Structural Transitions from Spherical to Nonspherical Micelles in Blends of Poly(styrene-butadiene) Diblock Copolymer and Polystyrene Homopolymers

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ABSTRACT: Blending of a block copolymer with a large amount of homopolymer can result in the formation of a micellar phase consisting of spherical domains of the aggregating copolymer block. We show that transitions in micelle shape and mesophase type(s) can occur by increasing the molecular weight of the homopolymer matrix, by increasing the aggregating block molecular weight, or by increasing the volume fraction of the copolymer. The new morphologies include cylindrical micelles, vesicles, and lamellar type structures. These transitions can be understood in terms of the general rule of domain morphology as a function of relative microphase volume fractions put forth by Molau[1] for neat block copolymers and later extended by Sadron and Gallot[2] to the case of block copolymers in preferential solvents.

Introduction

A number of reports have appeared in the literature regarding various domain morphologies in diblock-homopolymer blends. We are concerned with blends in which the diblock component is relatively dilute so that micelles of block copolymer are formed in the homopolymer matrix. We are also concerned with near-equilibrium conditions so that the microstructure is characteristic of the blend system's thermodynamics rather than a kinetically controlled state. In the present study we focus on the transitions from an initially single-phase spherical micelle state induced by variation of the diblock copolymer concentration, asymmetry, and molecular weight as well as by the homopolymer molecular weight.

The first theories for the critical micelle concentration in diblock-homopolymer blends[3,4] assumed micelles of spherical geometry. The structure of a spherical micelle consists of a core of radius R comprised of the aggregating block of the copolymer surrounded by a spherical shell of thickness L containing the outer diblock highly swollen with the homopolymer, Figure 1. Only in a recent treatment[5] has the case of a nonspherical (i.e., cylindrical) micelle geometry been considered. Much of the experimental work on the phase behavior of diblock-homopolymer blends has utilized scattering methods, which cannot unambiguously determine the morphology of the systems studied.[6-8] Direct TEM observations of the specific domain morphology in diblock copolymer-homopolymer blends containing micelles have been made by various groups.[9-15] Most of these observations were carried out on blends with a rather limited variation of composition, concentration, and molecular weight and without proper attention toward assuring that the system studied was near thermodynamic equilibrium.

We have recently made a systematical study of spherical micelles in PS/PB diblock-PS homopolymer blends.[16,17] A detailed comparison was made to the theory of Leibler, Orland, and Wheeler[3] as extended by Roe[18] to allow for the case of asymmetrical copolymers and the possibility of homopolymer residing in the micelle core. In the course of this study we observed transitions in the geometry of the micelles and the appearance of new mesophase morphologies (i.e., cylindrical micelles, vesicles, and other lamellar type structures) dependent on the particular molecular parameters of the blend system. In this paper we discuss the near-equilibrium structural transitions we have observed and show that these can be understood in terms of the variation of the relative volume fractions of the core and corona regions of a micelle.

Table I
Poly(styrene-butadiene) Diblock Copolymer Characteristics

sample	M_n, kg/mol PS	M_n, kg/mol PB	vol % PS
SB 10/10	12.0	10.0	51.2
SB 20/20	20.5	20.5	46.5
SB 40/40	42.3	45.0	44.7
SB 10/23	10.2	23.7	26.9
SB 10/65	10.7	63.1	12.7

Experimental Section

Table I lists the copolymer samples used in this study. Each sample is designated by a two letter code and two numbers. SB indicates a poly(styrene-butadiene) diblock copolymer. The first number refers to the number-average molecular weight (kg/mol) of the polystyrene block, and the second number refers to the number average molecular weight (kg/mol) of the polybutadiene block. The polydispersity of the polystyrene block and the copolymer is less than 1.05. Polystyrene homopolymers of various molecular weights (2100, 3900, 7400, 17 000, and 35 000) were obtained from Pressure Chemical Co. These samples were characterized by Dr. L. J. Fetters of Exxon and have a polydispersity of less than 1.09. Prior to use the polystyrene homopolymers were heated to 160 °C under vacuum (at which condition they foamed) for 30 min to remove any solvent or residual styrene monomer or oligomer.

