polymer papers

Micelle growth and clustering in blends of polystyrene and styrene–butadiene diblock copolymer

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(*Received 7 March 1994*)

This paper presents an investigation of the morphology of blends containing 5 wt% styrene–butadiene diblock copolymer in a high-molecular-weight polystyrene matrix. Different samples of these blends were prepared by melt compounding in an extruder and by solvent casting. Transmission electron microscopy was used to determine their morphology. The extruded blend contained well dispersed, disc-shaped micelles of the diblock. The morphology of the solvent-cast blend was strikingly different, with onion-skinned structures of diblock copolymer that spanned up to several micrometres. However, upon annealing at 200°C, the morphology of the extruded blend and of the solvent-cast blend evolved towards the same relaxed state. The micelles became more spherical, grew in size and slowly agglomerated into cluster formations. The kinetics of this evolution were observed for the extruded blend. Micelle growth and clustering rates at 200°C and also at 180°C were determined by characterizing their size, shape and spatial distribution. The micelles became more spherical quickly and formed clusters over a longer time period. The changes in micelle shape became apparent in blends annealed at 180°C for as little as 5 min. The micelle clustering, however, was only evident in the blends annealed at 200°C. The rate of clustering was quantified by plots of nearest-neighbour distributions at different times. Analysis of these plots indicates a diffusion mechanism for the clustering. The results seem to support theoretical assertions of Semenov on dynamics of block-copolymer micelles in a high-molecular-weight polymer matrix.

(Keywords: polystyrene; styrene–butadiene copolymer; blend morphology)

INTRODUCTION

The desired mechanical properties for a blend of incompatible homopolymers (A and B) may be achieved by tailoring the blend morphology through the addition of some AB diblock copolymer. Hence, an understanding of the morphology of blends with an AB diblock copolymer dispersed in an A polymer matrix is important. The A and B polymer block segments tend to phase-separate when combined in sufficient concentrations. When the AB diblock is a minor component of the blend, the B blocks segregate to form the cores of micellar structures with the attached A blocks forming surrounding coronae. The size, shape and spatial distribution of these micelles when processed can be very different from their equilibrium structure. Upon annealing at a temperature above the glass transition temperature of each blend component, the morphology can change with time. The work presented here is a description of this evolution in morphology for a high-molecular-weight A/AB polymer blend.

Considerable theoretical and experimental work has been reported on the morphologies of AB/A polymer blends at equilibrium. Leibler and coworkers[1] have presented a model for micellar formation at thermodynamic equilibrium in a low-molecular-weight homopolymer matrix. Their model is based upon a balance between enthalpic and entropic effects. The growth of the micelles results in a decrease in surface area at the A–B interphase, which is enthalpically favourable. The micelle growth also results in stretching of the diblock chains and compaction of the micelle corona, which is entropically unfavourable. The equilibrium morphology is defined by a balance between these two effects, which minimizes the free energy of the system. Kinning and coworkers[2] have experimentally observed the morphology of solvent-cast blends of styrene–butadiene diblock copolymer and polystyrene; the molecular weights of the polystyrenes were below the critical molecular weight for entanglement. They note an increase in micelle core radii and a decrease in corona thickness with increasing molecular weight of the matrix homopolymer below the entanglement molecular weight. The effect of temperature on the equilibrium morphology in such systems has been reported by Rigby and Roe[3]. As the temperature is increased, the micelle cores swell owing to greater dissolution of low-molecular-weight matrix homopolymer into them. These observations confirm the trends predicted by the theory of Leibler *et al.*[1] for such systems.

Annealing at elevated temperatures will lead to changes in the micellar structure from the processed state. The rate of such changes depends upon the molecular weights of components in the system. The transition to an

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0032-3861/94/23/5051-06

equilibrium morphology of AB micelles in a low-molecular-weight solvent A should occur relatively quickly. For blends with a high-molecular-weight matrix, the timescale for this transition may be much longer. Halperin and Alexander[4] have examined the mechanisms for relaxation of micelle structure in a low-molecular-weight homopolymer system. They propose that the rate-determining step for morphological evolution in such a system is the addition or extraction of individual AB macromolecules in a micelle. Balazs *et al.*[5] have analysed the formation of micelles by polymeric and non-polymeric constituents in low-molecular-weight solvents. Their numerical simulation predicts that simple scaling relationships derived for low-molecular-weight micelle constituents are not applicable for associating diblock copolymer molecules. Because of the limited mobility in high-molecular-weight polymeric systems, the morphology may never attain that of true equilibrium. Semenov[6] has predicted that micelle formation and agglomeration for high-molecular-weight systems may never achieve a true equilibrium morphology but may instead be limited by activation energy barriers.

