Correlation between Shear Viscosity and Anisotropic Domain Growth during Spinodal Decomposition under Shear Flow

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To investigate the influence of a simple shear flow on the late stage spinodal decomposition of a binary polymer blend, the shear viscosity and the domain growth have been studied by a combined rheo–small-angle-light-scattering technique. In a representation versus the applied strain, the viscosities as well as the structure deformation can be scaled on single curves for different shear rates. Both quantities show two characteristic crossovers at the same strain values. The behavior is compared with results of a recent computer simulation.

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Spinodal decomposition (SD) is a well-known demixing process for many systems (e.g., metallic alloys, binary liquid mixtures, solutions, and polymer blends) and due to its great importance many investigations are dealing with it. Although there are many interesting questions open, the main features of SD are well understood [1,2]. The spinodal demixing process which leads to a typical interconnected percolation structure can be separated into at least three regimes: the early, intermediate, and late stages [3,4]. In the early stage the decomposition is diffusion controlled and described by the linear Cahn theory [5], whereas in the later stages the phases have reached the final composition and the structure growth is driven by the interfacial tension. In the late stage the structure growth obeys the universal growth law $q_m \propto t^\alpha$ with $\alpha = -1$ for liquid and polymer mixtures. q_m represents the magnitude of the scattering vector at the maximum of the structure function and is related to the interdomain distance Λ_m by $\Lambda_m = 2\pi/q_m$.

If a shear flow acts on the system simultaneously to the SD, the picture is less clear. Experimental observations in the late stage on binary liquid mixtures [6,7] as well as on polymer mixtures [8,9] show an anisotropic structure development. The structure growth under a steady shear flow was quantitatively investigated by light scattering techniques on a low molecular system [10] and by our group on a binary polymer mixture [9]. In order to get a deeper insight in the interplay between the structure growth due to the demixing process and the structure deformation due to the shear flow we improved our previous experiments by the observation of rheological properties (i.e., the shear viscosities) simultaneous to small-angle-light-scattering (SALS) measurements which monitor the structure changes.

The polymer blend consists of polybutadiene (PB) and polyisoprene (PI), which are slightly different from those used previously. The molecular weights M_n of PB and PI are 85 000 and 75 000 g/mol, respectively, and the heterogeneity index of both polymers is $M_W/M_n = 1.05$. The content of 1,2 units of PB is 14.4% and sets the lower critical solution temperature of the blend to 32 °C as measured by differential scanning caliometry. Blends near the critical 47/53 wt% composition were used. Details of the polymerization, characterization, and blend preparation are given elsewhere [11].

The experiment was carried out by imposing a steady shear flow simultaneously to a temperature jump from room temperature to 60 °C into the unstable region of the phase diagram. Rheo-SALS measurements were performed with a previously described apparatus which combines a Bohlin CS50 rheometer and a homemade SALS device allowing quantitative detection of the two-dimensional SALS pattern [12]. The sample was located in a cone and plate geometry made of optical transparent quartz glass. Different constant shear rates in the range between $S = 0.0006$ and $0.012\ \mathrm{s}^{-1}$ were applied. SALS measurements without shear have shown that the PB/PI blends are clearly in the late stage of the SD process throughout the observable scattering vector range [11,13].

In Fig. 1 SALS patterns are shown for a shear rate of $S = 0.003\ \mathrm{s}^{-1}$ at various times after the temperature jump. The so-called spinodal ring typical for SALS during SD is deformed to an ellipse. The stretching direction of the scattering ellipse is perpendicular to the direction of the shear flow reflecting an elongation of the structure parallel to the flow direction. At the maxima of the scattering pattern the scattering vectors $q_{m\|}$ parallel and $q_{m\perp}$ perpendicular to the flow direction (i.e., along the minor and major axes of the scattering ellipse) were determined. As in the previous investigation the structure growth in the direction perpendicular to the flow direction, i.e., the neutral direction, is independent of the shear flow and therefore $\alpha_\perp(S) = \alpha\ (S = 0) = -1$ holds for the exponent. $\alpha\ (S = 0)$ is the exponent of the universal growth law. If the reciprocal of the structure deformation $\Lambda_m(t,0)/\Lambda_{m\|}(t,S) = q_{m\|}(t,S)/q_m(t,0)$ is plotted versus the total strain St, the influence of the shear in the direction parallel to the applied shear rate is described