Films of block copolymer/homopolymer blends for electron microscopy were cast from toluene, a nonpreferential solvent. Cast films were placed in a vacuum for 2 weeks in order to remove the solvent. Finally the films were annealed at 115 °C for 1 week under vacuum in order to approach equilibrium conditions. Thin (400-1000 Å) sections were prepared via cryoultramicrotomy at -110 °C. The films were then exposed for 4 h to osmium tetraoxide vapor and examined at 100 kV in the bright field mode of a JEOL 100CX TEMSCAN transmission electron microscope.

Results

Transitions in Morphology of Symmetric Diblock Copolymers in Homopolymer. As shown by the electron micrographs in Figure 2, blends containing 12.5 wt % copolymer SB 20/20 in 3900 and in 7400 PS homopolymer exhibit spherical micelles. However, when the molecular weight of the homopolystyrene matrix is further increased, cylindrical micelles occur, as in 12.5 wt % SB 20/20 in 17 000 PS (Figure 2C). As in the case of spherical micelles, the core of the cylindrical micelle is made up of polybutadiene blocks, with a corona surrounding the core consisting of polystyrene blocks and homopolystyrene. While the blends containing spherical micelles are transparent, the blend containing cylindrical micelles is turbid.

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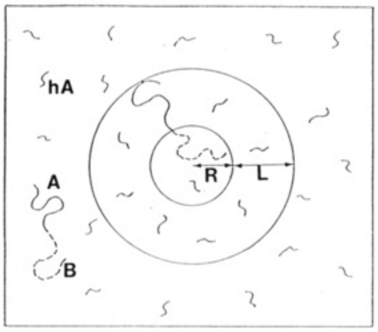

Figure 1. Schematic showing the structure of a spherical micelle in a blend of diblock copolymer (AB) and homopolymer (hA).

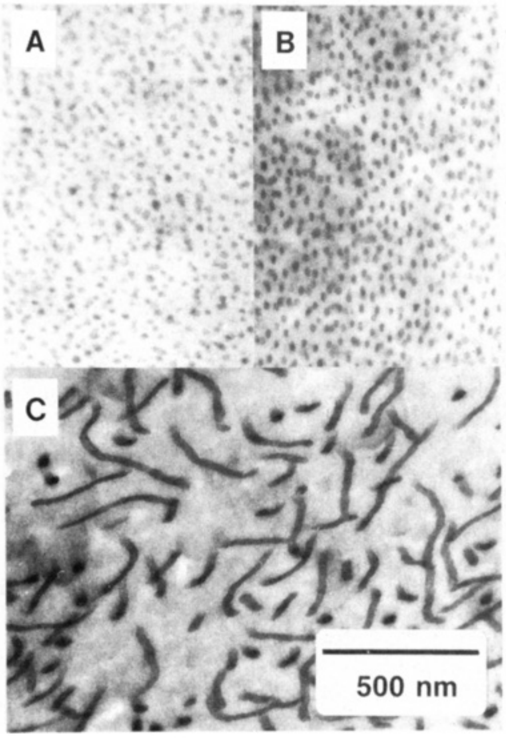

Figure 2. Electron micrographs showing the transition from spherical micelles to cylindrical micelles with increasing homopolymer molecular weight: 12.5 wt % SB 20/20 in (A) 3900 PS, (B) 7400 PS, and (C) 17 000 PS.

This is easily understood since the scale of the phase-separated structure (i.e., the micelle size) for the blend with cylindrical micelles is on the order of a few thousand angstroms and, thus, is expected to scatter light much more than the blend having spherical micelles, for which the scale of the phase-separated structure is only a few hundred angstroms. Without the electron microscopy evidence, however, this turbidity with increasing polystyrene homopolymer molecular weight could have been incorrectly interpreted as resulting from a macrophase separation of the polystyrene homopolymer or the formation of an additional phase. The electron micrograph shows that the cylindrical micelles are approximately uniformly distributed throughout the homopolymer matrix. Furthermore, no large regions containing exclusively polystyrene homopolymer are observed by electron microscopy, indicating that the system is a single homogeneous micellar phase. It is also clear that the micelles are wormlike rather than straight cylinders.