The object of this work is to study the changes in morphology upon annealing of a high-molecular-weight A/AB polymer blend produced by different processing methods, and the rate of changes in morphology. Blends consisting of 5% by weight styrene–butadiene diblock copolymer dispersed in a high-molecular-weight polystyrene homopolymer matrix are produced by melt compounding and by solvent casting. The size, shape and spatial distribution of the blend are compared for each blend before and after annealing at an elevated temperature to obtain a relaxed state morphology. The kinetics of the morphological evolution of the melt compounded blend are obtained by comparing the size and spatial distribution of the micelles of the blend after annealing over progressive time increments. The results seem to support theoretical assertions of Semenov[6] on dynamics of block-copolymer micelles in a high-molecular-weight polymer matrix.

EXPERIMENTAL

Materials

Blends consisting of 95% polystyrene and 5% styrene–butadiene diblock copolymer are examined. The matrix polymer is one of two different amorphous polystyrenes: Dow Styron 666D, with $M_w = 235\,000$ and a polydispersity index of 2.5, and Dow Styron 666APR, with a slightly lower M_w of 179 000 and a narrower molecular-weight distribution with a polydispersity index of 1.7. The latter polymer was used in the kinetics study. The AB component in each blend is Finaprene 315, a tapered diblock styrene–butadiene copolymer with $M_w = 136\,000$ and $M_n = 120\,000$. Some 70 wt% of the Finaprene is styrene and the remaining 30 wt% is butadiene. The styrene block makes up 50% of the copolymer, with the rest of the styrene of the copolymer found in the taper. The Finaprene contains a stabilizer and an antioxidant to reduce the likelihood of the temperature-sensitive butadiene degrading or crosslinking.

Blend preparation

The extruded blends were compounded in a Baker–Perkins (APV) co-rotating, fully intermeshing twin-screw extruder. Pre-dried polystyrene and styrene–butadiene copolymer pellets were each weighed out, shaken together and fed to the extruder as a mixture consisting of 5% copolymer. The extruder barrel length is 13 times its diameter of 30 mm. The extrusion was performed with the barrel temperature of each melt zone maintained at 170°C and a screw rotation rate of 250 rev min^{-1}. The highest feed rate consistent with the extruder torque capacity was used. This provided for a mean residence time of less than 2 min. The extruder was configured with two intensive mixing zones each consisting of six two-lobed kneading discs. The blend was extruded through a twin 3 mm diameter circular strand die and into a water bath. The strands were then pelletized and the extrusion procedure was repeated. Finally, the blend was extruded a third time and quenched in the water bath where the strands were collected. The blend was compounded three times to ensure the two components were well mixed. Stabilizer was used to ensure that no noticeable degradation of the material occurred during this process.

The solvent-cast specimens were prepared with Styron 666D as the matrix polymer. A mixture of 19 g of polystyrene and 1 g of Fina 315 were dissolved in 100 g of toluene. To remove the toluene solvent, the temperature of the solution was maintained at 30°C in an oven for four days with gentle agitation provided by a magnetic stirring rod. This was followed by three additional days at 30°C under vacuum. The sample was then annealed under vacuum at 70°C for three days followed by one day at 100°C and finally 1 h at 150°C. The samples were then allowed to cool slowly to room temperature while still under vacuum.

The extruded or solvent-cast specimens were annealed at 180 or 200°C under a blanket of nitrogen at a pressure of 1 psig (6.895 kPa). After the selected annealing period of up to 2 h, the sections were removed and quickly (within 3 s) quenched by submersion in a water bath.

