Memory Effects in Homopolymer Blends during Annealing

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Received April 25, 2002

ABSTRACT: We perform light scattering and direct optical experiments on a homopolymer blend of poly(methylphenylsiloxane) (PMPS) with polystyrene (PS). The system is subjected to the three-step process. The system is first quench to low temperature (T_1) and allowed to separate for 5 h; next it is heated to a high temperature (T_0) to the one-phase region where it mixes for a couple of minutes (1−10 min) and then quenched back to T_1 and observed for 5 h. We note that annealing at T_0 can be quantitatively studied by the analysis of the scattering intensity summed over a linear array of photodiodes. This quantity is very sensitive to the structure exisiting in the system. If the system is properly annealed, it has a noisy behavior and while the structure inside the system persists, it behaves very regularly. Moreover, one can observe the differences in the scattering intensity between the first and the second quench at very short wavevectors, indicating that large domains survived the annealing process for short annealing time (less than 4 min). However, the average area of the domains per unit volume is the same as obtained from the tail of the scattering intensity, indicating that small domains dominating in the system do not survive the mixing process even if it is very short (2 min). Finally, the direct observation under the microscope reveals that they dissolve in such a way that their size changes at the end of the process of dissolution, when as we suspect the size of the interface becomes comparable to the size of the dissolving domain. Domains inside the domains are also observed at short times after the second quench. In general, our methods allow the quantitative estimate of the annealing time for polymer mixtures and thus can save a lot of time, especially if we have to repeat the same measurements many times and we need to anneal the samples between measurements.

1. Introduction

The phase separation process is fairly well understood in AB homopolymer blends.[1−3] A typically studied process is a one-step process. First the sample is annealed for many hours or even days at high temperature in a one-phase region, and next it is quenched to a low temperature where it undergoes a phase separation. The domains of A-rich and B-rich phase form and grow in time, saturating in the process. Quite recently, the two-step quench−jump[4−11] and quench−quench[12−14] processes have started to be studied. Akcasu et al.[4,5] concentrated on the mixing (dissolution) in a one-phase region. The two-step process considered in their papers[4,5] was as follows: the system was quenched below the binodal temperature into the thermodynamically unstable region and allowed to demix for some time. Next, the system was heated above the binodal into the one-phase region, and decay of the scattering intensity was observed. They observed the exponential decay in time of the maximum scattering intensity and the algebraic shift of its location toward small wavevectors with the exponent −0.5. Vailati and Giglio[8] prepared a binary mixture at a temperature below the consolute temperature in a two-phase region. The system was completely separated with a sharp interface between two phases. Next they applied a temperature jump, and the diffusion process of mixing started. They observed large fluctuations in the composition during the mixing process, orders of magnitude larger than the fluctuations at equilibrium. Hashimoto et al.[12−14] studied the acceleration of the separation process by the double-quench method. First they quenched the system below the spinodal, and after some time they made the second quench to the lower temperature. They studied this two-step quench−quench process by light scattering. The increase of the scattering intensity at high wavevectors indicated that smaller domains started to form in the system. The intensity peak decreased at first just after the second quench, which could indicate that small domains formed inside large domains. This effect was only possible when the size of the big domains was larger than the typical size of the Cahn instability at the final temperature. If it was not the case, the small domains did not develop, and only the original domains grew faster. The number of unexpected observations shows that the process of mixing/demixing is far from being fully understood.

Here our main interest is to observe the three-step quench−jump−quench (demixing−mixing−demixing) process in an AB homopolymer blend. The system is first quenched from the one-phase region (temperature T_0) below the spinodal (to temperature T_1) and allowed to separate for many hours; next we heat up a sample (make a temperature jump) to the initial high temperature T_0 and allow the system to mix for a couple of minutes. Finally, we quench the system again to T_1. The main question which we would like to pose here is the following: *how long should be the annealing at high temperature so that the system would lose all infomation concerning the initial nonuniform state of the blend, and what are the memory effects if any?* The main objective of this paper is to provide a procedure that provides a test of a good annealing of polymer mixtures (no memory effects), and a *quantitative* estimate of the annealing time needed in this case. One of the simplest ways to study the problem is to compare the evolution of the system after the first quench with the evolution after the second quench. If the annealing at T_0 is not perfect, some traces of the old structure (which developed after the first quench) should affect the evolution

10.1021/ma0206467 CCC: $22.00

of the domains after the second quench. Here we perform the light scattering studies and analyze the evolution of the scattering intensity $S(q,t)$ as a function of the wavevector, q, and time, t. Additionally, we have made the optical observation under the microscope repeating the same procedure as in the experiment with the light scattering. Our results give a simple and clear procedure for the determination of the time necessary to mix two polymers at high temperature.

