

STRAIN FIELD INDUCED ANISOTROPIC PHASE SEPARATION OF POLYMER BLENDS

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Using a small angle light scattering (SALS) technique, we investigated the anisotropic SALS patterns formed in a phase separating polystyrene (PS) and poly(vinyl methyl ether) (PVME) blend under strain fields. We have found that, in addition to the interfacial relaxations, the stretching of the polymer chains plays an important role in the phase separation of the PS/PVME blend under a strain field. Two novel scattering patterns and the strain induced slowing down of the phase separation dynamics are observed. The experimental results are compared to a theoretical calculation based on a time-dependent Ginzburg-Landau equation incorporated with the chain stretching effect.

1. Introduction

Creating new materials by blending polymers with various intrinsic properties has been very active in recent decades. However, most of the multi-component polymers in the application conditions are multi-phase materials with very much different phase morphologies and a variety of macroscopic properties of the multi-phase polymers depend strongly on their mesoscopic morphologies. Experimentally, applying symmetrical breaking fields to control the morphologies of polymeric systems has been quite successful and many interesting phenomena are observed.^{1–10}

For polymer blends, it is well known that, depending on the composition and the phase separation mechanism, i.e., spinodal decomposition (SD) or nucleation and growth (NG), either bicontinuous phase or droplet phase can be obtained. These phase structures are macroscopically isotropic. The macroscopically anisotropic patterns can be generated by applying flow fields (one kind of symmetry breaking fields).¹ Besides the elongation of the domains in the flow fields, more complicated phenomena are observed, such as shear induced demixing,³ shear induced mixing,^{2,3} and string-like patterns.^{4,5} If the dynamics of the morphology evolution

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is slow enough (usually, it can always be satisfied for polymer melts), it can be investigated through the scattering technology by continuously recording the scattering patterns. In this paper, we report on the phase separation of polymer blends under an external shear strain by using the small angle light scattering (SALS) technique.

2. Experiments

The polymer blends used in the light scattering experiments are composed of polystyrene (PS) and poly(vinyl methyl ether) (PVME). The molecular weights of the PS and PVME are 38,000 and 95,000 g/mol, and the corresponding inhomogeneity indexes are 1.5 and 2.8, respectively. The phase diagram was measured by the cloud-point method and showed that the system has a lower critical solution temperature with a critical composition of 18 wt.% PS and a critical temperature of 108°C. The blend of 50/50 wt.% composition of a phase separation temperature 114°C was used in the experiment.

The shear strain is introduced by a rectilinear shear apparatus constructed in our laboratory.¹¹ The shearing cell is transparent and the He-Ne gas laser beam ($\lambda = 632.8\text{nm}$, 5mW) is normal to the cell plane. The scattering is imagined on a screen placed normal to the incident beam, whose intensity distribution is captured by a charge-coupled-device (CCD) camera. The polymer blend is filled between the two glasses with a distance of about 20 μm .

Domain relaxations after the cessation of shear. In these experiments, we first let the mixture proceed the phase separation at 125°C for 4 minutes after quenching under the quiescent condition and the isotropic domains were formed as clearly indicated by the presence of a spinodal ring in the scattering pattern. Then, the steady shear was applied for 20 strains at a shear rate of 1s⁻¹. After the shear was stopped, we started to record the SALS pattern. The results are shown in Fig. 1. It is seen that the scattering pattern after being sheared for 20 strains becomes an ellipse with very small minor axis. After the shear flow stopped, the phase separation proceeds further and the scattering intensity in the vorticity direction is becoming stronger while the scattering intensity in the flow direction does not change so much. When $t = 720\text{s}$, the scattering pattern looks like a “nut-shell” with very strong scattering intensity in the vorticity direction. At first, the possible mechanism of forming the “nut-shell-like” scattering pattern appears to be due to the interfacial relaxations of the shear-elongated domains that have high curvatures at the tips of the elongated domains. However, if it is so, the scattering pattern would go back to the spinodal-ring-like shape (which corresponds to isotropic domains) after the elongated domains relax back to the isotropic domains. It surely does not do so as we can clearly see from Fig. 1(d).

This subtle nut-shell-like relaxation pattern can be interpreted as follows. As polymers are chainlike molecules, it is easy to imagine that the chain coils in polymer mixtures could be stretched under a flow field. Once the flow field is turned off,