The shape of the micelles in blends containing copolymer SB 40/40 was also observed to change from spherical to cylindrical as the homopolymer molecular weight is increased. For homopolymer molecular weights less than 17 000, spherical micelles are observed up to the highest concentration of diblock examined (20 wt %). Blends of SB 40/40 in 17 000 PS exhibit both spherical and cylindrical micelles, as shown in Figure 3A–C. For 5.0 wt % copolymer only spherical micelles are present, while for 9.8 wt % copolymer a small number of short cylinders are observed. When the copolymer concentration is increased to 18.2 wt %, most of the copolymer forms long cylindrical micelles (this blend is also turbid). The micrographs suggest a relatively narrow size distribution of the spherical and cylindrical micelle diameters.

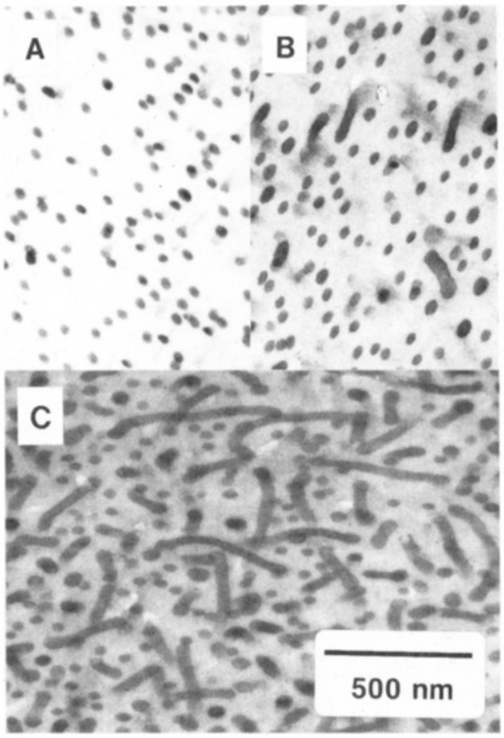

Figure 3. Electron micrographs of SB 40/40 in 17 000 PS showing the transition from spherical to cylindrical micelles with increasing copolymer concentration: (A) 5.0 wt, (B) 9.8 wt %, and (C) 18.2 wt %.

When the homopolymer molecular weight is increased even further, another structural transition occurs, as shown by the micrograph in Figure 4A for 5.0 wt % SB 40/40 in 35 000 PS homopolymer. The polybutadiene phase-separated structures seen in this micrograph are portions of approximately 0.5-μm-diameter spherical vesicles in which the vesicle wall is made up of polybutadiene block chains. In addition a small number of cylindrical micelles are also evident in this sample (see arrows). The vesicular structure is illustrated schematically in Figure 4B. The thickness of the vesicle wall (25 nm) is about 1.3 times the unperturbed end-to-end distance of the PB block chains, which are arranged similarly to the block chains in lamellar structures of neat block copolymers. Adjacent to the interior and exterior of the vesicle walls there is a corona region containing both PS block chains and PS homopolymer, analogous to the corona region of spherical and cylindrical micelles. Due to the excess homopolystyrene of the blend the lamellae sheets are highly separated by homopolystyrene. As expected from the scale of the phase separation, this blend is also turbid.