Characterization of morphology

The specimens were prepared for transmission electron microscopy (TEM) by a procedure similar to that described by Kato[7]. Sections were ultramicrotomed from the plane perpendicular to and a plane parallel to the strand axis of each annealed segment. These 90 nm thick sections were collected in 300 mesh copper grids and exposed to OsO_4. OsO_4 reacts with the unsaturated double bonds of the butadiene, thereby attaching osmium as a stain. The copper grids were then coated with a 1 nm thick copper film to provide stability under the electron beam. Micrographs were taken either on a Hitachi HU 800 or a JEOL 100 CX electron microscope. The chemically deposited osmium is electron-opaque relative to the carbon and hydrogen atoms of the polymer, so that butadiene-rich sections of the electron micrographs appear as dark areas. For the kinetics study, negatives of the micrographs were placed upon an overhead projector and projected onto a wall where the major and minor axis lengths of the micelle cores were measured with calipers. The distance of each micelle from its core edge to the edge of its nearest neighbour was also measured. At least two micrographs, each with 30 or more micelles evident, were examined for each set of annealing conditions. A minimum of 120 total micelle cores were measured for each reported case. The sectioning method results in a truncation of the micelles.

A correction derived by Berney *et al.*[8] was employed to determine the average radii for each set of conditions. The random error in micelle volume measurement due to the statistical sampling size is estimated to be 10%[9].

RESULTS AND DISCUSSION

First, the morphologies of extruded blends and solvent-cast blends are compared before and after annealing, with Styron 666D as the matrix polymer. The extruded blend morphology is shown in *Figure 1a*. The micelles in the extruded blend are well dispersed discs having an average radius of about 20 nm. This is markedly different from the solvent-cast blend morphology shown in *Figure 1b*. Here, large onion-skinned structures of butadiene and styrene that can span several micrometres are evident. However, these two markedly different morphologies evolve towards the same morphology upon annealing. The morphologies of the blends when annealed for 1 h at 200°C are compared in *Figures 2a* and *2b*. This similarity in the relaxed morphology, in contrast with the differences in the initial stressed morphologies, suggests an approach towards a stable morphology upon annealing at 200°C. The micelles of the extruded blend grow in size and become more spherical. The large onion-skinned structures in the solvent-cast blend break up to form small spherical micelles as seen in the extruded blend. In either blend, these spherical micelles are seen to agglomerate into cluster formations (cf. refs. 10, 11).

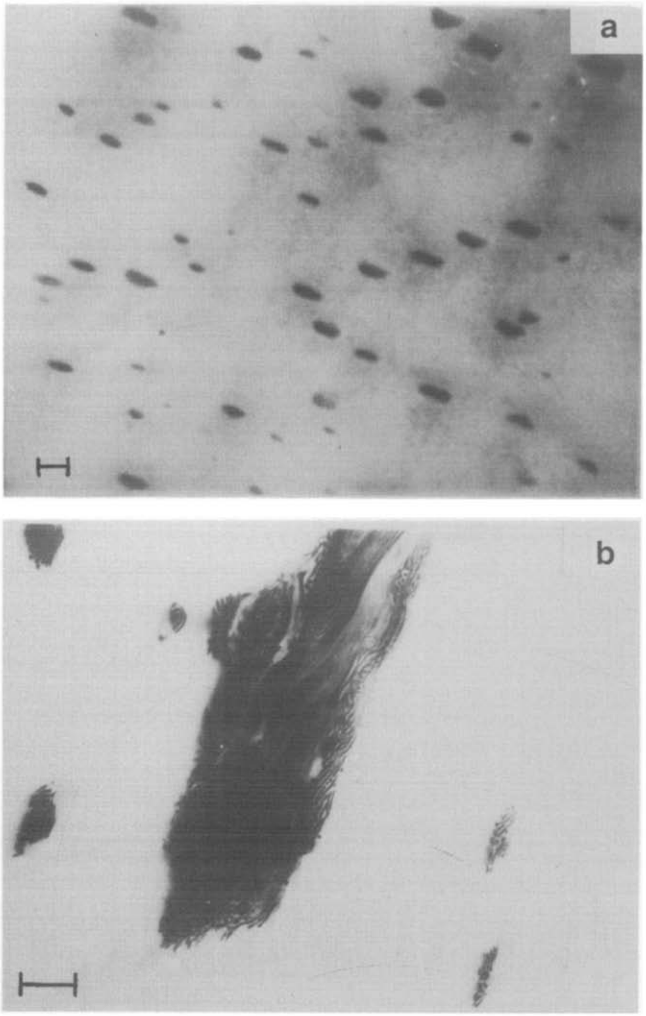

Figure 1 Morphology of unannealed Styron 666D blends: (a) extruded; (b) solvent-cast. Scale bars: (a) 0.1 μm; (b) 1.0 μm

