymers, which became more prominent during annealing. It is theorized that the rubbery PIB chains are able to relax, thereby protruding from the surface, anchored by the physically crosslinked PS phases.

Introduction

This paper reports the investigation of the nanostructured morphology of linear triblock and novel arborescent polyisobutylene-polystyrene (SIBS) copolymers by AFM in the tapping mode. SIBS type block copolymers are referred to as Thermoplastic Elastomers (TPE's[1]). While macroscopically homogeneous, they phase separate on a microscopic scale; the discreet plastic phases embedded in the continuous elastomer phase provide "physical crosslinks" and mechanical strength. TPEs behave like cured rubber at a temperature below the glass transition temperature (T_g) of the plastic phase. Above this temperature, however, they behave and can be processed as plastics. Upon cooling the physical crosslinks are reinstated and a "cured" rubber is obtained. TPE rubbers can be reprocessed, thus scraps can be reused. In order to get good phase separation in block-type TPEs leading to good mechanical properties, the length of the elastomer chains

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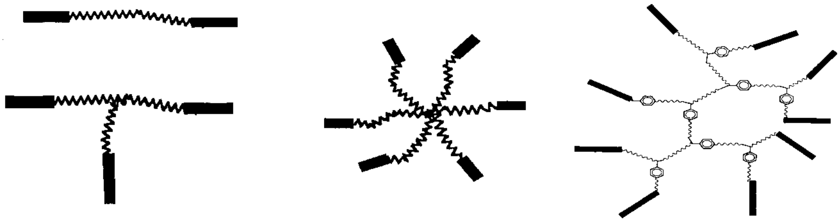
should be as uniform as possible. This can be achieved by living polymerization, a unique process without termination and other side reactions of the growing polymer chain. Living conditions producing relatively uniform polymers can be achieved in anionic, cationic and radical systems. The concept of living polymerization was first developed in anionic systems[2]. The first commercial block-type TPEs, Shell's Kraton family (polystyrene-polybutadiene-polystyrene, SBS), were produced by living anionic polymerization. Subsequent hydrogenation of the PBD segments imparted heat and environmental stability (Kraton-G family). It is only very recently that living conditions were achieved in cationic and radical polymerizations, both significant breakthroughs in polymer science. Polyisobutylene (PIB)-containing block copolymers can only be produced by carbocationic polymerization, thus they became a reality with the achievement of living carbocationic polymerization[3,4]. Novel SIBS TPEs show a unique combination of properties; good heat, chemical and environmental stability due to the saturated nature of PIB segment, coupled with good processability and outstanding barrier properties[5]. Recently published data confirmed the biostability and biocompatibility and lack of inflammation from the use of these TPEs as microporous stent-graft for long-term implant application[6]. The synthetic aspects of living carbocationic polymerization and PIB-based TPEs have been discussed and reviewed extensively[5,7]. The recent test-marketing of PIB-based TPEs by Kuraray of Japan indicate that commercial developments are underway[8]. Figure 1 shows the structure of three generations of novel PIB-based TPEs.



First generation Second generation Third generation

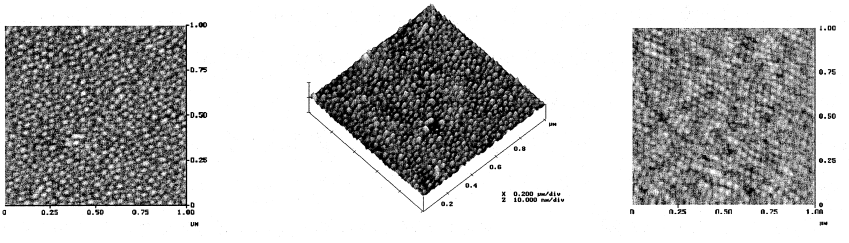
Figure 1. Schematic structure of PIB-based TPEs

The linear triblock and triarm-star block copolymers can be considered the first generation, and multiarm-stars the second generation of PIB-based TPEs. Branched polymers are attractive because of their higher moduli and lower viscosity, compared to their linear counterpart of similar molecular weight[9]. In addition, multiarm-star blocks impart good shear stability. Star-branched PIB-based blocks so far have been produced and studied under laboratory conditions only[7]. Arborescent (tree-like) PIB-based blocks are the most recent development[9] and can be considered the third generation of PIB-based TPEs.