It is of interest to ask whether such vesicular (or as we discuss later multilamellar vesicular type) structures are truly equilibrium structures. This can be addressed on two size scales. For micelle core and corona volume fractions near 0.5, a nearly planar interface is desired, and equilibrium can be readily attained locally. Globally, however,

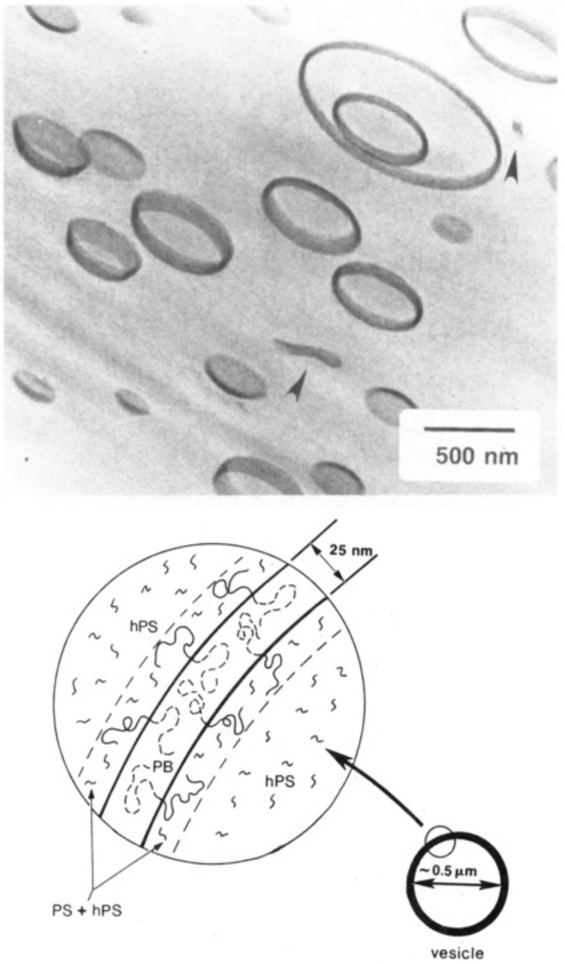

Figure 4. Vesicle morphology in SB–PS blends: (A, top) electron micrograph of 5.0 wt % SB 40/40 in 35 000 PS showing spherical vesicles and cylindrical micelles (arrows) and (B, bottom) schematic showing the arrangement of the copolymer and homopolymer chains in the spherical vesicle.

continuous surfaces (i.e., without edges, such as concentric spherical shells) of the aggregates will be favored, in order to avoid the excess energy of edges. Vesicular structures thus satisfy both local and global equilibrium considerations. If the concentration of the aggregates is high, an ordered arrangement of the surfaces will be favored (e.g., multilamellar vesicles), although with the relatively weak interaction between aggregates ordering will be difficult to achieve in practice.

These transitions in structure are similar to those observed for neat block copolymers[1] and block copolymer/solvent systems[2] as a function of the relative volume fractions of the microphases. Such transitions can be intuitively understood in terms of interface curvature and packing requirements of the blocks in the domain space. Consider the situation of a neat copolymer in which the two blocks have nearly the same volume (SB 20/20 or SB 40/40, for example) and which forms a lamellar domain structure having a planar interface, where the space available to the blocks on either side of the interface is comparable. Now when a preferential solvent is added to the domains of one of the blocks, it has the effect of increasing the effective volume fraction (i.e., molecular volume) of that block, and the interface therefore becomes curved so that the space available on the convex side (containing both block chain and preferential solvent) is larger than that available on the concave side. Therefore, cylindrical or spherical microdomains are formed, depending on the amount of added solvent, with the microphase having the smaller volume fraction occupying the concave side of the interface. In the case of micellar systems, the two volume fractions that must be considered are the relative volume fractions within the micelle. These consist of the core volume fraction υ and the corona volume fraction $(1-\upsilon)$. The value of υ is given by

$$\upsilon = (R/(R + L))^n$$

where R is the radius of the micelle core (for spheres or cylinders, or one-half the thickness of the aggregating block for lamellae), L is the thickness of the micelle corona region, and n is 3 for spheres, 2 for cylinders, and 1 for lamellae. One can thus anticipate that factors which increase the core and/or decrease the corona volume fraction could affect a transition in micelle geometry. The volume fractions at which the transitions in domain shape occur for neat block copolymers are at about 0.2 for the spherical to cylindrical transition and at about 0.35 for the cylindrical to lamellar transition.[20]

