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Time Change in the Maximum of Scattering Intensity during Spinodal Decomposition

Scaling Postulate. We consider a phase-separation process which occurs after a binary mixture is suddenly quenched from a homogeneous state to the region inside the spinodal. During this process, usually called spinodal decomposition, the intensity $I(q,t)$ of light scattered from the mixture, measured at a fixed value of q (the magnitude of the wave vector for incident light), varies with time t in a complex fashion. The $I(q,t)$ data as a function of q give a series of bell-shaped curves, which change with the increase in t, sometimes except at small t. The overall change is characterized by a monotonic increase of the peak height $I_m(t)$ and a gradual shift of the peak position q_m to small q. One of the central tasks in spinodal decomposition studies is to investigate how the time changes in the peak height and position depend on the quench temperature and the composition of the solution. In the following, we limit our discussion to the critical mixture, i.e., one having the critical composition, and denote $I_m(t)$ and $q_m(t)$ as functions of the quench temperature, T, by $I_m(t;T)$ and $q_m(t;T)$, respectively. Furthermore, we introduce a reduced peak height, $\bar{I}_m(t;T)$, defined by

$$\bar{I}_m(t;T) = I_m(t;T) \Big/ \int_{q'}^{q''} I(q,t;T) q^2 \, dq \qquad (1)$$

where q' and q'' are the q values at which $I(q,t;T)$ virtually becomes zero.

Chou and Goldburg[1] were probably the first to postulate that $q_m(t;T)$ and $\bar{I}_m(t;T)$ at T near the critical temperature, T_c, are scaled by a T-dependent correlation length, $\xi_c(T)$, and a time constant, $t_c(T)$, with the latter defined by

$$t_c(T) \equiv [\xi_c(T)]^2/D(T) \qquad (2)$$

Here, $D(T)$ denotes the mutual diffusion coefficient of the system at temperature T. This postulate means that the dimensionless peak position and height defined by

$$\tilde{q}_m(t;T) \equiv q_m(t;T)\xi_c(T) \qquad (3)$$

$$\tilde{I}_m(t;T) \equiv \bar{I}_m(t;T)[\xi_c(T)]^{-3} \qquad (4)$$

depend only on a reduced time $t/t_c(T)$; i.e.

$$\tilde{q}_m(t;T) = f(t/t_c) \qquad (5)$$

$$\tilde{I}_m(t;T) = g(t/t_c) \qquad (6)$$

Chou and Goldburg[1] indeed showed that their data on the critically quenched isobutyric acid-water and 2,6-lutidine-water mixtures obeyed eq 5 and 6 by estimating $\xi_c(T)$ and $D(T)$ from Chu et al.'s data[2] for the former and Gulari et al.'s data[3] for the latter. The applicability of the Chou-Goldburg scaling postulate to polymer systems was first examined by Snyder and Meakin,[4] who studied a blend of mutually miscible polystyrene (PS) and poly(vinyl methyl ether) (PVME). Because of the lack of available data, they estimated $\xi_c(T)$ by equating it to $1/q_m(0;T)$. This maneuver was then used by Yang et al.[5] and Hasimoto et al.[6] in studies of another critical PS-PVME blends. However, the experimental determination of $q_m(0,T)$ is not always feasible, since measured curves for $I(q,t)$ vs q often show no peak in the early stage of spinodal decomposition. In this note, we offer a method to test the Chou-Goldburg scaling laws, eq 5 and 6, without explicit information about ξ_c.

New Method. We introduce two experimentally determinable quantities $X(t,T)$ and $Y(t,T)$ defined by

$$X(t;T) \equiv q_m(t;T)[D(T)t]^{1/2} \qquad (7)$$

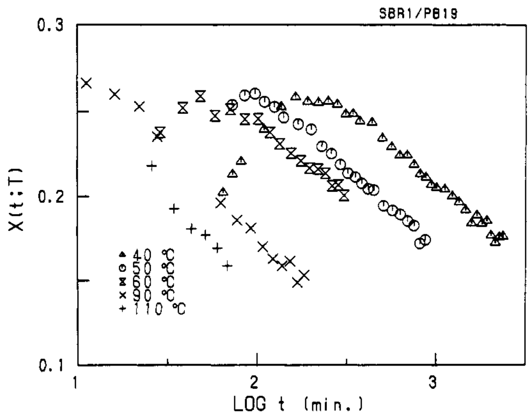

Figure 1. $X(t;T)$ plotted against log t at the indicated quench temperatures for a critical SBR1-PB19 blend.

