# LCST-type phase behaviour and extremely slow demixing phenomenon in polymer blends of poly(acrylonitrile-co-styrene) and poly(maleic anhydride-co-styrene)

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Phase behaviour of the binary blends of poly(acrylonitrile-co-styrene) and poly(maleic anhydride-co-styrene) was investigated by the cloud point method, using very long isothermal annealing (up to 97 h). A lower critical solution temperature (LCST) type phase diagram was found. Kinetic studies on demixing at the two-phase region above the LCST were carried out by light scattering. The demixing rate was very slow. This extremely slow demixing was interpreted in terms of the overlap of two effects: first, the interaction parameter $\chi_{12}$ is a slowly increasing function of temperature, i.e. the thermodynamic driving force for the demixing is not as large as expected from the quench depth in the phase diagram; and, secondly, the chain mobility is small, due to the small deviation of the LCST from the glass transition temperature of the mixture.

(**Keywords:** poly(acrylonitrile-co-styrene); poly(maleic anhydride-co-styrene); blend; phase diagram; demixing; light scattering)

## INTRODUCTION

There has been much interest in miscible polymer blends in which one or both of the component polymers are random copolymers. The blends are miscible without any specific interaction such as hydrogen bonding. This is considered to be due to the negative exchange interaction originated from an intrachain repulsive interaction in copolymer[1-4]. An interesting example is a binary blend of poly(acrylonitrile-co-styrene) (SAN) and poly(maleic anhydride-co-styrene) (SMA). The miscibility depends on the copolymer composition of SAN ($x$) and that of SMA ($y$). The miscibility map in the $x$–$y$ plane at a fixed temperature was given by Hall *et al.*[5,6] (*Figure 1*).

Generally, the miscible mixtures tend to phase-separate at elevated temperatures. This lower critical solution temperature (LCST) behaviour is typical for miscible polymer blends. Some miscible polymers also exhibit phase separation at low temperatures. This upper critical solution temperature (UCST) behaviour was found in copolymer/copolymer and copolymer/homopolymer blends by Ougizawa *et al.*[7,8] and Cong *et al.*[9]. Along the same lines, we were interested in the phase behaviour in SAN/SMA systems. During studies on the phase diagram, we found a very interesting phenomenon: extremely slow demixing even under a sufficiently deep quench.

In this Paper, we described LCST type phase behaviour in SAN/SMA blends and the kinetics of demixing after the temperature jump from the single-phase region to the two-phase region. An interpretation of the very slow demixing is given in terms of the temperature dependence of the interaction parameter $\chi_{12}$ and that of chain mobility.

## EXPERIMENTAL

The polymer specimens used in this study and their characteristics are shown in *Table 1*. SANs were kindly supplied by Dr Y. Aoki, Mitsubishi Monsanto Chemicals Co. Ltd. SMA was supplied by Arco Polymers Inc.: Dylark 332. As indicated in *Figure 1*, we selected three combinations of SAN and SMA. A pair of different polymers was dissolved at 8 wt% of total polymer in tetrahydrofuran. The solution was cast onto a cover glass (for microscopy). After the solvent had been evaporated at room temperature, the cast film was further dried under vacuum ($10^{-4}$ mmHg $\approx 10^{-2}$ Pa) for 7 h.

The blend film on the cover glass was inserted in a hot chamber kept at a constant temperature and was annealed for 22 h. When the film became opaque and two-phase morphology was observed under an optical microscope, we judged that the blend was in the two-phase region in the phase diagram. When no appreciable change with annealing was detected, the film was further annealed at the same temperature for 94 h. When the film was still clear and phase separation could not be detected under a microscope, even after this long annealing time, we judged that the blend was in the single-phase region*.

**Table 1** Polymer specimens

| Code | Composition (wt%) | $10^{-4} M_w$ |
|---|---|---|
| SMA | MA 15.3 | 13.2 |
| SAN15 | AN 15.0 | 12.9 |
| SAN20 | AN 19.5 | 8.9 |
| SAN25 | AN 25.0 | 19.4 |

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* Owing to the small difference in the glass transition temperatures ($T_g$) of SAN and SMA, it is impossible to verify the single-phase nature from measurements of $T_g$.

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These annealing experiments were repeated at various isothermal settings.

To discuss the kinetics of demixing, similar isothermal experiments were carried out in a hot chamber set in a light scattering photometer[10]. The goniometer trace of the intensity of the scattered light was given at appropriate intervals during the isothermal annealing.