This simple model based on considering the core volume fraction of the micelle is in quite reasonable agreement with the available data. For example, a higher molecular weight homopolystyrene will mix with the styrene block in the corona to a lesser extent than a lower molecular weight homopolystyrene. A lower content of homopolymer in the corona region will serve to increase the core volume fraction and may induce a transition to a nonspherical micelle geometry. Specifically, in the 12.5 wt % 20/20 SB in PS blends, the core volume fractions υ calculated from core radii and corona thicknesses (data in ref 16 and 17) are 0.12, 0.19, and 0.23 for homopolystyrenes of 2100, 3900, and 7400 molecular weight, all of which exhibit spherical micelles (Figure 2). However, for 17 000 molecular weight homopolystyrene, cylindrical micelles are found. By extrapolating the data in ref 16 and 17 on the micelle core size and the micelle corona size relationship with homopolymer molecular weight to a molecular weight of 17 000, the calculated υ (based on spherical micelles) is 0.31, in good correspondence with the observation of cylindrical micelles for this blend. The further decreased solubility of still higher molecular weight homopolymer in the corona region causes a smaller corona volume fraction and results in the appearance of vesicles for SB 40/40 in the 35 000 PS system. Since the vesicle diameter is large and the vesicle wall thickness is small, the domain curvature is very small, and this type of structure is essentially lamellar in nature.

Figure 3 shows that the micelles in blends of SB 40/40 in 17 000 PS change from spherical to cylindrical as the concentration of copolymer increases from 5 to 18.2 wt %. In our previous study[16,17] we have shown that the aggregation number and hence the core radius increase about 10% over this concentration range for copolymer SB 20/20. The same trend is expected to occur for copolymer SB 40/40. Thus an increase in the core volume fraction with copolymer concentration is presumably responsible for the transition in micelle shape. While one type of micelle geometry should have a slightly lower free energy and therefore be expected to occur exclusively, the difference in free energy between the spherical and cylindrical micellar structures near the transition may be small enough that a metastable (i.e., nonequilibrium) morphology, in which both spherical and cylindrical micelles coexist, may be present.

Transitions in Morphology of Nonsymmetric Diblock Copolymers in Homopolymer

Increasing the aggregating polybutadiene block length with respect to the polystyrene block length is the most

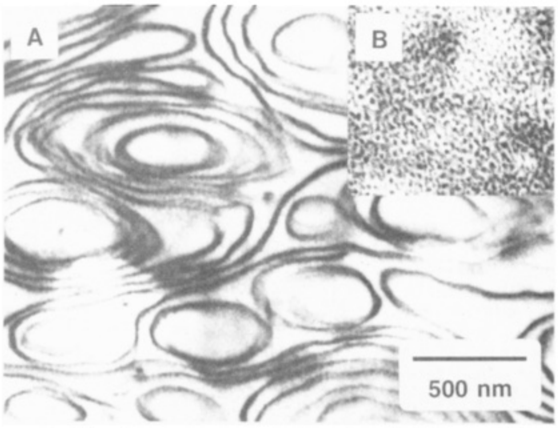

Figure 5. Electron micrographs showing (A) the multilamellar vesicle morphology of 18.4 wt % SB 10/23 in 3900 PS and (B) the spherical micelle structure of 17.8 wt % SB 10/23 in 2100 PS.

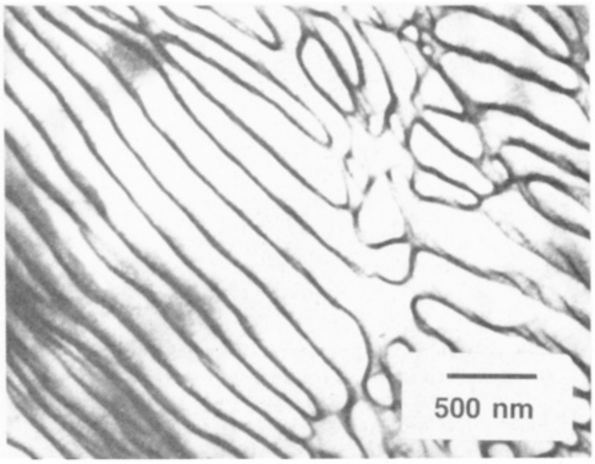

Figure 6. Electron micrograph showing the lamellar structure of 13 wt % SB 10/65 in 2100 PS.