2. Experimental Section

We have used a poly(methylphenylsiloxane) (PMPS) from Aldrich Chemical Co. characterized by $M_w = 2274$ and $M_w/M_n = 1.35$ and polystyrene (PS) from Fluka Chemical Co., $M_w = 10\,700$ and $M_w/M_n = 1.03$ characterized in the melt by the following radii of gyration:[15] PMPS, 6.54 Å; PS, 25.4 Å. PMPS was dried at 70° C under vacuum and next dissolved with PS in benzene in 55/45% (PMPS/PS) proportions for polymers by weight. Thin films were prepared by casting from 20% benzene solution on glass of size 1 cm in diameter. The films were dried at high temperature (70° C) under vacuum for 1 day and the next 3 days on a hot stage at 132° C before making the measurements. The samples were covered with a second glass plate, and the sample thickness was 50 ± 5 μm. Because the temperatures are high, the chemical composition of the samples starts to change appreciably (probably due to increased oxidation at high temperature), resulting in a change of the binodal temperature after 3 days of measurements. The samples have not degraded at room temperature because the last results obtained at high temperature were reproducible after 1 year. For practical purposes a single sample was used for 1 day only (a single measurements took about 11 h), and then it was discarded. The temperature was controlled up to 0.01 deg, and the typical time for the stabilization of the temperature after a sudden change was 50 s. (This effect was checked experimentally, since for example the average wavevector increases for 50 s when the sample is suddenly brought to a lower temperature.) The scattered intensity was detected on a linear array of 512 photodiodes. The measurements were taken every 0.5 s during heating and every 20 s during the quenches. The scattering angles, θ, which are accessible in this experiment are 0.5°−42°, and the corresponding wavevectors ($q = 4\pi/\lambda \sin \theta/2$) are 0.2−11 μm^{-1}. It means that in the real space it corresponds to the domains of size $L = 2\pi/q$ between 0.5 and 30 μm. We use the standard laser (He−Ne, 5 mW) of $\lambda = 632.8$ nm and a parabolic mirror to reflect the scattered intensity toward the array of photodiodes. We smoothed the noisy data by averaging them over 20 neighbor photodiodes; i.e., each point shown in the plot of $S(q,t)$ vs q has been integrated over the q range corresponding to 20 nearest photodiodes and divided by the range of integration. The range of integration for the points overlapped always for 10 photodiodes; i.e., we made such averaging for 51 photodiodes out of the total number of 512. Another method of averaging consisted in averaging each signal from a photodiode over the five nearest neighbors and keeping all 512 points. Apart from the determination of $S(q,t)$, we have done the analysis of the evolution of the scattering intensity summed over the linear array of photodiodes, defined as

$$\delta = \int S(q,t)\, \mathrm{d}q \tag{1}$$

and the first moment of such defined distribution, q_{av}:

$$q_{av} = \frac{\int q S(q,t)\, \mathrm{d}q}{\int S(q,t)\, \mathrm{d}q} \tag{2}$$

Please note that δ is not the total scattered intensity since we do not integrate in eq 1 with a proper measure q^2 but only sum the intensity over the linear array of photodiodes. We have used this definition for practical purposes, since it is easy to implement in the experiment and was simply used to reduce the noise level on the photodiodes and quantitatively study the proper annealing. The analysis of both q_{av} and δ is also helpful in the study of the scaling in the system as we show below.

It is well-known that after a single quench below the spinodal[1−3] the system at long times gets into the late stage regime, where the morphological properties of the system are governed by the single length scale: average domain size $L(t)$. In the late regime, one finds a power law growth of $L(t)$ and scaling; i.e., a morphological pattern of the domains at earlier times looks statistically similar to a pattern at later times apart from the global change of scale implied by the growth of $L(t)$. Quantitatively, it means for example that the correlation function of the homopolymer concentration has the following functional form:

$$g(\mathbf{r},t) = g(\mathbf{r}/L(t)) \tag{3}$$

where

$$L(t) \sim t^{\beta} \tag{4}$$

the characteristic length scale in the system, scales algebraically with time t with the exponent β. The scattering intensity is the Fourier transform of $g(\mathbf{r},t)$

$$S(q,t) = \int \mathrm{d}^3\mathbf{r}\, g(\mathbf{r},t) \mathrm{e}^{i\mathbf{qr}} \tag{5}$$

and because of the isotropy of the system depends only on the length of the scattering vector. It follows from the scaling hypothesis and eq 5 that

$$S(q,t) = L^3(t) I(x) \tag{6}$$

where $x = L(t)q$. It implies that

$$\delta = L^2(t) \int \mathrm{d}x\, I(x) \tag{7}$$

and

$$q_{av} = L^{-1}(t) \frac{\int x I(x)\, \mathrm{d}x}{\int I(x)\, \mathrm{d}x} \tag{8}$$

Thus, scaling implies that

$$\delta \sim {q_{av}}^{-2} \tag{9}$$

irrespective of the exponent β.