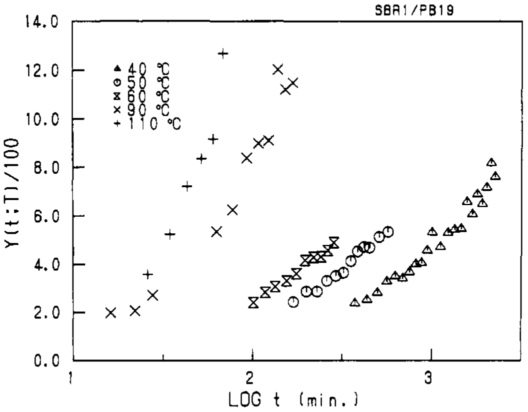

Figure 2. $Y(t;T)$ plotted against log t at the indicated quench temperatures for the same blend as in Figure 1.

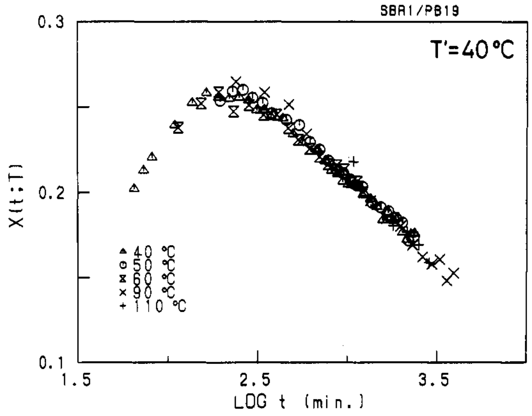

Figure 3. Reduction of X data at different quench temperatures to a master curve at 40 °C.

$$Y(t,T) \equiv \bar{I}_m(t,T)[D(T)t]^{-3/2} \qquad (8)$$

Then, with eq 2, 5, and 6, $X(t;T)$ and $Y(t;T)$ are written

$$X(t;T) = (t/t_c(T))^{1/2} f(t/t_c(T)) \qquad (9)$$

$$Y(t,T) = (t/t_c(T))^{-3/2} g(t/t_c(T)) \qquad (10)$$

Equation 9 indicates that $X(t;T)$ depends on a single variable $t/t_c(T)$. Hence, plots of $X(t,T)$ against ln t for different T should be superimposable on a master curve by horizontal shifting. The master curve gives us the form of $(t/t_c(T'))^{1/2} f(t/t_c(T'))$ at a reference temperature T' over a wider range of t. Thus, if the master curve is multiplied by $t^{-1/2}$, the resulting curve yields the values of $(t_c')^{-1/2} f$-

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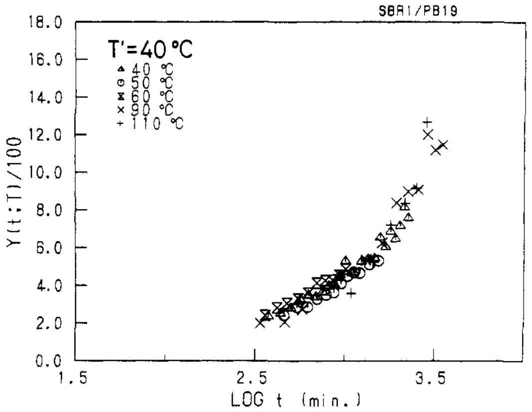

Figure 4. Reduction of Y data at different quench temperatures to a master curve at 40 °C.

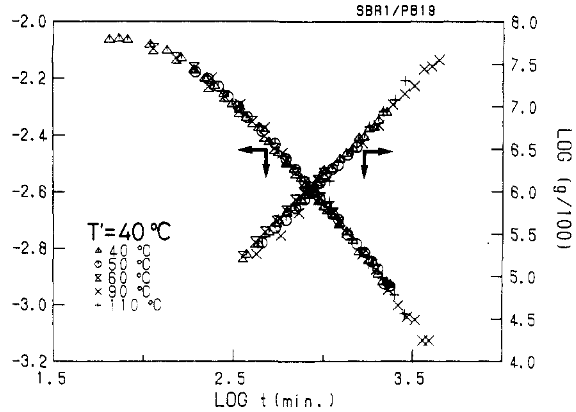

Figure 5. Time changes in f ($\sim \tilde{q}_m$) and g ($\sim \tilde{I}_m$) at 40 °C for a critical SBR1-PB19 blend.

(t/t_c'), where t_c' is the value of $t_c(T)$ at the reference temperature T'; i.e., $t_c' = [\xi_c(T')]^2/D(T')$.

From eq 10 it follows that plots of $Y(t;T)$ against ln t for different T can be reduced to a master curve by horizontal shifting and that multiplication of the master curve $Y(t,T')$ by $t^{3/2}$ gives the values of $(t_c')^{3/2}g(t/t_c')$.