## RESULTS AND DISCUSSION

### *Phase diagram*

All of the solution cast films of SAN15/SMA blends with different compositions were optically clear. Even after annealing for 97 h at high temperatures (up to 320°C), they were transparent and no indication of phase separation was seen under an optical microscope. These results imply that SAN15 is miscible with SMA at any composition and the expected LCST may locate far above the thermal decomposition temperature of the polymers.

The solution cast films of SAN20/SMA blends were also optically clear. The clarity was maintained even after annealing for 22 h at fairly low temperatures. This behaviour is indicated by open circles in *Figure 2*. After 22 h annealing, some films became translucent and a modulated structure* with a periodic distance of a few micrometres was observed under a microscope; see, for example, *Figure 3a*. This is indicated by squares in

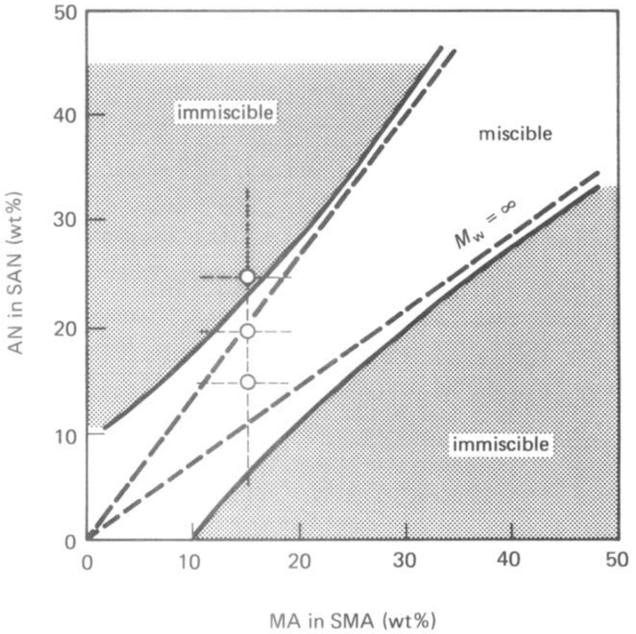

**Figure 1** Miscibility map for the SAN/SMA blends (reproduced from Reference 6): ——, observed; – – –, expected for infinite molecular weight polymer system. Open circles indicate the three combinations in this paper