In each case the base scattering (at high temperature) was subtracted from $S(q,t)$. The samples were first annealed at 132 °C and then quenched to temperature 112 °C below the spinodal, where they were allowed to demix for 5 h. Next the system was heated back to 132 °C, and after a few minutes (1−10 min) it was quenched back to 112 °C and observed for 5 h. The results of both quenches are compared in the next section.

Furthermore, we have done the complemetary observation of the system under the microscope Nikon Eclipse E400. The observation has been done under a magnification of 750×, but the photographs were taken with a magnification of 250×. The samples were placed on the heating stage, under the microscope, with the 0.01 deg control of the temperature, the same as in the scattering experiment.

3. Results and Discussion

In Figure 1 we show a schematic picture of the experiment. The binodal curve separates a one-phase region above from the two-phase region below the curve. The system is brought by a temperature quench into the two-phase region to temperature $T_1 = 112$ °C, and

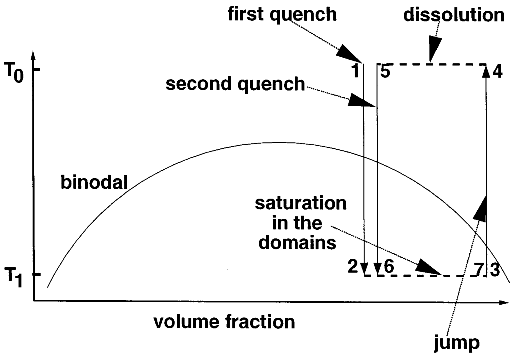

Figure 1. The schematic picture of the general idea of our measurements. The binodal curve, given by the solid line, divides the one-phase (above) from the two-phase region (below). The system of a fixed volume fraction is quenched from the high temperature, T_0, to the temperature T_1 into the two-phase region (process 1 → 2) and allowed to demix at this temperature for 5 h (process 2 → 3). Next it is heated back to temperature T_0 (process 3 → 4), and the domains originally formed at T_1 dissolve by diffusion for a couple of minutes (from 1 to 10 min) (process 4 → 5). Then the system is quenched for the second time to temperature T_1 (process 5 → 6) and allowed to separate for the second time for 5 h (process 6 → 7). The dashed line shows schematic evolution of the average volume fraction inside a typical domain in the system. In principle, it is hard to show the kinetic pathway of these processes on a two-dimensional diagram since it involves the whole non-uniform distribution of the volume fraction in the system. Our goal is to see what are the memory effects in the dissolution process. In principle, we compare the process 2 → 3 (after the first quench) with the process 6 → 7 (after the second quench). Without any trace of the original structure in the annealing process 4 → 5 the evolution 2 → 3 should be the same as 6 → 7.

the temperature jump (to $T_0 = 132$ °C) brings the system back into the one-phase region and after some time we quench it back to T_1. The whole processes can be divided into the following steps: $T_0 \rightarrow T_1$ temperature quench, phase separation at T_1, $T_1 \rightarrow T_0$ temperature jump, dissolution of the domains at T_0, again $T_0 \rightarrow T_1$ second temperature quench, and finally the phase separation at T_1. We will compare the results for the separation after the first quench to the separation after the second quench.

In Figure 2 we show the scattering intensity, $S(q,t)$, as a function of the wavevector q obtained for different times after the first quench. The peak increases and the peak position moves toward small wavevectors. We have found $\delta \sim t^{0.6\pm0.1}$ and $q_{\mathrm{av}} \sim t^{-0.3\pm0.05}$, and from eq 9 it follows that we have reached the late stage growth regime where scaling is satisfied. It also means that the PS- and PMPS-rich domains which formed in the system are very well saturated. The domain grows exponent $^1/_3$, and a high density of droplets (as seen under the microscope) indicates that the growth of the domains proceed by the Binder−Stauffer mechanism of droplet coalescence.

In Figure 3 we show the decay of $S(q,t)$ after the temperature jump. The prediction of the mode-coupling analysis of Akcasu[4] gives the shift of the maximum of the scattering $q_{\max} \sim t^{-0.5}$ for long times of the decay and exponential decay of the intensity. Unfortunately, it seems that this is by no means universal and might depend on the state of the system before the temperature jump. For example, Haloubek[9] found an exponential behavior of $q_{\max}$ as a function of time, and we have found also a very fast decay of $q_{\max}$ which if fitted to the algebraic form gave $q_{\max} \sim t^{-2.5}$. It is also possible that the prediction of Akcasu[4] are valid for a very narrow range of time just before the scattering intensity reaches the noise level, and thus this time interval is practically not accessible in our experiment.

