Colloid & Polymer Science Colloid Polym Sci 272:1373–1379 (1994)

On the microphase separation kinetics of symmetric diblock copolymers*)

T. P. Russell and I. Chin¹)

IBM Research Division Almaden Research Center, San Jose, California USA
¹) Department of Polymer Science and Engineering Inha University, Inchon, South Korea

*) *In celebration of his 65th birthday, this article is dedicated to Prof. E. W. Fischer whose methodic and thorough approach to research has been and continues to be a model for us to follow.*
Es freut mich, daß ich mit Herrn Fischer gearbeitet habe. Ich habe vieles von ihm gelernt. Ich hoffe, daß auch ich so fleißig sein werde, wenn ich so jung bin wie er.

Abstract: Time-resolved small-angle x-ray scattering studies were performed on symmetric diblock copolymers of polystyrene and poly(methyl methacrylate), P(S-b-MMA). Freeze-dried powders of P(S-b-MMA) having a molecular weight of 8.4×10^4 were rapidly heated to temperatures above the glass transition temperature to initiate the microphase separation. The microphase separation process was found to consist of a rapid, local microphase separation followed by a long-term coarsening process. The period characterizing the lamellar microphase separated structure was found to increase initially and then saturate at longer times. These results are discussed in light of recent theoretical developments.

Key words: Time-resolved small-angle x-ray scattering – microphase separation – symmetric diblock copolymers

Introduction

Symmetric diblock copolymers can exist in either the phase mixed or microphase separated state [1]. If $\chi N < 10.5$, where χ is the Flory–Huggins segmental interaction parameter and N is the number of monomer units in the copolymer chain, the copolymers will be phase mixed where the segments of the two blocks are intimately mixed. This spatial distribution of chains segments is not completely random due to the interconnectivity of segments which gives rise to the now classic correlation hole scattering observed for phase mixed diblock copolymers [2]. If $\chi N > 10.5$, the symmetric diblock copolymer microphase separates into lamellar microdomains with a period that can be described in terms of the molecular weight and the segmental interaction parameter [3–6]. It should be noted that, in most cases, the microphase separation of the copolymer occurs on cooling. χ has usually been characterized by a $\frac{1}{T}$ dependence which causes χ to increase with decreasing temperature. Recently, however, it has been shown [7] that diblock copolymers can microphase separate upon heating. Here, equation of state effects cause χ to increase with increasing temperature in a manner similar to that of polymer mixtures [8, 9]. In analogy to polymer mixtures, what has been termed the order-to-disorder transition in diblock copolymers can be termed the upper critical ordering transition, UCOT, and this new transition can be termed the lower critical ordering transition, LCOT.

Whether a diblock copolymer exhibits an LCOT or UCOT, as the measurement temperature approaches the transition temperature, the concentration fluctuations in the disordered state increase in amplitude and induce the phase transition [10, 11]. As the transition temperature is increased, the dominant period of the fluctuations increases and gives rise to a pretransitional chain stretching [12–14]. The increase in the correlation length and amplitude of the fluctuations is similar to that exhibited by simple homopolymer mixtures. It is tempting, therefore, to consider the microphase separation of diblock copolymers in a similar light. However, due to the connectivity of the two blocks, the period of the fluctuations is limited [15–17]. Thus, one may expect that the short wavelength fluctuations will be suppressed since the gradient energy term in the free energy will be too large to support these fluctuations. The long wavelength fluctuations, on the other hand, will be fully suppressed since the connectivity of the two blocks will preclude these fluctuations. Herein, experimental data is presented on the kinetics of microphase separation of diblock copolymers after the copolymer has been rapidly brought from a condition where $\chi N < 10.5$ to one where $\chi N > 10.5$. A novel preparation condition is introduced whereby such quenching is made easily.