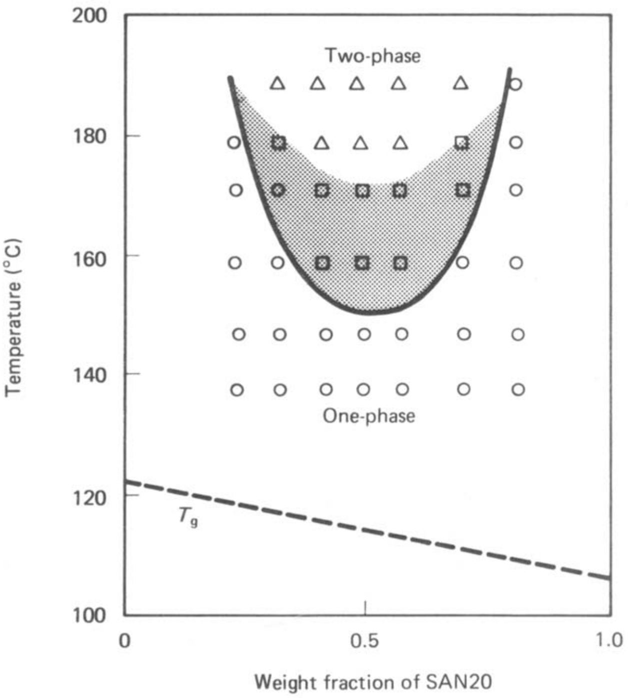

**Figure 2** Phase diagram of SAN20/SMA system

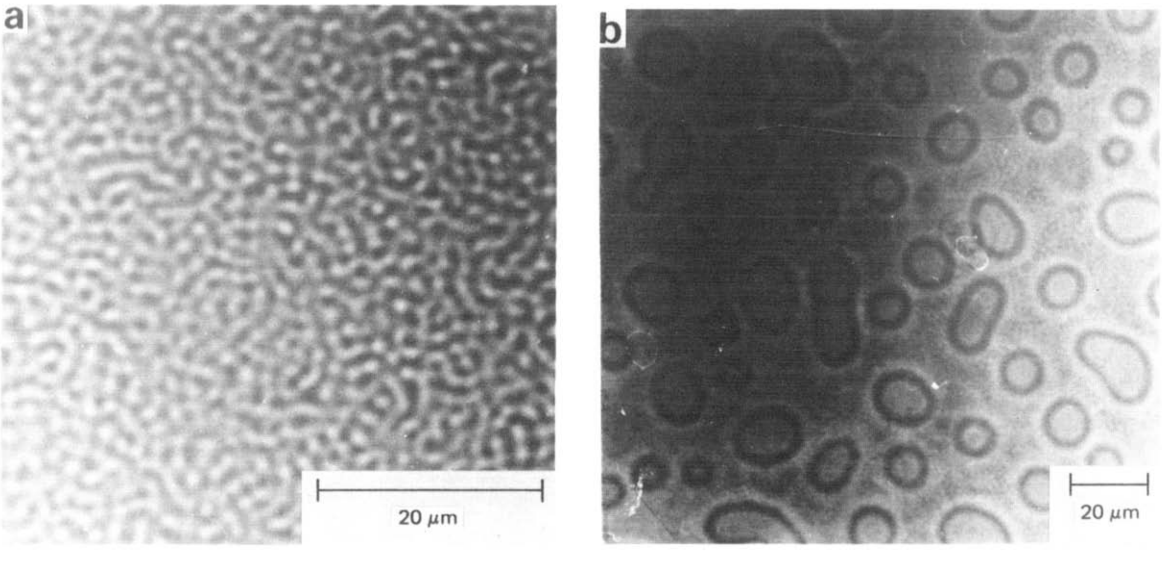

**Figure 3** Optical micrographs of the SAN25/SMA films after isothermal annealing: (a) 25/75, 170°C, 24 h; (b) 50/50, 190°C, 6 h

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* A regular two-phase structure with unique periodicity and a high level of phase connectivity, which is characteristic of the early stage of demixing by spinodal decomposition[7].

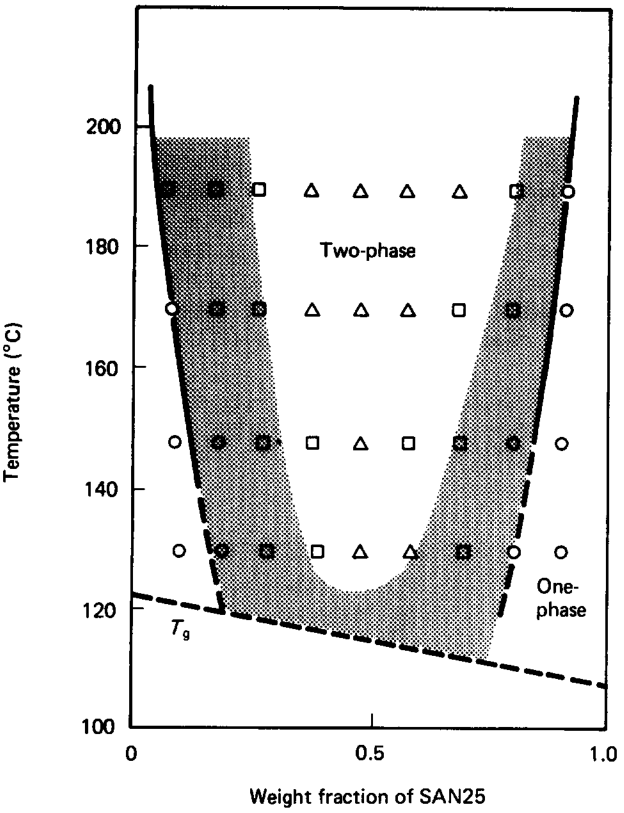

Figure 4 Phase diagram of SAN25/SMA system. Open circles in two-phase region change to rectangular sign after annealing for 97 h

*Figure 2*. The triangles in *Figure 2* represent the situation where the irregular two-phase morphology, of which a typical example is shown in *Figure 3b*, had already developed before 22 h annealing. On the basis of these observations, the LCST line was drawn somewhat arbitrarily in *Figure 2*. The single-phase nature was carefully confirmed by annealing for 94 h.