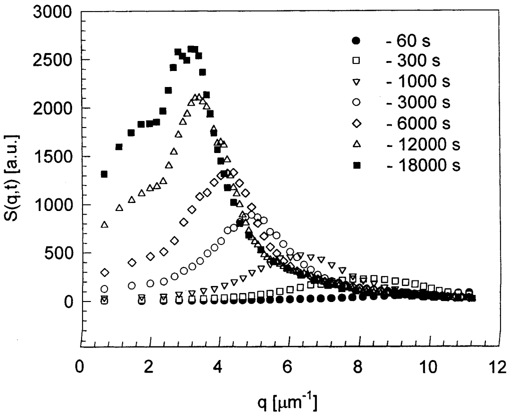

Figure 2. Scattering intensity, $S(q,t)$, after a quench from a high temperature $T_0 = 132$ °C (above the binodal (see Figure 1)) to the temperature $T_1 = 112$ °C, as a function of the wavevector q for different times. It shows the known behavior during the spinodal decomposition. The peak grows and its location shifts toward smaller wavevectors, indicating the growth of the average size of the PS-rich and PMPS-rich domains (coarsening process).

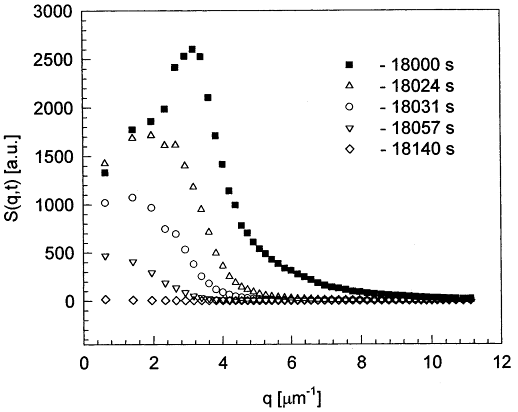

Figure 3. Scattering intensity, $S(q,t)$, after a temperature jump from $T_1 = 112$ °C to the one-phase region $T_0 = 132$ °C above the binodal as a function of the wavevector q. The peak decreases (indicating the decrease of the saturation of the domains) and its location shifts toward smaller wavevectors, indicating the increase of the average size of the PS-rich and PMPS-rich domains following a global disappearance of small domains (reverse coarsening process) by pure diffusion across domains boundaries.

The sample was kept at high temperature for 2 min (Figure 3), and then we made another quench to $T_1 = 112$ °C. In Figure 4 we show the growth of $S(q,t)$ as a function of time after the second quench. The close inspection shows the differences between Figure 2 (first quench) and Figure 4 (second quench). They strongly differ at very small wavevectors, indicating that the number of big domains is larger in the system after the second quench. It is a clear sign of the memory effect. The large domains survived the annealing for 2 min at high temperature, and their number after the second quench increased. At high wavevectors there is practically no difference in $S(q,t)$ between the first and second quench, which means that the surface area per volume is the same in both cases. It is best visible at the log−log plot of $S(q,t)$ (Figure 5). The differences are only at small wavevectors, and the tail behaves as $1/q^4$ (Porod

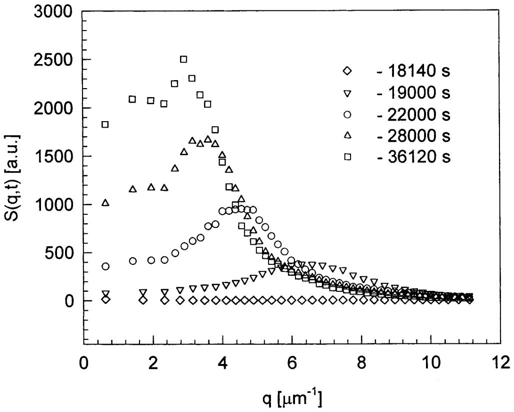

Figure 4. Scattering intensity, $S(q,t)$, after a second quench to the temperature $T_1 = 112$ °C (see Figure 1) after being kept at high temperature $T_0 = 132$ °C for 2 min. It is shown as a function of the wavevector q for different times. The peak grows and its location shifts toward smaller wavevectors, indicating the growth of the average size of the PS-rich and PMPS-rich domains (coarsening process); compare with Figure 2. The differences at small wavevectors are due to the larger number of big domains after the second quench. These domains survived the annealing process.

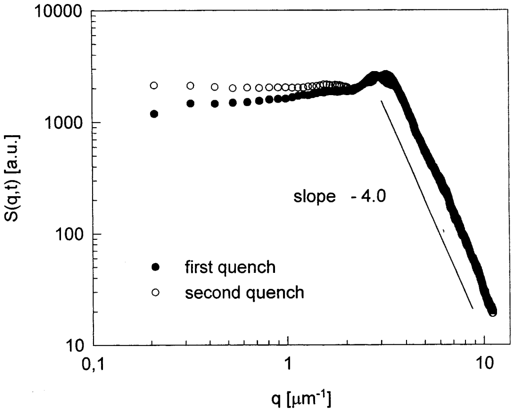

Figure 5. Scattering intensity, $S(q,t)$, on a log–log plot as a function of the wavevector q for $t = 5$ h for the first and second quench (see also Figures 2 and 4). The annealing was done for 2 min. The fit to the tail of $S(q,t)$ shows that it behaves according to the Porod law $1/q^4$, and since both tails are the same, it means that the area per unit volume is the same after the first and second quench. Differences are visible at small q vectors, indicating that the number of large domains survived 2 min of annealing process.