An additional driving force for these studies stems from some recent work dealing with the kinetics of ordering of thin diblock copolymer films on a surface [18, 19]. In these studies it was observed that copolymer films initially spin coated onto a silicon substrate were microphase separated. However, the average period of the microphase separated structure was ~ 1/3 that of the equilibrium period of the equilibrium, lamellar microphase separated structure. After a short period of annealing at temperatures above the glass transition temperature, T_g, a rapid local reorganization of the copolymer chains occurred, giving rise to a period that was close to the equilibrium period. However, the morphology could be described as a bicontinuous network structure which provided an easy mechanism by which the ordering of the lamellar microdomains parallel to the surface could occur. With further annealing above T_g, the ordering of the lamellar microdomains propagated into the sample from both surfaces at the expense of the bicontinuous structure. After extensive annealing, the ordering of the lamellar microdomains saturated the sample. These results suggested that the microphase separation of the diblock copolymer occurred at least in a two-step process. Initially, there was a local relaxation of the chains to a structure that approximated the equilibrium period. However, a long-term coarsening process occurred. This behavior should be directly observable by time-resolved x-ray scattering studies on bulk samples.

Experiment

The copolymers used in this study were symmetric diblock copolymers of polystyrene, PS, and poly(methyl methacrylate), PMMA, denoted P(S-b-MMA). The copolymer has an $M_w = 8.4 \times 10^4$ with an $M_w/M_n = 1.04$. The interaction parameter, χ, between PS and PMMA segments of this copolymer has been shown to be given by [20, 21] $\chi = 0.021 + \frac{3.20}{T}$ where T is the temperature in Kelvin. χ is seen to be weakly temperature dependent and, for temperatures below ~ 220 °C, $\chi N \sim 24$. Consequently, the copolymer will microphase separate into lamellar microdomains for all temperatures above T_g. To force the copolymer into a phase mixed state, the copolymer was dissolved in benzene. The solution was then frozen at 0 °C and the benzene was sublimed into a liquid nitrogen trap. This left a diaphanous powder which was collected and cold pressed into a pellet which was used for the scattering experiments. Consequently, the copolymer was trapped in a highly non-equilibrium state. The pellets were then placed in a sample cell and rapidly heated to a specific temperature above T_g using a Mettler FP-85 hot stage. The cell is designed such that incident and scattered x-ray could pass through the cell unhindered.

Time-resolved x-ray scattering studies were performed on Beamline I-4 at the Stanford Synchrotron Radiation Laboratory. The specifics of the scattering geometry can be found elsewhere [22]. Briefly, the x-rays from the storage ring were focussed vertically by a symmetrically bent float glass mirror coated with platinum. The x-rays then impinged upon an asymmetric bent Si crystal which served to monochromate the x-ray beam and focus the beam horizontally. The horizontal and vertical focal plane of the x-rays was at the linear photodiode array detector. Data from the detector was stored at specified time intervals on an IBM PS/2. Slits were used to eliminate parasitic radiation. A 50 μm sheet of Kapton, inclined 45° to the incident beam, placed just prior to the sample scattered a small fraction of the incident radiation into a NaI crystal scintillation detector which served to monitor the flux incident on the sample.

Approximately 15 s were required to heat the sample to the temperature of the experiment as indicated by a thermocouple mounted onto the sample cell. For each experiment the temperature was stable to within ± 0.2 °C. The scattering from the sample was recorded once the sample had reached the desired temperature.

Results and discussion

Shown in Fig. 1 is the scattering profile obtained for the freeze-dried P(S-b-MMA) after cold pressing. This profile represents the scattering at time zero ($t = 0$). As can be seen, the scattered intensity is a monotonically decreasing function of the scattering vector Q where $Q = \frac{4\pi}{\lambda} \sin \theta$ where 2θ is the scattering angle and λ is the wavelength. For a diblock copolymer in the disordered state, a weak scattering maximum, characterized by the molecular weight of the copolymer and the segmental interaction parameter would be expected. This is not seen here since the x-ray contrast between the PS and PMMA blocks is low. The angular dependence of the scattering arises from small microvoids which are present in the sample due to the preparation conditions. From a Guinier analysis of the scattering, one can estimate an average void size of ~ 80 Å. The data was not placed on an absolute level and, consequently, no information could be derived pertaining to the volume fraction of the voids in the sample. However, it is very clear that the microphase separation of the copolymer has been fully suppressed by the preparation conditions used. This sample was annealed for 24 h under vacuum and the scattering profile shown in Fig. 2 was obtained. Here, a maximum characteristic of the lamellar microphase separated morphology is evident. The maximum the scattering profile occurs at $Q = 0.019$ Å which corresponds to a period of 330 Å. This scattering profile represents the structure of the copolymer after microphase separation and it is the change in the scattering profile as a function of time from that shown in Fig. 1 to that in Fig. 2 which is the focus of this work. It should be noted that a third order reflection is not evident in the scattering profiles. While this would be expected. Porod analysis of the tail