direct way to increase the PB micelle core volume fraction. For example, the micelles in blends of 13.0 wt % SB 10/10 in 3900 PS and in 7400 PS are spherical. On the other hand, Figure 5A shows that 18.4 wt % SB 10/23 in 3900 PS has a multilamellar vesicular structure in which multiple layers of concentric polybutadiene spherical shells are present, uniformly dispersed throughout the sample. In the blends studied here, no large areas of nearly pure homopolymer are observed. The distance between the concentric PB layers suggests that a significant amount of homopolymer is contained between them.

Reducing the homopolymer molecular weight should cause an increase in the corona thickness and a decrease in the core size, resulting in a reduction of the core volume fraction. Therefore, a transition from the lamellar type structure of 18.4 wt % SB 10/23 in 3900 PS (Figure 5A) to polybutadiene cylinders or spheres should occur with a lower molecular weight homopolystyrene. Indeed, as the micrograph in Figure 5B shows, a blend containing 17.8 wt % SB 10/23 in 2100 PS exhibits spherical micelles. In order for this copolymer to form spherical micelles, the amount of homopolystyrene in the micelle corona must be quite large. As expected from the scale of the phase separation, this blend is transparent, while the former blend is slightly turbid.

Figure 6 shows an electron micrograph of 13 wt % SB 10/65 in 2100 PS. While SB 10/23 in this same homopolymer exhibits spherical domains, the blend containing SB 10/65 has a lamellar structure as a result of the increased PB block length. The large distance between the PB lamellae, relative to their width, indicates that a large amount of homopolystyrene is contained between them. It should be remarked that the morphology of this blend is uniform throughout the entire sample. On the other hand, a blend containing 4.0 wt % SB 10/65 in 7400 PS exhibits two distinct mesophases, as shown in Figure 7. Mesosphase M_1 has the same spherical domain morphology as the pure block copolymer, except that the polystyrene spheres are swollen with polystyrene homopolymer (from TEM measurements: for the neat diblock R is approximately 90 Å[17] whereas for the blend R is approximately 125 Å). Mesophase M_2 contains isolated spherical vesicles having polybutadiene walls suspended in a homopolystyrene matrix. This is the only blend presented here which exhibited two distinct mesophases.

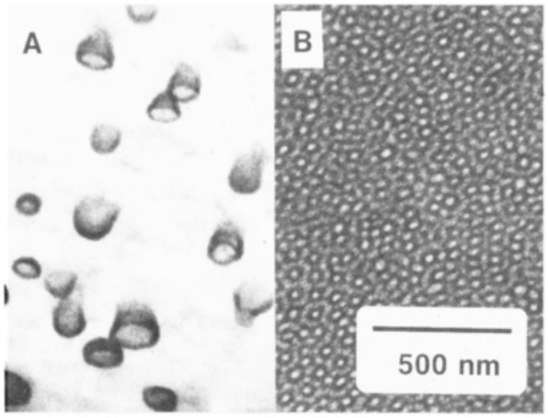

Figure 7. Electron micrographs of the two mesophases in the blend containing 4.0 wt % SB 10/65 in 7400 PS. (a) Mesophase M_2 contains isolated spherical vesicles, and (b) mesophase M_1 contains swollen spherical micelles.