For the AFM studies in this work, SIBS block copolymers were synthesized by living cabocationic polymerization with sequential monomer addition. The process has been scaled up to the pound/batch scale. Details of the synthesis procedures have been described elsewhere[7]. A sample of a commercially test-marketed SIBS was obtained by courtesy of Kuraray America, Inc., New York, USA (TS-Polymer, PS = 30 wt.%). Arborescent SIBS was synthesized by blocking PS from arborescent PIBs synthesized by inimer-type living carbocationic polymerization[10-12]; the details of the synthetic procedure will be described elsewhere. Thin films of SIBS block copolymers were prepared by spin coating 3 wt.% solutions in toluene onto silicon wafers by using a headway resist spinner at 6000 rpm for 30 sec. The spin-coated films had a final thickness of ~ 150 nm. AFM was performed on these samples and on samples annealed at 115 °C for 6-90 hrs.The AFM images were recorded with a Nanoscope III from Digital Instruments, operated in the tapping mode in air using microfabricated cantilevers with a spring constant of 30 Nm^{-1}. For the analysis of the observed surface structures, the Nanoscope image processing software was employed.

AFM Studies

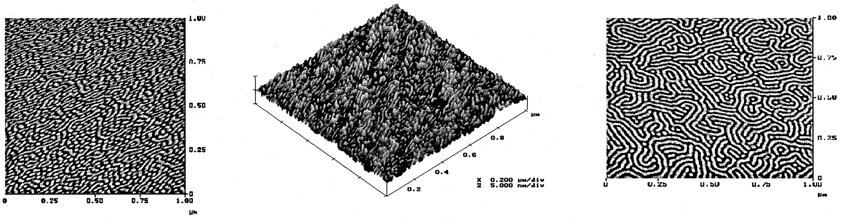
Figure 2(a) and (b) show the morphology and the three-dimensional height image of a linear triblock with 20 wt% PS. The hard PS phase forms structural domains



(a) (b) (c)

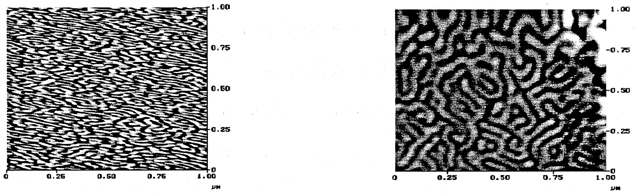
Figure 2. AFM images of a linear triblock SIBS with 20 wt% PS.

(spheres/cylinders) with diameters of 25-35 nm, which are dispersed in the continuous PIB phase. A possible explanation for the height variations between two phases (high and low-lying plateaus (hills and valleys)) is the fact that the rubbery phase, being above its glass transition temperature, is able to relax by expanding out of the surface of the film. Figure 2(c) shows that the structural features became more ordered after annealing the sample at 115 °C. Figure 3 shows the morphology of TS30; PS spheres with some cylinders with a domain size of 10-14 nm can be seen. After annealing the morphology became more ordered and stable (c), in which the PS formed a combination of cylinders and lamellae with a domain size of 25-31 nm. Our experimental samples with 30 wt% PS showed very similar morphologies. Figure 4 shows an interpenetrating network structure or a gyroid bicontinuous morphology (i.e. a combination of hexagonal-packed cylinder and spheres), with cylinders of 40-50 nm and spheres of 50-70 nm diameter, for a linear triblock with 40 wt % PS. The disappearance of the gyroid morphology after annealing (b) indicates that thismorphology is not thermally stable; the gyroid structure has rearranged into a more stable morphology consisting of cylinders and lamellae with a PS domain size of 35-45 nm.



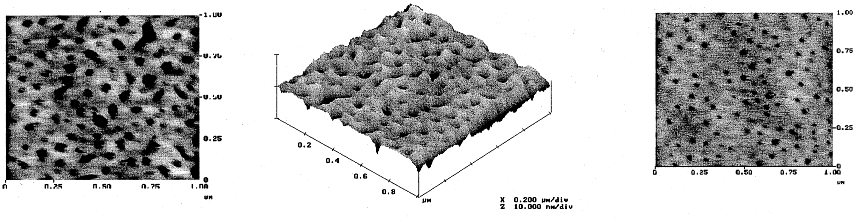
(a) (b) (c)

Figure 3. AFM images of the semicommercial TS polymer.