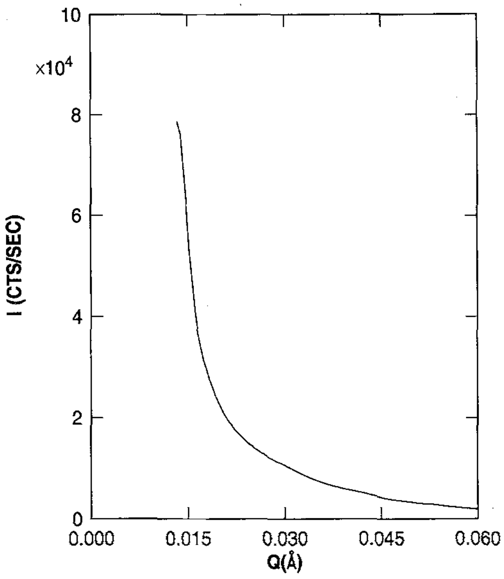

Fig. 1. Small-angle x-ray scattering of a freeze-dried P(S-b-MMA) copolymer as a function of the scattering vector, Q. The profile shown was obtained at room temperature prior to the quenching experiment

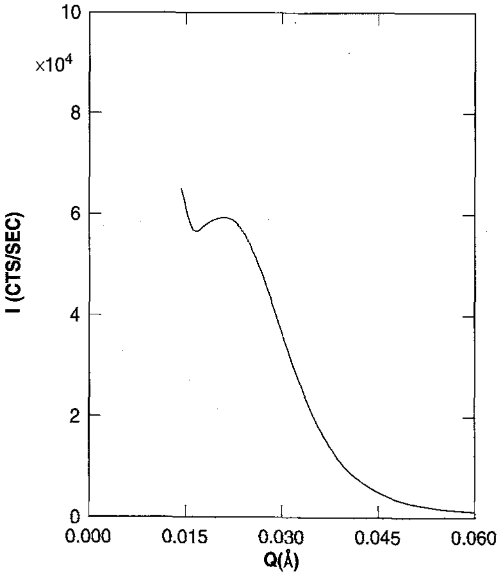

Fig. 2. Small-angle x-ray scattering profile of a P(S-b-MMA) copolymer that was freeze-dried and then annealed for 24 h at 140 °C

part of the scattering profile and independent neutron reflectivity studies [23, 24] show that the interface between the PS and PMMA microdomains is ~ 50 Å. This large interfacial width serves to suppress the scattering at higher scattering vectors and, consequently, makes the observation of higher order reflections difficult. Extended data accumulation times reveals the presence of the third order reflection as shown previously [25]. It is important to compare the two scattering profiles. The dominant amount of scattering in the initial sample has decreased substantially at the position where the scattering maximum of the microphase separated morphology is observed. Consequently, while the presence of microvoids in the initial sample may place some limitations on the interpretation of the results, the extent to which it will change the overall conclusions will be minimal.

Shown in Fig. 3 is the time-resolved x-ray scattering of P(S-b-MMA) after a rapid heating to 140 °C. The full time scale of the measurements is 1100 s. From these data it is evident that the scattering increases markedly as a function of time with the gradual development of the characteristic scattering of the microphase separated structure. It is also evident that the increase in scattering at longer times is less dramatic than at shorter times.