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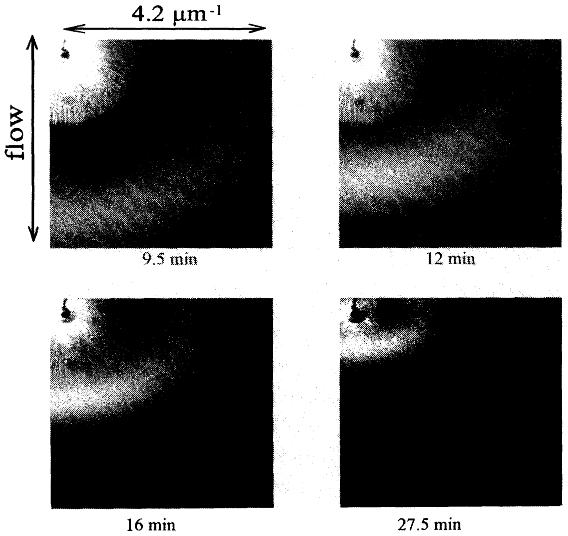

FIG. 1. Scattering patterns at various times after the simultaneous temperature jump into the two phase region at 60 °C and the onset of a shear flow with a shear rate of $S = 0.003\ \mathrm{s}^{-1}$.

by a single master curve for the various shear rates. Figure 2 is a log-log plot of this master curve. In Fig. 2 the previous measurements on a blend with different molecular weights are additionally shown [9]. The small deviations of the actual measurements at the highest shear rate are explained by the early appearance of deformation when the temperature equilibrium after the temperature jump was not yet attained.

In contrast to the earlier work the observed range is expanded to smaller strain values, so that the interesting region of $St \approx 1$ is accessible. At $St > 1$ the velocity difference $\Lambda_m S$ across the domains is greater than the growth rate $d\Lambda_m/dt$ of the domains due to the SD process. Therefore a deformation of the growing domains is expected for $St > 1$. As can be seen from Fig. 2 a deviation from the unperturbed behavior where $q_{m\|}(t,S)/q_m(t,0) = 1$ appears at strain values slightly greater than $St = 1$. For strains $St < 1$ no shear deformation is observed. At higher strain values a deviation from the unsheared behavior occurs and the structure deformation obeys again a power law with a new exponent as in the unsheared case: $q_{m\|}(t,S)/q_m(t,0) \propto t^{\alpha'}$ with $\alpha' = \alpha_\| - \alpha = -(0.8 \pm 0.1)$. As found and discussed in the earlier work where a somewhat different blend was used this exponent deviates significantly from the value $\alpha' = -1.0$, which was found for low molecular mixtures [10].

For the forthcoming discussion it is worth noting that the crossover to the power law behavior occurs at a strain value of $St = 4 \pm 0.5$ also in accordance with the previous work. In conclusion, there are two characteristic strain values: $St \approx 1$ where the structure begins to be deformed and the crossover to the power law behavior at $St \approx 4$.

Figure 3 shows the shear viscosities at different shear rates measured in parallel to the SALS pattern. During the first 2 min a strong decrease of the viscosities occurs due to the heating process. After the temperature reaches its final value, the viscosities first are nearly constant for a short period of time and then begin to increase until a maximum is reached after a shear rate dependent time. It has been checked that the temperature equilibration after the temperature jump is independent of the small shear rates applied and is completed after ≈250 sec, i.e., the appearance of the maximum in the viscosity is not caused by a temperature fluctuation. If the viscosities are plotted versus the strain St in Fig. 4, the curves fall on a single curve for the various shear rates with a maximum at $St \approx 4$ and the onset of the viscosity increase at $St \approx 1$, respectively. These are the same characteristic values observed in SALS for the crossovers to the power law regime and the onset of the deformation, respectively. At