law). Since the tails are the same, also the area per unit volume in both cases is the same. Nonetheless, there are more larger domains after the second quench than after the first one. We have repeated the same experiment, but this time we kept the sample at high temperature for 4 min. The results indicate that after 4 min at high temperature the memory effects are almost but not entirely lost. We also did experiment for 10 min at high temperature. In Figure 6 we show the results for $S(q,t = 5$ h) for the samples which were kept at $T_0 = 132$ °C for 2, 4, and 10 min. It is clear that at small q-vectors there are differences between the results of two quenches. For 4 min of annealing the scattering is almost the same for both quenches. For 10 min of annealing there are no traces of the old structure, and the scattering intensity after 5 h of spinodal decomposition is identical for both quenches. One can also plot δ (Figure 7) and q_{av} (Figure 8) as a function of time. We see that there is a noisy behavior of both of them, during annealing, with a plateau, which indicates a good annealing with no memory effects for the annealing longer than 4 min. Such a plateau is absent for 2 min of annealing, showing that the old structure survived the annealing at high temperature. Therefore, the noisy plateau in δ and q_{av} is a good test for annealing time. Of course, the noisy behavior arises from the weak scattering of the homogeneous mixture obtained after a proper annealing.

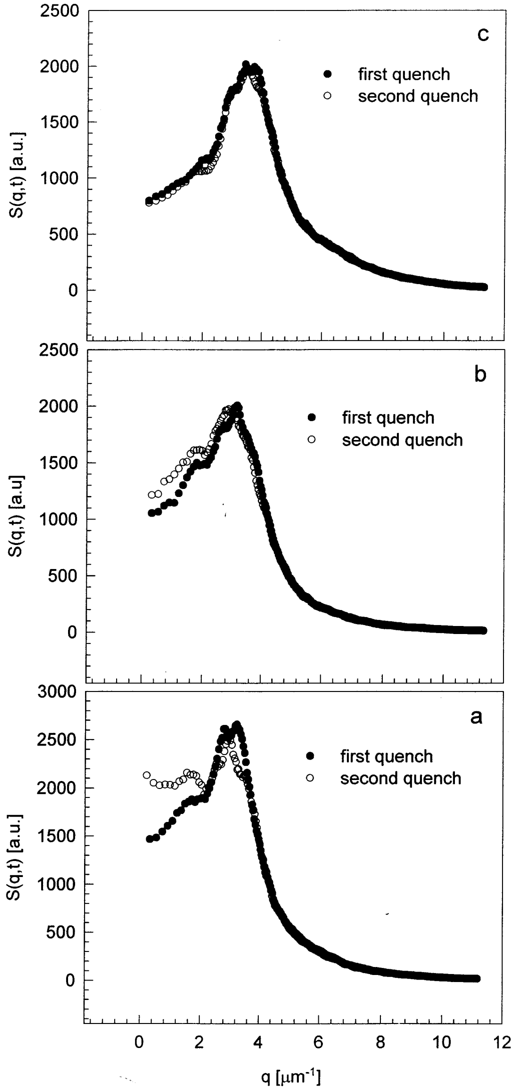

Figure 6. Scattering intensity, $S(q,t)$, as a function of the wavevector q for $t = 5$ h for the first and second quench for three different cases: (a) the sample kept for 2 min at high temperature, (b) for 4 min at high temperature, and (c) for 10 min at high temperature. As we can see, the memory effects are gone if we anneal the sample at high temperature longer than for 4 min. In (c) we see that for 10 min of annealing the scattering intensity is identical for both quenches.

To confirm our observation obtained in the light scattering experiment, we have repeated the experimental procedure in order to observe the domains and the memory effects directly under the microscope. In Figure 9 we see the formation of the domains after 295 min of the first quench (at 112 °C), its decay for 1 min at high temperature (132 °C), and the subsequent evolution for 180 min once again at 112 °C. The scale shown in Figure 9d (valid for all) is 10 μm. From Figure 9d we see that some of the large domains survived the annealing process. Comparing Figure 9b (295 min after