When we find that the data for $X(t;T)$ and $Y(t;T)$ can be reduced to master curves, we can conclude that the system under study obeys the Chou–Goldburg scaling laws. Though incapable of determining the absolute values of f and g, the master curves obtained allow us to see how the exponents α and β in the relations $\tilde{q}_m \sim t^{-\alpha}$ and $\tilde{I}_m \sim t^{\beta}$ vary with time. This information should be important for elucidating the molecular mechanism responsible for the spinodal decomposition of critical binary mixtures.

Application. We made a test of the Chou–Goldburg postulate by applying the above method to the unpublished experimental data of Hashimoto and Takenaka on the critical mixture of a styrene–butadiene rubber 1 (SBR1)/polybutadiene 19 (PB19) blend. (SBR1: $M_w = 1.18 \times 10^5$, $M_w/M_n = 1.18$; styrene content = 20 wt %; trans:cis:vinyl = 0.16:0.23:0.61. PB19: $M_w = 1.90 \times 10^5$, $M_w/M_n = 1.16$; cis:trans:vinyl = 0.19:0.35:0.46.) In so doing, we estimated the necessary values of $D(T)$ by analyzing $I(q,t)$ data for the initial stage of spinodal decomposition in the usual way.[7]

Figures 1 and 2 show the values of $X(t;T)$ and $Y(t;T)$ at five temperatures plotted against log t. These plots can be reduced to master curves by adequate horizontal shifting. Figures 3 and 4 show the results obtained when 40 °C is chosen as the reference temperature T'. Here, the variable t on the abscissa axis refers to the real time scale in the measurement at T'. The amounts of horizontal shifting that were needed for the construction of the master curves are reported by Izumitani et al.[8] in a forthcoming paper. We see that the experimental data of Hashimoto and Takenaka are consistent with the Chou–Goldburg postulate. However, this finding is surprising, because the data are concerned with quench temperatures (40–110 °C) far below T_c of the blend, which was estimated by Izumitani and Hashimoto[9] to be about 400 °C.

The master curves for f and g in Figure 5 have been derived from the data points in Figures 3 and 4. The abscissa variable t again refers to the real time in the measurement at 40 °C. The time scale in which these curves appear is only a little more than one decade. Experimental data covering a wider time scale are needed for checking the range of validity of the Chou–Goldburg postulate. In Figure 5, the master curve for f is distinctly curved, giving α which increases smoothly from about 0.2 to about 0.8 with increasing t. On the other hand, the corresponding curve for g is almost linear, giving β equal to about 2.4. Thus, these results essentially satisfy the relation $\beta = 3\alpha$ in the time scale $t > 370$ min (or log t (min) > 2.4).

References and Notes

(1) Chou, Y. C.; Goldburg, W. I. *Phys. Rev. A* **1979**, *20*, 2105.
(2) Chu, B.; Schoenes, F. J.; Kao, W. I. *J. Am. Chem. Soc.* **1969**, *90*, 3402.
(3) Gulari, E.; Collings, A. F.; Schmidt, R. L.; Pings, C. J. *J. Chem. Phys.* **1972**, *56*, 6169.
(4) Snyder, H. L.; Meakin, P. *J. Chem. Phys.* **1983**, *79*, 5588.
(5) Yang, H.; Shibayama, M.; Stein, R. S.; Shimizu, N.; Hashimoto, T. *Macromolecules* **1986**, *19*, 1667.
(6) Hashimoto, T.; Itakura, M.; Shimidzu, N. *J. Chem. Phys.* **1986**, *85*, 6773.
(7) Hashimoto, T. *Phase Transitions* **1988**, *12*, 47.
(8) Izumitani, T.; Takenaka, M.; Hashimoto, T. *J. Chem. Phys.*, in press.
(9) Izumitani, T.; Hashimoto, T. *J. Chem. Phys.* **1985**, *83*, 3694.

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Effect of Increasing Propyl Group Substitution on Permethyl Polyazine

The study of polymers with conjugated π systems that can be oxidatively or reductively doped into a highly conductive state has been of great interest recently.[1] The prototype polymer in this class is polyacetylene,[2] $-(CH{=}CH)_x-$. We have been studying polyazines,[3] $-(N{=}C(R_1)\text{-}C(R_2){=}N)_x-$, that are formally isoelectronic to, but topologically distinct from, polyacetylene. Unlike polyacetylene, polyazines are environmentally stable and so are attractive candidates for useful conducting polymers. Polyazines ($R_1 = R_2 = H$ or $R_1 = R_2 = CH_3$) can be doped to give conducting materials,[3c,3g] but these polymers lack processing characteristics. Organic soluble polyazines are known,[4,5] but these materials do not dope into a highly conductive state.

This report describes the preparation and IR and NMR characterization of long-chain soluble permethyl ($R_1 = R_2 = CH_3$) polyazines with a controlled number of propyl

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