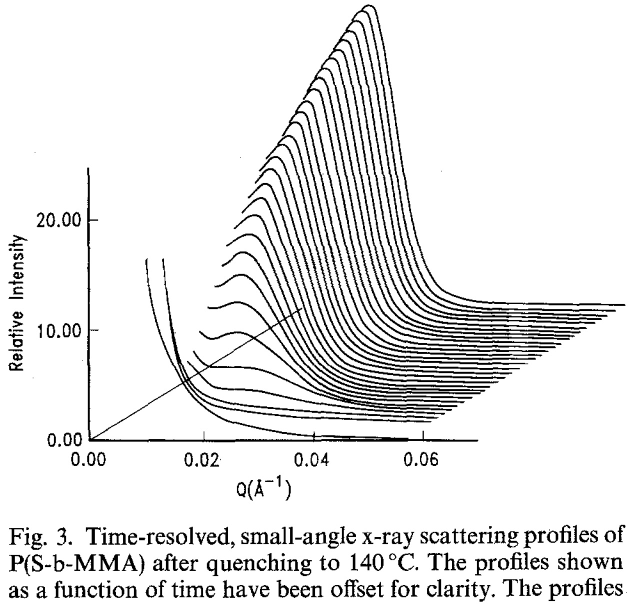

Fig. 3. Time-resolved, small-angle x-ray scattering profiles of P(S-b-MMA) after quenching to 140 °C. The profiles shown as a function of time have been offset for clarity. The profiles are equally incremented in time with the full time range of this experiment being 1100 s

According to the linearized Cahn–Hilliard–Cook theory [26–28], for a system undergoing a spinodal phase separation, the intensity of scattering at a given Q as a function of time is given by:

$$I(Q), t) = I(Q, \infty (+ (I(Q, 0) - (I(Q, \infty)) \exp(2R(Q)t) , \qquad (1)$$

where $I(Q, 0)$ is the scattering at $t = 0$, $I(Q\ \infty)$ is the virtual structure factor, and $R(Q)$ is the amplification factor for fluctuations at a given Q. The virtual structure factor, in the case of simple mixtures, is the scattering characteristics of fluctuations at the quench temperature. For quenches within the spinodal region, $I(Q, \infty)$ can never be observed since the mixture phase separates [29]. In the case of copolymers, $I(Q, \infty)$ is given by the correlation hole scattering of the copolymer at the quench temperature. This would, of course, lead to negative scattering intensities according to mean field arguments.

Attempting to pursue the microphase separation of block copolymers via the Cahn–Hilliar–Cook formalism has several severe limitations. First. the size scale over which the concentrations fluctuations of interest occurs is of the order of tens of nanometers. The amplification factor is Eq. (1) is given by:

$$R(Q) = -DQ^2 - M\kappa Q^4 , \qquad (2)$$

where D is the diffusivity, M is the mobility and κ is the interfacial energy. If one considers typical diffusion coefficients for polymers ($\sim 10^{-17}$ cm^2/s), the time required for the polymer to move the distances of interest is on the order of seconds. Consequently, unless one is very near the T_g of the polymers, it is exceptionally difficult to measure the kinetics of interest for this purpose. In fact, the copolymer will have relaxed sufficiently by the time the sample has thermally equilibrated to make the measurements nearly impossible. One possible means to circumvent this is via pressure quenches where the changes are essentially instantaneous. A second problem with the use of Eq. (1) is that the peak in the correlation hole scattering is not invariant. As the temperature is brought near the lower or upper critical ordering transition, the copolymer chains undergo a pretransitional stretching [12–14]. In the microphase separated state the copolymer chains are stretched at the interface due to the non-favourable interactions of the blocks at the interface. In homopolymer mixtures the scattering function has a maximum value at $Q = 0$ Å^{-1} and the concentration fluctuation are not sensitive to the chain configuration.

Rather than attempting to extract quantitative information on the mechanism of microphase separation, be it via a spinodal process or by a nucleation and growth process, it is worthwhile to examine the experimental findings. Shown in Fig. 4 is the period *L*, calculated from the position of the peak in the scattering, as a function of time. The data, plotted in a log-log manner, show several interesting features. Initially, the period is constant as a function of time. This is followed by a gradual increase in the period up to a value corresponding to the equilibrium period. With further time, the period is constant to within experimental error. The increase in the period as a function of time appears to obey a power law with an exponent of 0.1. Shown in Fig. 5 is the relative intensity of the scattering maximum at 140 °C as a function of time. Over the entire time interval the intensity of the scattering increases in a power law manner with time with an exponent of 0.53. At longer times, the intensity begins to increase less rapidly as noted by the curvature. Similar results were obtained at 130° and 150 °C. Taken together, these results indicate that the microphase separation of the P(S-b-MMA) involves at least three stages. Initially, concentration fluctuations are established at the quench temperature which grow in amplitude. However, soon the magnitude of the concentration fluctuations are sufficiently large that the copolymer chain begins to stretch as noted by the increase in the period. These fluctuations continue to grow with stretching of the copolymer chains. Finally, the fluctuations saturate and the equilibrium period is established. But, the phase separation continues by a coarsening of the microphases. This coarsening process can be characterized by a continuous decrease in the interfacial width. The interfacial width is initially large and, with time, diminishes, giving rise to the increase in the scattering. This essentially translates into an increase in the fraction of the period occupied by pure PS and PMMA. These results are in accord with recent experimental findings of Stühn and coworkers [30] on diblock copolymers of polystyrene and polyisoprene.