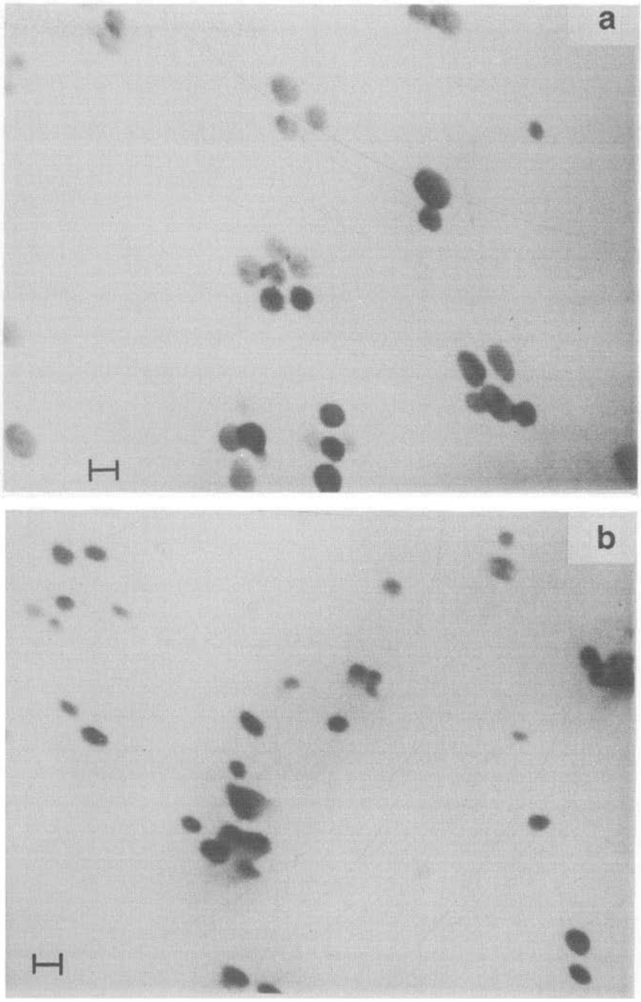

Figure 2 Morphology of Styron 666D blends after annealing for 1 h at 200°C: (a) extruded; (b) solvent-cast. Scale bars: (a) 0.1 μm; (b) 0.1 μm

Next, the kinetics of morphological evolution are presented for extruded blends during annealing at 180 and at 200°C. These observations were made on blends consisting of the Styron 666APR and the same concentration (5 wt%) of Fina 315. Before annealing, the micelles formed in the lower-molecular-weight polystyrene are approximately half as large as those in the Styron 666D. The aspect ratio, defined as the average ratio of the major to minor axis length of the micelle core, is 2.3 in either plane. *Figure 3* shows that about 10% of the cores in the plane containing the strand axis are significantly elongated with an aspect ratio of 10 or more. The axes of these cylinders are aligned with the axis of the extrudate strands. The average micelle core radius is 12.8 nm. This is the radius of a sphere with a projected area equal to that of the ellipsoidal micelle cores.

Upon annealing at either 180 or 200°C, the fraction of highly elongated ellipsoids or cylinders in the axial plane disappears. This transformation occurs quickly; for example, no cylinders are evident in the axial plane after the blend is annealed for 5 min at 180°C, as shown in

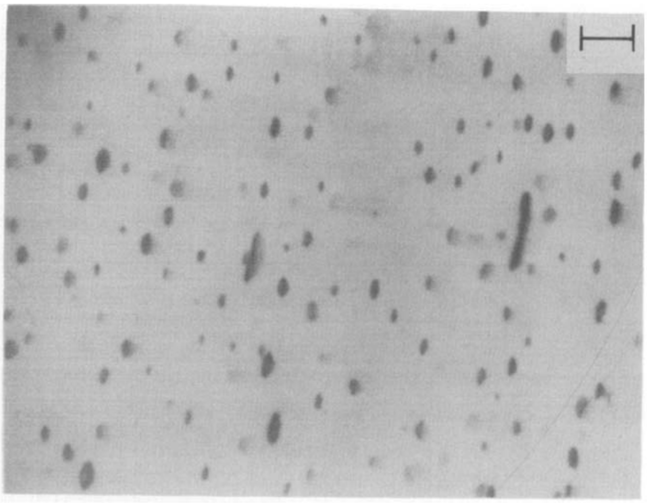

Figure 3 Morphology of extruded Styron 666APR blend (in plane of extrudate axis). Scale bar: 0.1 μm

Figure 4. The timescale for other changes described below is much longer. Because of the relatively small number of highly elongated micelles, the average aspect ratio of micelles does not change significantly at this temperature. The micelle cores also become noticeably more spherical after annealing at 200°C. The average aspect ratio decreases from 2.3 to 1.6 after 2 h of annealing.