*Figure 4* is the phase diagram of a SAN25/SMA blend estimated in the same way as in *Figure 2*. This system seems to have an LCST type phase diagram, with its critical point below the glass transition temperatures of both component polymers.

From these results, one may note that the miscibility of SAN with SMA is in the order SAN15 > SAN20 > SAN25. This situation is interpreted by the binary interaction argument as follows. Since our system is the binary blend of copolymer 1, composed of monomers A (acrylonitrile) and B (styrene), and copolymer 2, composed of monomers B and C (maleic anhydride), the interaction parameter is given by

$$\chi_{12}=\chi_{AB}x^2+(\chi_{AC}-\chi_{BC}-\chi_{AB})xy+\chi_{BC}y^2 \qquad (1)$$

where $x$ and $y$ are the copolymer compositions in terms of volume fractions of A and C, respectively, i.e. copolymer 1 is $(A_xB_{1-x})$ and copolymer-2 is $(C_yB_{1-y})$. Assuming that

$$\chi_{AC}/\chi_{BC}=-0.07, \chi_{AB}/\chi_{BC}=1$$

(Reference 3), the values of $\chi_{12}$ are estimated to be $-0.00158\chi_{BC}$, $0.0004\chi_{BC}$ and $0.00738\chi_{BC}$, for SAN15/SMA, SAN20/SMA and SAN25/SMA systems, respectively. When $\chi_{BC}$ is positive, these results give the above order of miscibility.

### *Temperature dependence of $\chi_{12}$*

Once the phase diagram has been obtained, one can estimate the temperature dependence of $\chi_{12}$ by assuming[11]

$$\chi_{12}=A/T+BT+C \qquad (2)$$

where $T$ is temperature and $A$, $B$ and $C$ are constants. The first term on the right-hand side of equation (2) corresponds to the exchange energy contribution to the free energy of mixing. The second term corresponds to the so-called free-volume contribution. In this equation we omitted the composition dependence of $\chi_{12}$, which was found to be very small.

On the basis of the Flory–Huggins equation, one can calculate the binodal curve for a given set of parameters in equation (2) and the molecular weights of component polymers. We selected the best set of parameters $A$, $B$, and $C$ to fit the calculated binodal curve to the phase diagram observed (*Figures 2* and *4*). The results are shown by $\chi_{12}$–$T$ curves in *Figure 5*. Note here that $A$ is negative while $B$ and $C$ are positive in our binary systems.

*Figure 5* also shows the temperature dependence of $\chi_{12}$ for polystyrene (PS)/poly(vinyl methyl ether) (PVME). This $\chi_{12}(T)$ curve was similarly estimated from the phase diagram by Shibayama *et al.*[12]. This curve is included in *Figure 5* for comparison, demonstrating that the $\chi_{12}(T)$ of the SAN/SMA system is a slowly increasing curve. It implies that, in the two-phase region of SAN/SMA systems, the thermodynamic quench depth $|\chi_{12}(T)-\chi_{12}(T_s)|$ is not as large as expected from the deviation from the spinodal temperature $|T-T_s|$ in the phase diagram, compared with the situation in PS/PVME systems.

### *Kinetics of demixing*

In the shaded areas of *Figures 2* and *4*, we observed the modulated structure with periodic distance $<2\,\mu m$ even after very long annealing times (22 h), demonstrating that the demixing is very slow and still remained a modulated structure even after 22 h. In contrast, the demixing in the PS/PVME system is fast: e.g. modulated structure is maintained for only $\approx 10$ min and it coarsens to an isolated droplet morphology under $|T-T_s|=15$ K

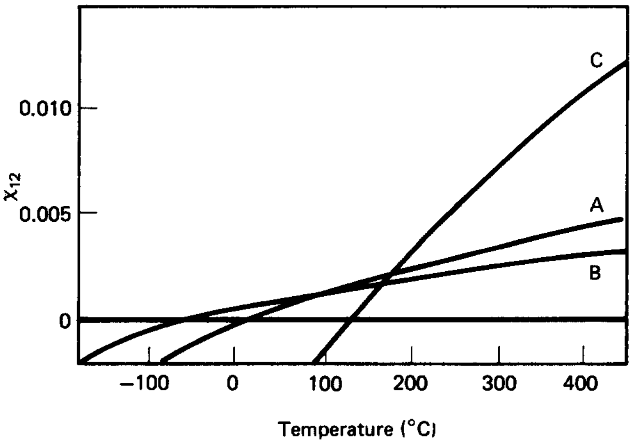

**Figure 5** Temperature dependence of $\chi_{12}$, estimated by parameter fitting of equation (2) to the phase diagram observed, assuming a segment volume of 100 ml mol$^{-1}$: curve A, SAN20/SMA; curve B, SAN25/SMA; curve C, PS/PVME

(Reference 13). The rate of demixing is discussed more quantitatively by light scattering measurements.