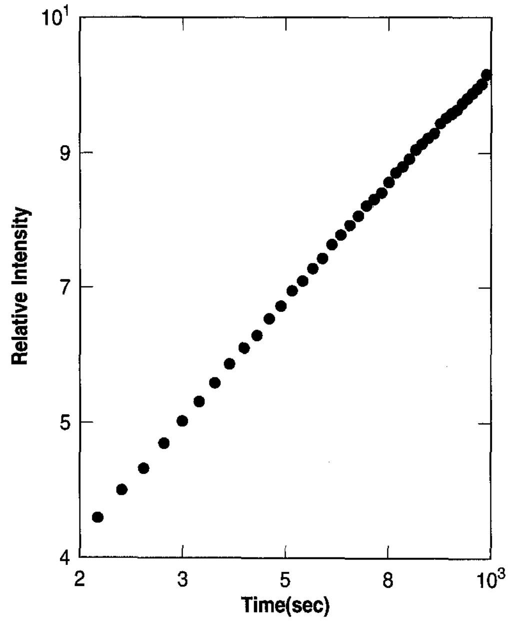

Fig. 5. The intensity of the small-angle x-ray scattering peak as a function of time. The data are plotted in a log-log manner

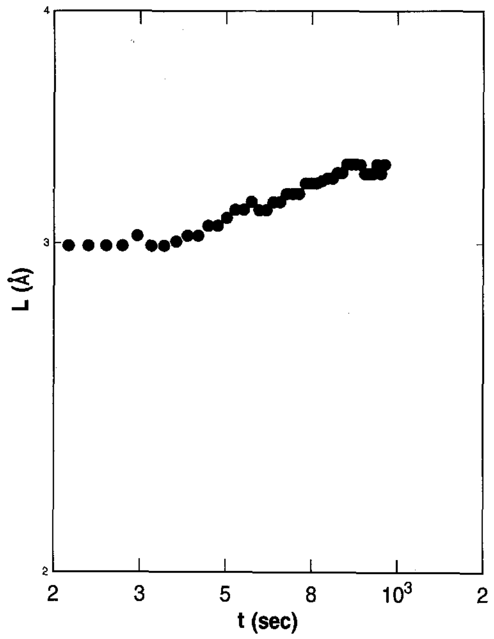

Fig. 4. The period, *L*, of P(S-b-MMA) as a function of time after quenching to 140 °C. *L* was calculated from the position of the scattering maximum. The data are plotted in a log-log manner

Recently, Muthukumar [31] had extended the linear analysis of phase separation to include the case of the microphase separation of diblock copolymers. Here, the fluctuations present in a copolymer melt are restricted on short and long wavelength scales. Short wavelength fluctuations are suppressed because of the gradient energy term, whereas the longer wavelength fluctuations are suppressed due to the connectivity of the blocks. This treatment, which is limited to very high, essentially infinite, molecular weight copolymers makes distinct predictions for shallow and deep quenches. These correspond to copolymers in the weak and strong segregation limits, respectively. For shallow quenches, the period is initially constant as a function of time. With increasing time the period then begins to increase in a power law manner with an exponent of 0.24. At longer times the period attains its equilibrium value and remains constant as a function of time. In the deep quench, the period increases with a power law exponent of 1/3. Qualitatively, these predictions describe the data presented here. In the case of P(S-b-MMA), $\chi N \sim 25$, which places the system between the weak and strong segregation limits. Consequently, an exponent of at least 1/4 would be expected. However, the exponent observed experimentally is significantly less at ~ 0.1. This discrepancy may arise from the finite molecular weight of the copolymer studied experimentally which may negate some of the approximations used in the theory. However, the qualitative aspects of the theory are in accord with the experimental observations. More work, however, is required experimentally and theoretically to elucidate the origin of the discrepancies.