The increases in average micelle core radius upon annealing at 180 and 200°C are shown in *Figure 5*. A marginal 15% increase in core radius was noted after heating the blend for 1 h at 180°C. When annealed at 200°C, the micelle cores increased over 60% in radius in 1 h and increased over 100% in 2 h. The distribution of micelle radii is shown before and after annealing for 2 h at 200°C in *Figure 6*. The error due to truncation of micelles during sectioning is present in these distributions since the correction can only be applied to the average values. Upon annealing, the number of micelles in a given area decreases and the distribution of sizes becomes broader. The micelle cores with radii below 10 nm dissolve into the matrix or merge to form larger micelles, while much larger micelles having a radius of 20 to 30 nm or more are formed.

Micelle clustering

The micelles in the blend are well separated when extruded. Upon annealing at an elevated temperature for a sufficient time, the micelles agglomerate into clusters, as seen in *Figure 2a*. In order to quantify the rate of clustering, the edge-to-edge distance between each micelle and its nearest neighbour was measured from the micrographs of the blend. This clustering phenomenon is only evident in the 200°C annealed specimens. Distributions of nearest-micelle-neighbour distances are shown in *Figure 7* for the extruded blend before and after annealing for 2 h at 200°C. A large increase in the count of closely spaced micelles occurs upon annealing. The rate of clustering at 200°C is illustrated in *Figure 8*, where the median nearest-neighbour distances are plotted *versus* the square root of time. The median distance is proportional to the square root of time; this trend is consistent with a diffusion process. The diffusion rate determined from the slope of this line is $1.3 \times 10^{-17}\ \mathrm{cm^2\,s^{-1}}$.

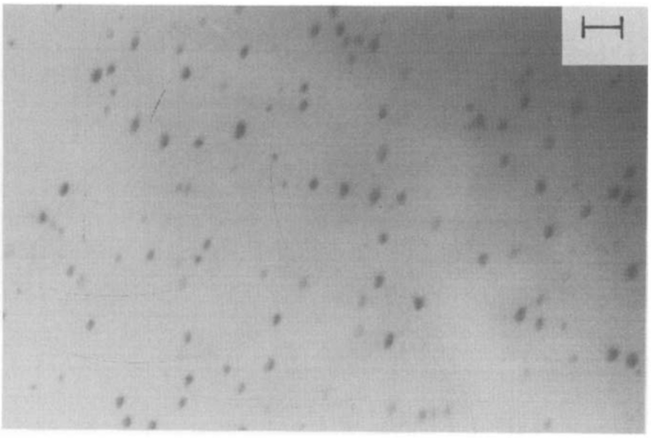

Figure 4 Morphology of Styron 666APR blend after annealing for 5 min at 180°C (in plane of extrudate axis). Scale bar: 0.1 μm

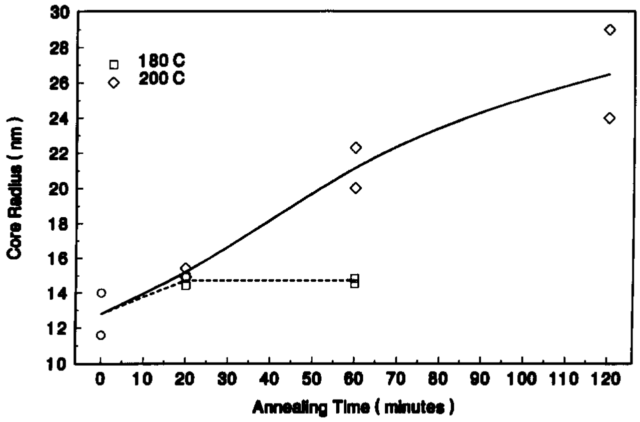

Figure 5 Growth of micelle cores upon annealing at 180 and 200°C (values corrected for truncation error)