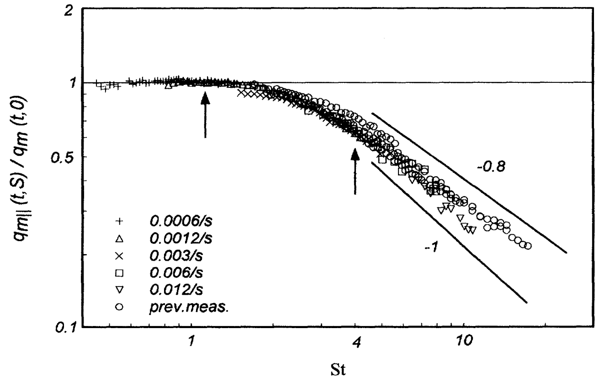

FIG. 2. Reciprocal of the structure deformation for the various shear rates and previous measurements vs the applied shear deformation.

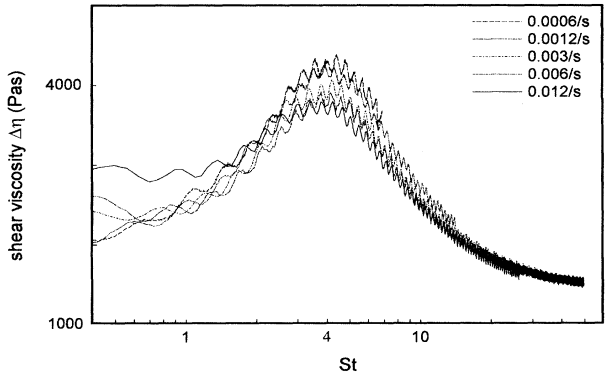

FIG. 3. Shear viscosities for the various applied shear rates S : +: 0.0006 s^{-1}, △: 0.0012 s^{-1}, ×: 0.003 s^{-1}, □: 0.006 s^{-1}, ▽: 0.012 s^{-1}.

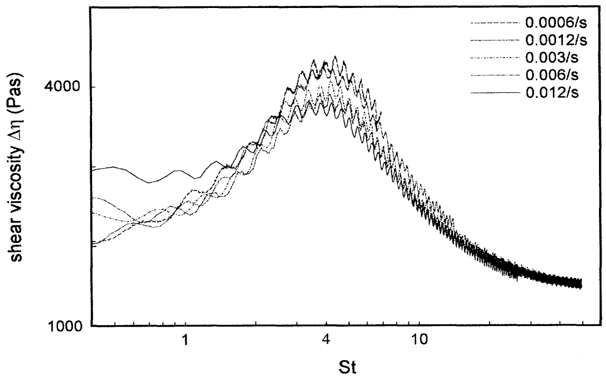

FIG. 4. Strain dependence of the shear viscosity.

long times the viscosities decrease to a constant value independent on the shear rate.

It is possible to compare these results with a recent computer simulation of Ohta, Nozaki, and Doi [14,15] with a model depending on a theoretical investigation of Doi and Ohta on the rheology of complex interfaces [16]. Although a quantitative comparison of the structure development is not possible because geometries in their calculations were different from our experimental setup, the measured strain dependence of the shear viscosity can be compared with their calculated anisotropy factor which is proportional to the shear viscosity. It is interesting to note that the computer simulation produced a similar behavior with an increase at $St \approx 1$ and a maximum at $St \approx 4$ though this behavior was obtained for the case of an off-critical mixture where a dispersed structure is exposed to the shear flow. In the case of a critical mixture, i.e., an interconnected percolation structure, the viscosity increases immediately after the onset of flow and reaches a maximum at strain values of $St \approx 1$. The simulations assume *not* a simultaneous onset of shear flow and SD in contrast to our experiments. We believe that this is the reason for the observed discrepancy. The flow in the simulations is applied on a structure which has developed during unperturbed SD for a period of time. In this case the dimensions of the domains are sufficiently large and, therefore, the shear flow does deform the domains immediately after the onset of flow. For the off-critical case, following an argument of Ohta, Nozaki, and Doi [14,15], the nearly constant viscosity in the initial regime reflects the fact that the dimensions of the dispersed particles are too small to be deformed immediately. But this is also the case when the flow is applied simultaneously to the onset of the SD. First the structures are very small and only after a period of time are the dimensions sufficiently large to be deformed by the flow. Therefore we believe that our experiment on a critical mixture rather has to be compared with the off-critical case of the computer simulation. This statement has to be verified by experiments where the shear flow is switched on after a certain period of unperturbed SD which might be directly comparable to the computer simulations or by investigations on off-critical mixtures. Both kinds of experiments are in progress.