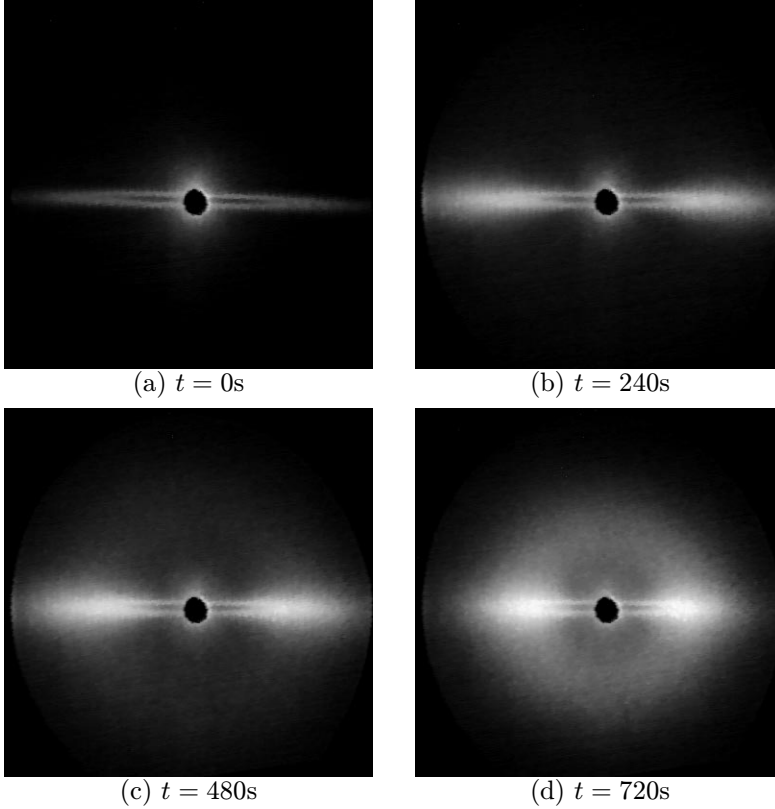


Fig. 1. Experimental SALS patterns of PS/PVME blend. Before recording the scattering patterns, the sample first phase separated at 125°C for 4 minutes. Then, the sample was sheared for 20 shear strains at a shear rate of 1s^{-1} . The shear and vorticity are along the vertical and horizontal directions in the figure, respectively. After stopping the shear (at $t = 0\text{s}$), the scattering patterns were recorded. The half width of each figure corresponds to $6\mu\text{m}^{-1}$.

the stretched coils will relax back to the equilibrium state due to the stored elastic energy. It is obvious that the relaxations of the chains is mainly along the shear direction, that is to say, the relaxations of the chains are anisotropic. At the same time, the phase separation is ongoing. Because it arises from the inhomogeneity of the chemical potential, although under a strain field, the random concentration fluctuations itself is, however, isotropic. We believe, it is the coupling between the isotropic concentration fluctuations and the anisotropic chain relaxation that causes the new scattering pattern under a strain field. To go beyond these intuitive considerations, we have done a theoretical treatment on the relaxations of the scattering function in a phase-separating polymer mixture upon flow cessation. The equation of motion for the concentration fluctuations is the time-dependent Ginzburg-Landau (TDGL) equation and the free energy functional incorporates the chain stretching explicitly.^{12,13} The scattering patterns for just after the cessation

of shear and a later time during the relaxation are given in Fig. 2. As can be seen there is a qualitative agreement between the SALS experiment and the theory.

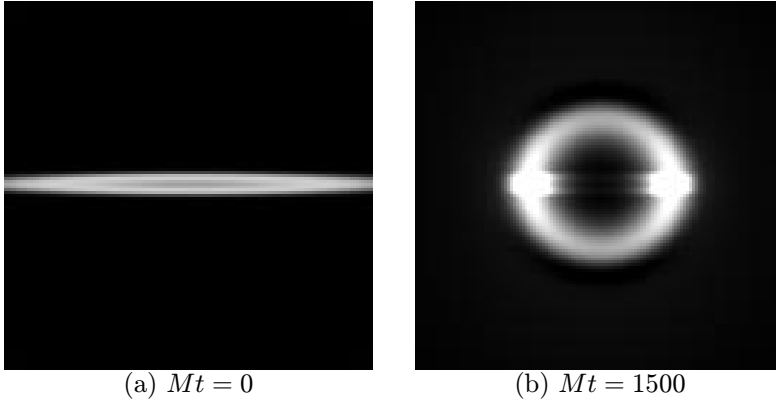


Fig. 2. Theoretical scattering patterns at two subsequent times (in unit of Mt , where M is the mobility of the polymers) after the cessation of the shear, both the wave vectors ranging from $-\pi$ to π . The pre-sheared flow direction is along vertical direction. The shear and vorticity are along the vertical and horizontal directions in the figure, respectively.

Phase separation in strain field. To further remove the ambiguity, we designed a second kind of experiments for getting ride of the interference from the interfacial relaxations. In these experiments, we first sheared the same sample in a homogenous state (at 105°C). Therefore, one can completely ignore the effect of the interfacial relaxations and expect that the polymer chains would be stretched to some extent in the homogenous state. After stopping the shear flow, the sample was immediately quenched into the spinodal region and the phase separation proceeded. Then, the SALS pattern was recorded under the quiescent condition. The results are shown in Fig. 3. It is seen that, after quenching, the scattering intensity appears first in the vorticity direction and forms what is like a “butterfly” pattern. The scattering intensity of the “butterfly” pattern increases with evolution time. When $t = 5100\text{s}$, the intensity in the vorticity direction is still stronger than that in the flow direction while keeping its shape basically a spinodal ring. In this experiment, since the phase separation is proceeding without the influence of the interfaces, we can conclude that the non-uniform distribution of the scattering intensity is certainly resulted from the chain stretching effect. Therefore, we can conclude that the chain stretching effect may be responsible for the appearing of the “nut-shell-like” and “butterfly-like” SALS patterns.