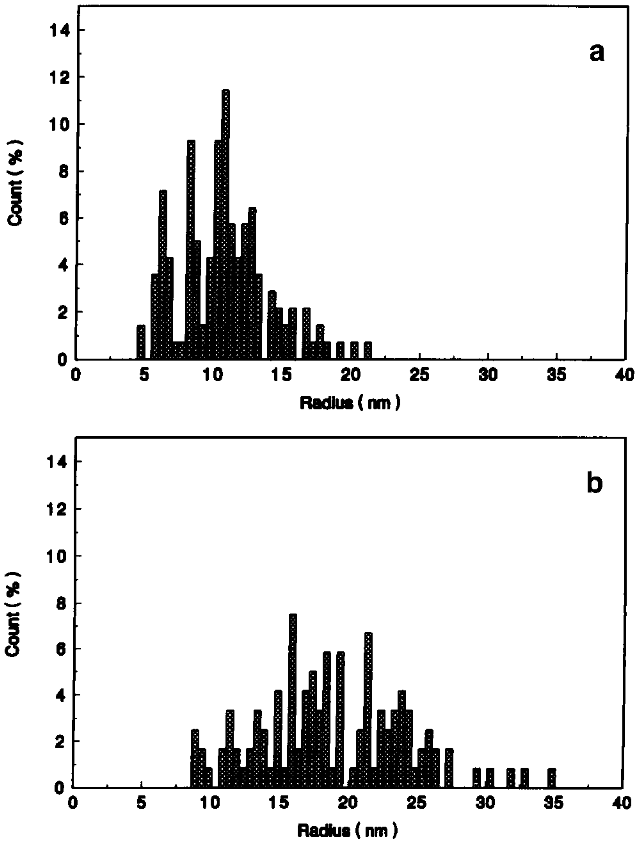

Figure 6 Distributions of micelle core radii: (a) before annealing; (b) after annealing 2 h at 200°C

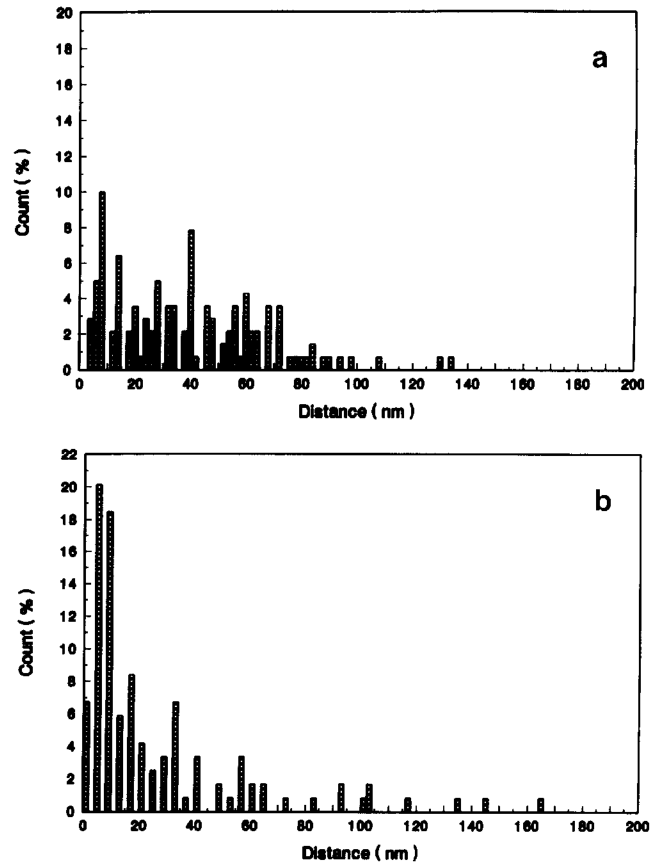

Figure 7 Distributions of nearest-neighbour distances of micelles: (a) before annealing; (b) after annealing 2 h at 200°C

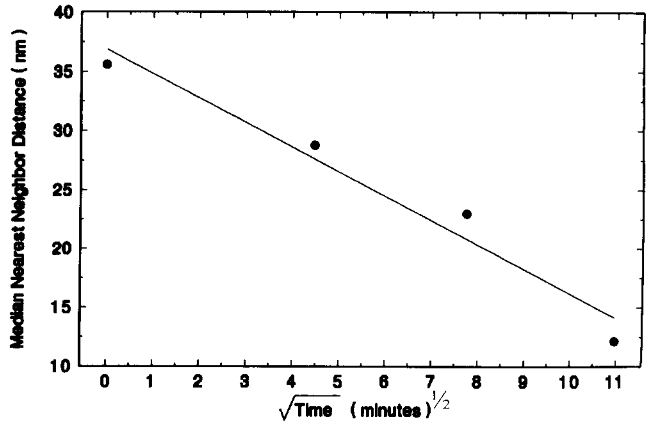

Figure 8 Change in median nearest-neighbour distance at 200°C with the square root of time. The linear curve suggests a diffusional mechanism