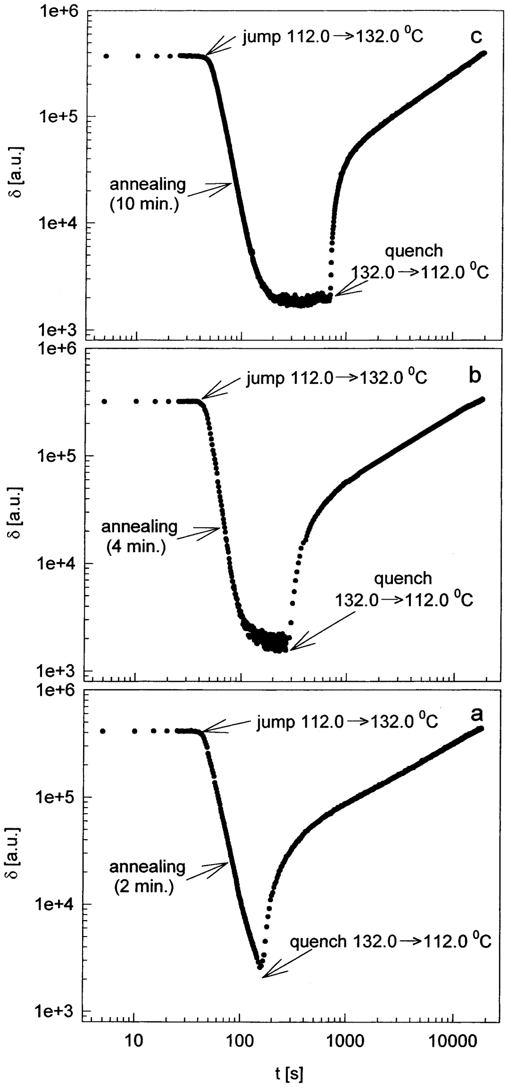

Figure 7. δ (see eq 1) as a function of time for three cases: (a) the sample kept for 2 min at high temperature, (b) for 4 min at high temperature, and (c) for 10 min at high temperature. The starting point shown in this figure is after 5 h of the evolution after the first quench and just before the temperature jump. The annealing for 10 min results in a noisy plateau, an indicator that annealing was complete with no memory of the old structure left.

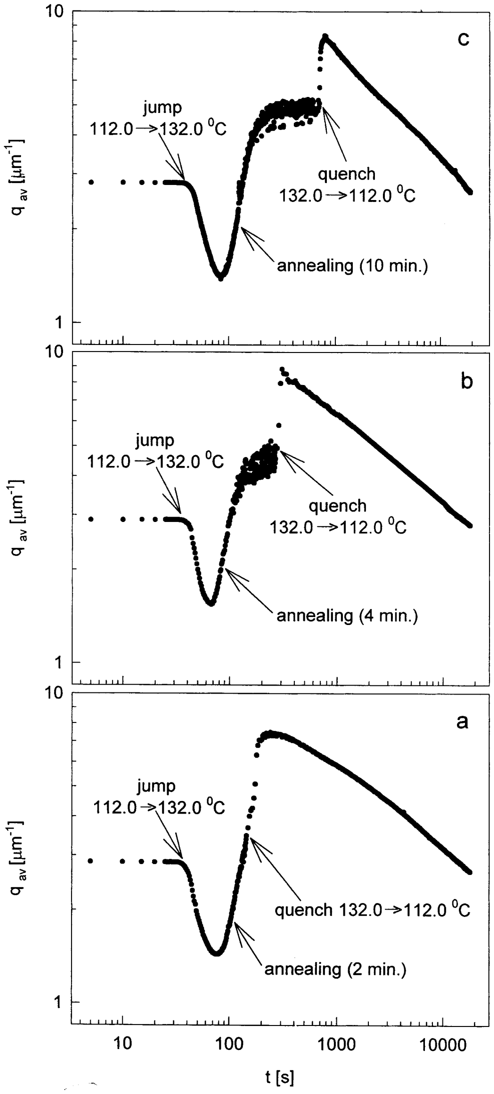

Figure 8. q_{av} (eq 2) as a function of time for three cases: (a) the sample kept for 2 min at high temperature, (b) for 4 min at high temperature, and (c) for 10 min at high temperature. The starting point shown in this figure is after 5 h of the evolution after the first quench and just before the temperature jump. The annealing for 10 min results in a noisy plateau, an indicator that annealing was complete with no memory of the old structure (produced during the first quench) left.

the first quench) and Figure 9f (180 min after the second quench) shows that the spinodal decomposition process goes faster in the second case as far as the size of large domains is concerned; i.e., there are more large domains in the system after the second quench, supporting our results obtained in the light scattering experiment (see the increase in the scattering intensity in Figure 6 after the second quench). In Figure 10 we show yet another phenomenon which would be hard to observe in the light scattering experiment. After 240 min of the first quench (Figure 10a) we made an annealing for 1 min and subsequent quench. By comparing parts a and b of Figure 10, we see that the boundaries of the largest domains (bigger than 30 μm) stayed intact and survived the annealing process. It means that the annealing proceed in two steps: first the concentration inside the domains changes and next the domains start to change their size and shift their boundaries. Moreover, in Figure 10b we see that after the second quench the formation of smaller domains started inside the big domains; the same observation was made in the quench–quench process by Hashimoto et al. We interpret this process as the spinodal decomposition, since the temperature of the system is below the spinodal temperature. However, we cannot rule out the possibility that due to the confinement the uniform (partially saturated) state of the system inside the big domains is metastable, and the small droplets form not by the spinodal mechanism but rather by nucleation.