The strain field not only gives rise to anisotropic scattering patterns, but also affects the dynamics of the phase separation of the polymer blend. Fig. 4 shows the comparison between the SALS patterns with similar characteristic domain size (or the similar q_m value) for the samples without and with pre-shear in the homogeneous state before quenching. For the sample sheared in the homogenous state before quenching, the evolution of the phase separation is much slower, i.e., it takes

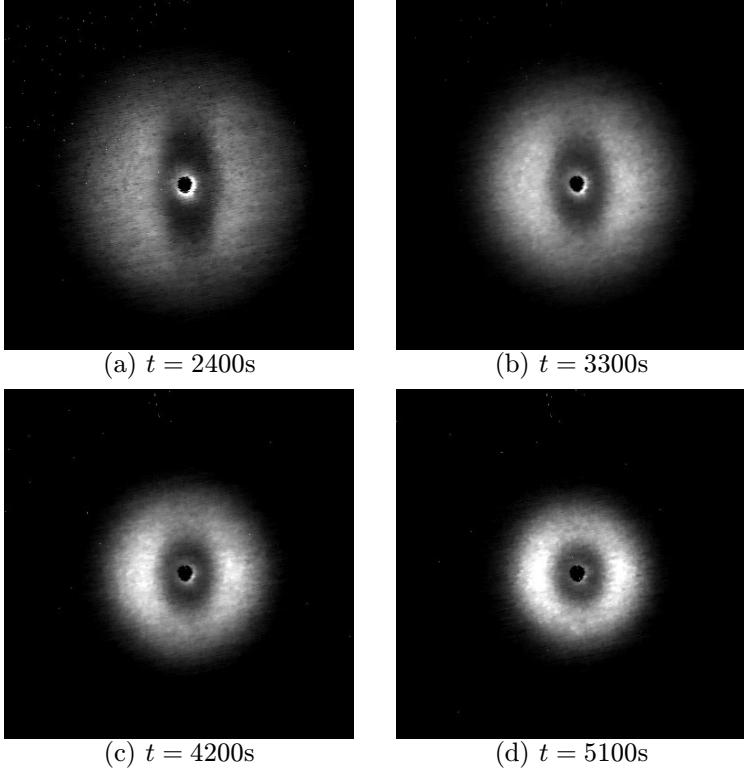


Fig. 3. Experimental SALS patterns of PS/PVME blend. The sample was first sheared for 20 strains in the homogenous state (at 105°C) at a shear rate of 1s^{-1} . The shear and vorticity are along the vertical and horizontal directions in the figure, respectively. Then the SALS patterns were taken, after immediate quenching to 125°C , under quiescent condition. The half width of each figure corresponds to $6\mu\text{m}^{-1}$.

much longer time for the domains in the pre-sheared sample (Fig. 3(d), $t = 5100\text{s}$) to grow to the same size as that in the sample without pre-shear (Fig. 4, $t = 480\text{s}$). It reveals that the shear flow (even sheared at the homogenous state) suppresses the concentration fluctuations and thus slows down the morphology evolution.

3. Conclusion

We have investigated the anisotropic SALS patterns formed in a phase separating PS/PVME blend under strain fields. We have found that, in addition to the interfacial relaxations, the stretching of the polymer chains plays an important role in the SD process under a strain field. Two novel scattering patterns and the strain induced slowing down of the SD are observed and our theoretical calculation shows that the chain stretching indeed is responsible for these interesting features.

We note that the chain stretching effect is observed not only in polymer blends under shear flow, but also in block copolymers. Especially, when the shear rate is

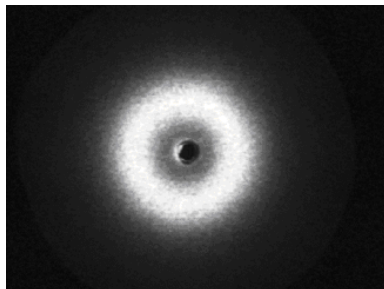


Fig. 4. Experimental SD SALS patterns of PS/PVME blend without shear. The scattering pattern was recorded at $t = 480$ s after heating the sample into the biphasic region. The characteristic domain size λ (or q_m value, which is related to the characteristic domain size as $q_m = 2\pi/\lambda$) is similar to that in Fig. 3(d). The half width of the figure corresponds to $6\mu\text{m}^{-1}$.

high, the transverse orientation of the lamellae of a microphase separated block copolymer is observed. The theoretical calculation incorporating the chain stretching of the block copolymers can reproduce all the experimental observations.¹⁴ It reveals that when the shear rate is high, the copolymer chains are stretched along the flow direction and thus the micro-phase separated lamellae can only take the transverse orientation. However, in order to understand the detailed mechanism of the chain stretching effect, it still deserves further theoretical and experimental investigations.

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