Interactions between micelles may be repulsive or attractive. This is governed in part by the coronae of the micelles. The effect of the corona on micellar interactions depends upon the molecular weight of the matrix polymer. In low-molecular-weight solvent systems, matrix polymer swells the micelle coronae, thereby causing the diblock chains to become extended. Repulsion between the coronae of adjacent micelles in these systems arises from entropy considerations[12]. In high-molecular-weight systems such as those in this work, the matrix polymer does not swell the micelle corona[3]. The A block cilia are therefore compacted against the micelle core rather than extended. For such a system, Semenov[6,13] has predicted a strong attractive force between the micelles at equilibrium. However, the true equilibrium morphology may never be reached because of the limited mobility in the high-molecular-weight polymer matrix. The observable morphology of the blend may be determined by potential-energy barriers rather than equilibrium free energy.

The diffusivity for Brownian motions of spheres is given by equation (1) for comparison:

$$D = \frac{kT}{6\pi\eta a} \tag{1}$$

With the viscosity η of the Styron 666APR melt at 200°C equal to 400 Pa s, the Brownian diffusion coefficient for well separated spherical particles the size of the micelle cores is about $4 \times 10^{-13}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. This value is four orders of magnitude greater than the measured diffusion rate. The effect of the corona on the mobility of the micelle may be at least partially responsible for this tremendous discrepancy. The cilia may intermingle and entangle to some limited degree with the matrix homopolymer, thereby inhibiting micellar diffusion. The diffusion may be hindered by strong energy barriers to the diffusion of block copolymer chains in the high-molecular-weight polymer matrix discussed by Semenov[6]. Similar experiments on micellar clustering with a range of block copolymer molecular weights are required to elucidate further the dynamics of clustering.

CONCLUSIONS

The morphology of blends comprised of a high-molecular-weight polystyrene matrix and a styrene–butadiene diblock copolymer depends on processing method and on annealing history. The morphology of the solvent-cast blend was strikingly different from that of the extruded blend. Upon annealing at 200°C, these two blends evolved towards the same relaxed state morphology. The micelles became more spherical quickly and formed clusters over a longer time period. The rate of clustering may be quantified by plots of nearest-neighbour distributions at different times. Analysis of these plots indicates a diffusion mechanism for the clustering. The slow rate of micelle clustering indicates strongly hindered diffusion in these systems.

ACKNOWLEDGEMENTS

This work was made possible with REF funds from the State of Michigan and administered by the Composite Materials and Structures Center at Michigan State University. We wish to express our appreciation to Dr Andre Lee at Michigan State University for discussions on the experimental approach to the kinetics investigation and to Dr John Heckman of the Center for Electron Optics at Michigan State University who supervised the preparation of TEM specimens.

REFERENCES

1 Leibler, L., Orland, H. and Wheeler, J. *J. Chem. Phys.* 1983, **79**, 3550
2 Kinning, D., Thomas, E. and Fetters, L. *J. Chem. Phys.* 1989, **90**, 5806
3 Rigby, D. and Roe, R. *Macromolecules* 1986, **19**, 721

4 Halperin, A. and Alexander, S. *Macromolecules* 1989, **22**, 2403
5 Balazs, A., Gempe, M. and Brady, J. *J. Chem. Phys.*, 1990, **92**, 2036
6 Semenov, A. *Macromolecules* 1992, **25**, 4967
7 Kato, K. *Polym. Eng. Sci.* 1967, 38
8 Berney, C. B., Cohen, R. E. and Bates, F. S. *Polymer* 1986, **23**, 1222
9 Gebizlioglu, O. S., Argon, A. S. and Cohen, R. E. *Polymer* 1985, **26**, 519
10 Nichols, K. and Jayaraman, K. Proc. Xth Int. Congr. on Rheology, Sydney, Australia, August 1988, p. 148
11 Nichols, K. PhD Dissertation, Michigan State University, 1989
12 Leibler, L. and Pincus, P. *Macromolecules* 1984, **17**, 2922
13 Semenov, A. *Macromolecules* 1989, **22**, 2849