4. Summary

We have performed a three-step (temperature quench–jump–quench) process for a homopolymer blend of poly(methylphenylsiloxane) and polystyrene to study the memory effects during annealing at high temperature. We have observed the differences in the light scattering intensity between the first and the second quench at very short wavevectors, indicating that large domains survived the short annealing process (2 min). This observation has been also confirmed by the direct

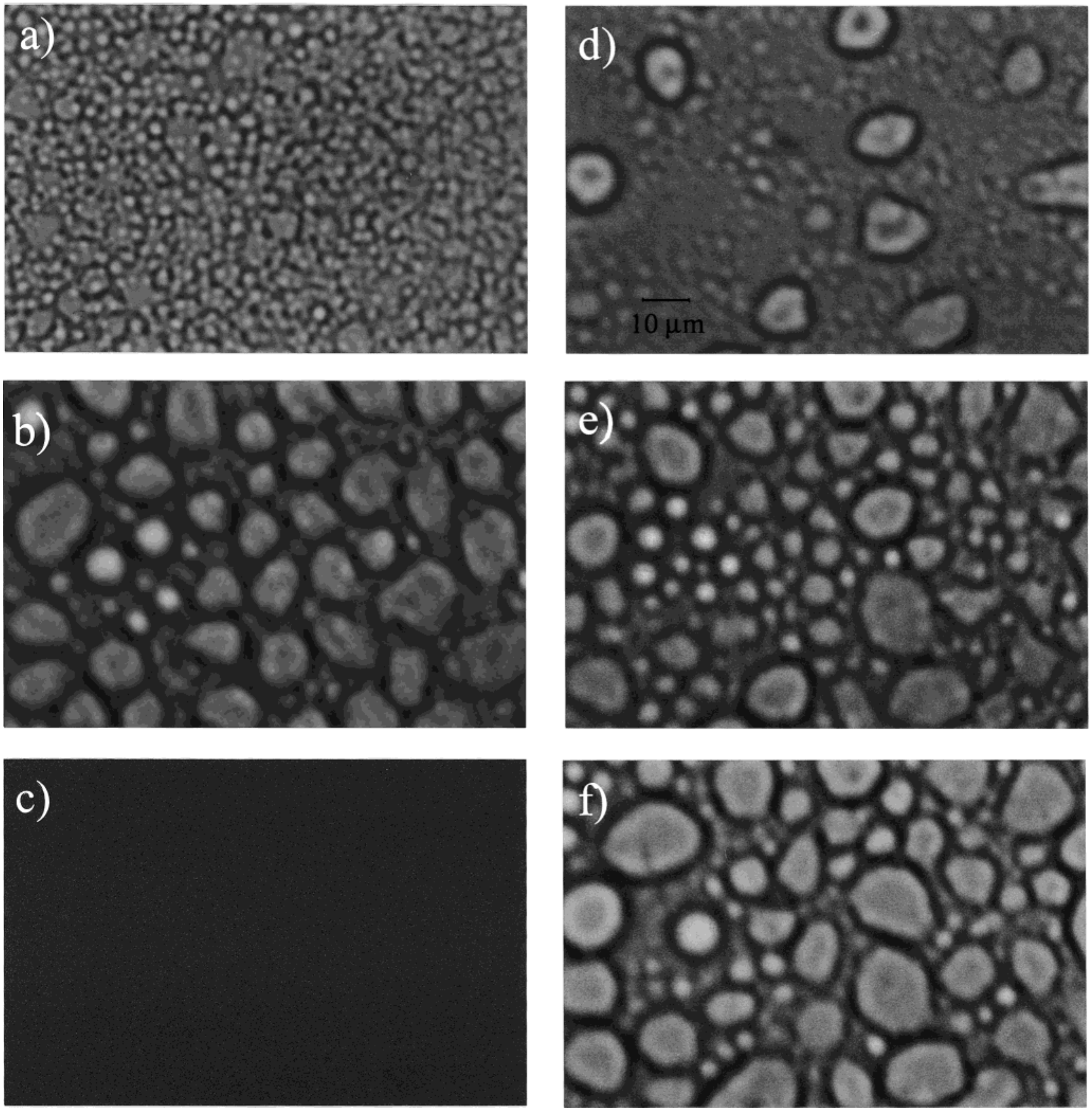

Figure 9. Photographs obtained from the direct observation under the microscope. The size bar of 10 μm is shown in photograph (d). The times are as follows: 20 min (a), 295 min (b) (during the first quench), 1 min after the annealing (c), 1 min of the second quench (d), 60 min after the second quench (e), and 180 min (f). As we can see, big domains survive the annealing process.