Summary

The transitions in micelle geometry are found to be correlated with the relative volume fractions of the core and corona regions of the micelle, in analogy with the transitions in domain geometry found in neat copolymers and copolymer/solvent systems. The micelle core volume fraction can be most directly raised by increasing the aggregating block molecular weight. A larger micelle core volume fraction can also result from an increase in homopolymer molecular weight, which decreases the corona thickness as a result of a lower degree of mixing. The micelle core volume fraction can also be increased by raising the block copolymer concentration, which results in a higher aggregation number. It is observed that the transitions from spherical to nonspherical micelles are accompanied by an increase in the turbidity of the blends resulting from the larger length scale of the phase-separated structures. Without the electron microscopy evidence however, this turbidity could be incorrectly attributed to a macrophase separation of the polystyrene homopolymer or the formation of an additional mesophase. For this reason, the micellar regions of block copolymer/homopolymer phase diagrams based on cloud point measuremenets alone are somewhat tentative.

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Registry No. (S)(B) (block copolymer), 106107-54-4; PS, 9003-53-6.

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Complexation of Stereoregular Poly(methyl methacrylates). 13. Influence of Chain Length on the Process of Complexation in Dilute Solution

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ABSTRACT: The complexation process between long i matrices and much shorter s oligomers was investigated by means of DSC on complexed material, isolated from dilute solution, as a function of i/s mixing ratio, time after mixing, and chain length of the oligomers. It was confirmed that the previously observed second level of cooperativity in this system is caused by subsequent crystallization of complexed sections. In line with the recently published general mechanism, two endotherms were found, originating from decomplexation of complexed sections, partly organized into fringed micellar clusters (T_m^1), and the simultaneous decomplexation and melting of lamellarly crystallized complexes (T_m^3). A dependence of T_m^3 on oligomer chain length was observed, suggesting that the (maximum) lamellar thickness was limited by this parameter. For the heat of complexation, a value of 20 kJ/base mol of complex was found, while further evidence was obtained that the additional heat of crystallization of complexed sections is negligible, compared to the heat of complexation.

Introduction

The process of stereocomplexation between isotactic (i) and syndiotactic (s) PMMA has been subject of extensive investigations ever since the first report of Fox et al. on mixtures of i- and s-PMMA showing anomalous WAXS patterns.[1] The investigations on this subject were reviewed by Spevâcek and Schneider.[2]

Very recently we published an investigation on the mechanism of the complexation process in bulk as well as dilute solution.[3,4] The so-called critical sequence length for complexation, at the conditions employed, appears to be an important parameter in describing the overall process, which is mainly kinetically determined; i.e., a true thermodynamic equilibrium is not reached. The critical sequence length is defined as the minimum length of the complexed chain sections, above which the complexes are stable with respect to thermal fluctuations, and it is derived from the more familiar concept of critical chain length in complexation reactions.[5-10] It appeared that in the overall process of stereocomplexation two processes can be distinguished:[3,4] complexation of i- and s-PMMA, giving the well-known 1 i/2 s stereocomplex[11] and crystallization of complexed chain sections. With respect to crystallization, two modes were proposed: fringed micellar and lamellar growth, depending on the critical sequence length at the conditions employed and the mobility of the chain sections. When a so-called strongly complexing solvent is employed, like DMF at room temperature,[12] the critical length for complexation is small. In that case, complexation proceeds much faster than lamellar crystallization, and the system will be immobilized quickly. Lamellar crystallization is hindered, resulting in a large amount of complex, only partly clustered into small fringed micellar crystallites. When the material obtained is isolated and dried and subsequently investigated by means of DSC, two main endotherms are detected, respectively, called T_m^1 and T_m^3,[3,4] identified as (i) decomplexation of complexed sections, partly organized into small fringed micellar clusters of complexed sections; and (ii) melting and decomplexation of lamellar crystallites of complexed sections. In addition, it should be mentioned that it was postulated that the greater part of the heats involved should be ascribed to decomplexation, i.e., the heat of melting is negligible compared to the heat of decomplexation.[3,4]

Apart from the formation of stereocomplex by mixing the components in bulk or in solution, the stereocomplex can also be formed in situ by free-radical polymerization of methyl methacrylate in the presence of an i-PMMA matrix.[13,14] In this system, oligomeric radicals, created in free solution, grow until they reach the critical chain length, followed by complexation with the i matrix. From then on, the matrix controls their growth, resulting in predom-

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