Conclusions

The kinetics of the microphase separation of P(S-b-MMA) symmetric diblock copolymers was investigated by time-resolved, small-angle x-ray scattering. Using a freeze-drying technique, the copolymers were brought into the phase mixed state. Quenching the copolymer to temperatures above the glass transition temperature placed the copolymer within the envelope defined by the spinodal where lamellar microphase separated domains would form. The scattering data clearly show that the microphase separation process occurs via at least a three-stage process. First, concentration fluctuations over a restricted wavelength range grow with time. When the fluctuations become sufficiently large, the copolymer chains undergo a stretching which causes the period to increase. After the fluctuations saturate at pure PS and PMMA concentrations, there is a slow coarsening process in which the interfacial width of the copolymer microdomains narrows with time.

Acknowledgements

This work was partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contrast DE-FG03-88ER45375. I.C. acknowledges the financial support of the Pohang Institute of Science and Technology, Pohang, Korea. This work was partially done at the Stanford Synchrotron Radiation Laboratory which is operated by the Department of Energy, Office of Basic Energy Sciences.

References

1. Bates FS, Fredrickson GH (1990) Ann Rev Phys Chem 41:525
2. Leibler I (1980) Macromolecules 13:1602
3. Meier D (1969) J Polym Sci C 26:81
4. Leary DF, Williams MC (1970) J Poly Sci B 8:335
5. Helfand E (1975) Macromolecules, 8:552
6. Helfand E, Wasserman ZR (1976) Macromolecules 9:879
7. Russell TP, Karis TE, Mayes AM, Gallot Y (1994) Nature
8. Sanchez IC, Lacombe RH (1976) J Phys Chem 80:2439
9. McMaster LP (1973) Macromolecules 6:760
10. Bates FS (1984) Macromolecules 17:3607
11. Fredrickson GH, Helfand E (1987) J Chem Phys 24:3456
12. Owens JN, Gancarz IC, Koberstein JT, Russell TP (1989) 22:3388
13. Almdahl K, Rosedale JH, Bates FS, Wignal GD, Fredrickson G (1990) 65:1112
14. Fried H, Binder K (1991) Europhys Lett 16:237
15. Hashimoto T, Kowsaka K, Shibayama M, Suchiro S (1986) Macromolecules 19:750
16. Hashimoto T, Kowsaka K, Shibayama M, Kawai H (1986) Macromolecules 19:754
17. Hashimoto T (1987) Macromolecules 20:465
18. Russell TP, Mayes AM, Kunz M, (1994) Teramoto A, Kabayshi M, Norisuye T (eds.) Ordering in Macromolecuar System. Springer-Verlag, Berlin p 217
19. Mayes AM, Russell TP, Bassereau P, Backer SM, Smith GS (1994) Macromolecules 27:749
20. Callaghan TA, Paul DR (1993) Macromolecules 26:2439
21. Russell TP (1993) Macromolecules 26:5819
22. Russell in Hand book of Synchrotrom Radiation. Vol. 3, Brown G, Moncton DE, eds, North-Holland Pub. Co., 1991.

23. Anastasiadis SH, Russell TP, Satija SK, Majkrazak CE (1989) Phys Rev Lett 62:1852
24. Anastasiadis, Russell TP, Satija SK, Majkrzak CF (1990) J Chem Phys 92:5677
25. Green PF, Jerome R, Christensen TM, Russell TP, Jerome R (1989) Macromolecules 22:2189
26. Cahn JW (1965) J Chem Phys 42:93
27. Hilliard JE (1970) in Phase Transformations. Aronson HI, ed., Am Soc Metals, Metals Park, OH
28. Cook HE (1970) Acta Metall 18:297
29. See for example, Strobl GR (1985) Macromolecules 18:558
30. Stühn B, Vilesov A, Zachmann HG (1994) Macromolecules submitted
31. Muthukumar M (1994) J Polym Sci Polym Phys Ed, submitted

Received May 2, 1994;
accepted June 17, 1994

Authors' address:

T.P. Russell
IBM Research Division
Almaden Research Center
650 Harry Road
San Jose, California 95120-6099, USA