observation under the microscope. The tails of the scattering intensity were the same, indicating that small domains dominating in the system do not survive the mixing process even if it is very short (1 min). Finally, the direct observation of very large domains, under the microscope, reveals that the mixing process changes the saturation of the domains but not their shape and size. They dissolve in such a way that their size changes at the end of the process of dissolution, when as we suspect the size of the interface becomes comparable to the size of the dissolving domain. Perfect annealing in our system with no memory effects is obtained after 4 min at high temperature. It should be borne in mind that time scales are not universal, and different systems may anneal differently. We simply pointed out in this paper how one can precisely study the annealing process and that many interesting phenomena may be associated with the memory effects in polymers. In general, our methods allow the *quantitative* estimate of the annealing time for any polymer mixtures and thus can save a lot of time, especially if we have to repeat the same measurements many times, and we need to anneal the samples between the measurements.

Miscibility denotes the tendency or capacity of two or more liquids to form a uniform blend. An old alchemist maxim, “similia similibus solvuntur” (“like dissolves like”), is the oldest rule of mixing. This rule can be a very good guide in the study of mixing, providing one can precisely define what in a given case is the degree of likeness. For example, two simple liquids of low molecular mass can easily mix, say, at room temperature, while after polymerization they

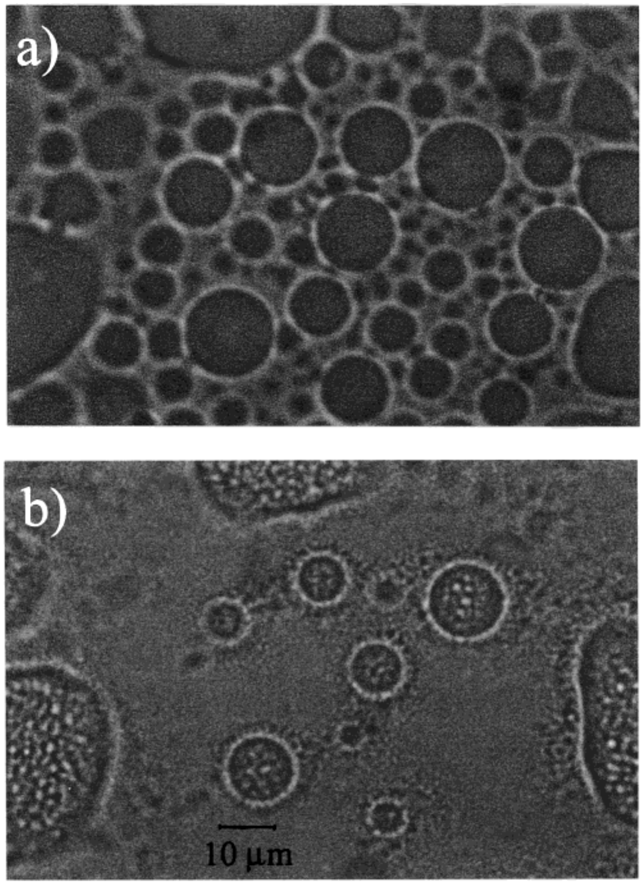

Figure 10. Photographs obtained from the direct observation under the microscope. The size bar of 10 μm is shown in photograph (b). The times are as follows: 240 min after the first quench (a) and 1 min after the second quench (b) As we can see, big domains survive the annealing process without change of shape. Inside the domains the small domains are clearly visible, meaning that after the second quench the spinodal decompostion starts inside the biggest domains which survived the annealing process.

demix well above the room temperature. Moreover, as we could observe in the multistep process that mixing, although proceeding simply, via diffusion can be very complicated depending strongly on the initial distribution of the components. The process of mixing and demixing is important from the technological point of view since many modern materials are composed of several components (mostly polymers) which in the process of preparation of the material are mixed in a liquid state before being quenched below the glass temperature.

One of the important problems in demixing/mixing studies concerns the kinetic pathways along which the transformation of the metastable or unstable states proceed toward equilibrium state. To learn more about the kinetic pathways, one needs more detailed knowledge about the Gibbs free energy as a functional of the order parameter field describing the phase transition (in the case of the blend it is the concentration of one component), in particular its minima, maxima, and the saddle points. We know that the Gibbs free energy has only one minimum above the critical temperature corresponding to the uniform mixed state. Below the spinodal it has two minima corresponding to the two uniform unmixed states—one rich in one component and one in the other. This knowledge is insufficient to learn about the kinetic pathways by which the phase transition proceeds or can proceed. We believe that the multistep processes can give us access to the Gibbs energy landscape and kinetic pathways.

Acknowledgment. This work has been supported by the KBN under Grant 5P03B09421 and 2P03B00923.

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MA0206467