(a) (b)

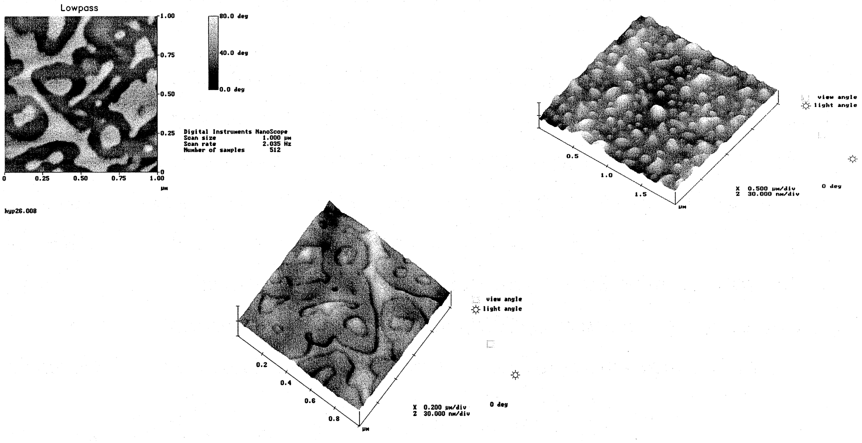
Figure 4. AFM images of a linear triblock with 40 wt% PS.



(a) (b) (c)

Figure 5. AFM images of an arborescent SIBS with 10 wt% PS.

The AFM image of an arborescent SIBS is shown in Figure 5. This sample has low PS content, thus it is very clear that the valleys are the PS phase dispersed in the continuous PIB phase. The PS spheres are distributed very irregularly, indicating that the structure depicted in Figure 1 is very likely the actual structure of the arborescent block. Annealing again resulted in more defined contours with a PS domain size of 39-50 (c). Figure 6 displays the AFM picture of an arborescent SIBS with 30 wt% PS. The structure is very irregular, and changes considerably upon annealing (c). Surprisingly, the novel arborescent block copolymers displayed TPE properties with 4-10 MPa



(a) (b) (c)

Figure 6. AFM images of an arborescent SIBS with 30wt% PS.

tensile strength and unusually high (over 1000 %) elongation. The mechanical strength of block-type TPEs is traditionally attributed to good phase separation between the soft and hard phases, for which uniform block length is believed to be a prerequisite. This is not the case in the novel arborescent blocks presented here. It can be theorized that the mechanical strength in fact is due to the nanometer size of the PS phases. It can also be theorized that the unusually large elongation of these blocks is due to the migration of PS blocks from one phase to the other. These third generation PIB-based TPEs have great commercial potential since they are much easier to produce than their first and third generation counterpart. Further investigation of these novel arborescent PIB-based TPEs is in progress in our laboratory.

Conclusions

Linear triblock and novel arborescent polyisobutylene-polystyrene (SIBS) block copolymers were produced on a pound/batch scale and their phase morphology was studied by using AFM in tapping mode; this is the first report of such studies. The block copolymers displayed various phase morphologies on a nanometer scale, due to the basic thermodynamic incompatibility of the individual polymer blocks. The observed equilibrium morphologies corresponded to domains of the minor component dispersed in a matrix of the major component. The microphase separation and the resultant nanostructured morphology of the block copolymers varied with the hard PS and soft PIB segment composition, ranging from spherical to lamellar nanometer-sized discreet PS phases dispersed in a continuous PIB matrix. Annealing increased the PS domain size and resulted in a more stable and ordered morphology. Interestingly, at 40.3 wt.% PS content an interpenetrating network structure was observed. The disappearance of the gyroid after annealing indicated that this morphology is not thermally stable. For the arborescent block copolymers unusual, irregular morphologies were observed. Three-dimensional AFM image and section analysis showed height differences between the two phases - high-lying plateaus (hills) and low-lying plateaus (valleys) were observed, which became more prominent during annealing.

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