A closer inspection of Figs. 3 and 4 shows a slow increase of the shear viscosities $\Delta\eta$ at the maximum with decreasing shear rate S. Following Ohta, Nozaki, and Doi [14,15] an empirical formula of the form $\max(\Delta\eta\, S) \propto S^{\nu}$ is assumed [17]. According to our experiment in Fig. 5 an exponent of $\nu = 0.96$ is attained. This value deviates from the exponents found by the computer simulations. However, the exponents strongly depend on the model of the theoretical calculations. It is believed that the exponent is a very sensitive quantity for comparing experimental results with theoretical models.

Ohta, Nozaki, and Doi [14,15] showed that the maximum of the shear viscosity occurs when the structures are deformed and elongated to such an extent that burst and recombination of the domains starts. With regard to this theoretical picture we interpret our results as follows. The structure is to be deformed at strain values of $St \approx 1$, i.e., a deviation of $q_{m\|}(t,S)/q_m(t,0)$ from the value 1, and simultaneously the shear viscosity increases. At strain values of $St \approx 4$ the deformed domains begin to burst and recombine and the shear viscosity attains the maximum. This is the point where the power law regime of the deformation $q_{m\|}(t,S)/q_m(t,0)$ begins.

In conclusion, we find in our combined rheo-SALS measurements a direct correlation between the shear viscosity and the structural changes during SD of a binary polymer blend under shear flow. The results are in qualitative agreement with computer simulations. Because of the complexity of the process many questions need further investigations. As far as we are aware, our study reports for the first time measurements of the correlated observation of time and shear rate dependence of the rheological and structural properties of a polymer system with complex interfaces.

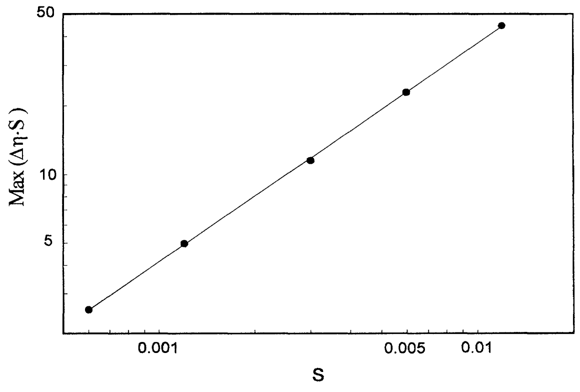

FIG. 5. Shear rate dependence of $\max(\Delta\eta\, S)$.

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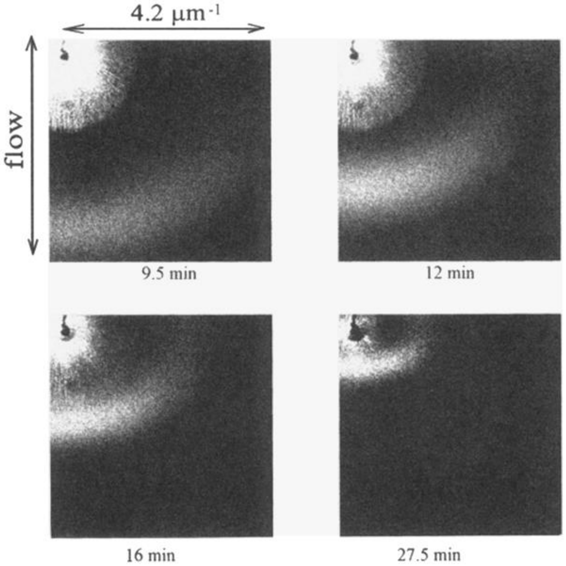
[17] ν is not the exponent usually linking ξ to ε.



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