*Figure 6* shows the change of light scattering profile with time after the temperature jump from the single-phase region (150°C) to the two-phase region (230°C). The scattering peak is due to the periodic structure developed by demixing. This is confirmed by comparing the Bragg spacing ($\Lambda_m$) from the peak angle ($\theta_m$) and the periodic distance by microscope. The peak position shifts to smaller angles with annealing time. The change of $\theta_m$ at various temperatures is shown in *Figure 7* in terms of the time development of the wave number $q_m$ ($=2\pi/\Lambda_m$).

The $q_m(t)$ curves in *Figure 7* suggest that the demixing is very slow. A rate constant defined by $\Delta\Lambda_m/\Delta t$ in a limited range $1 \leq \Lambda_m \leq 2$ $\mu$m is 0.13 nm s$^{-1}$ at 198°C, 0.62 nm s$^{-1}$ at 215°C and 2.32 nm s$^{-1}$ at 230°C. Note here that the lowest temperature, 198°C, is 80°C higher than the $T_g$ of the mixture.

The three curves in *Figure 7* seem to be capable of being reduced to a master curve by vertical and horizontal

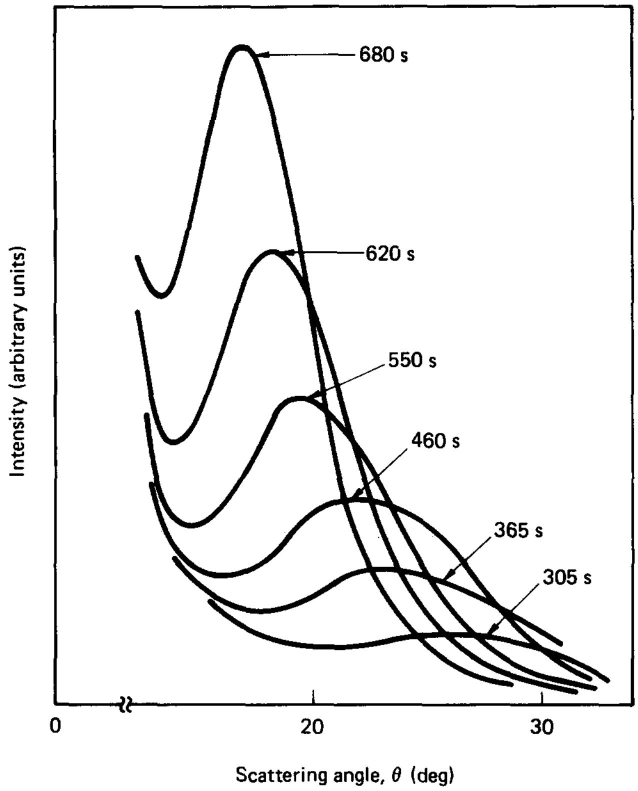

**Figure 6** Change of light scattering profile with annealing at 230°C for 40/60 SAN20/SMA. Numbers give annealing times after the temperature jump

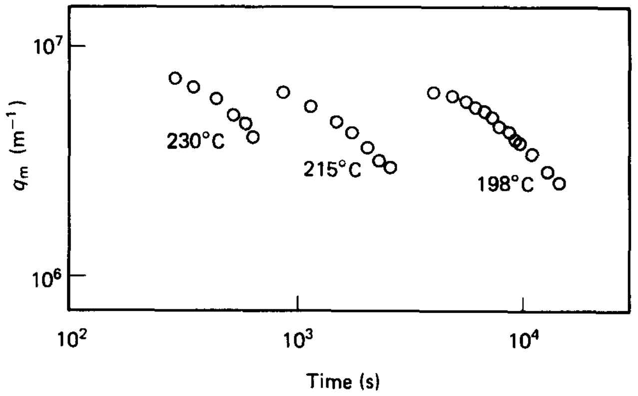

**Figure 7** Time development of wavenumber $q_m$ at different temperatures for 40/60 SAN20/SMA

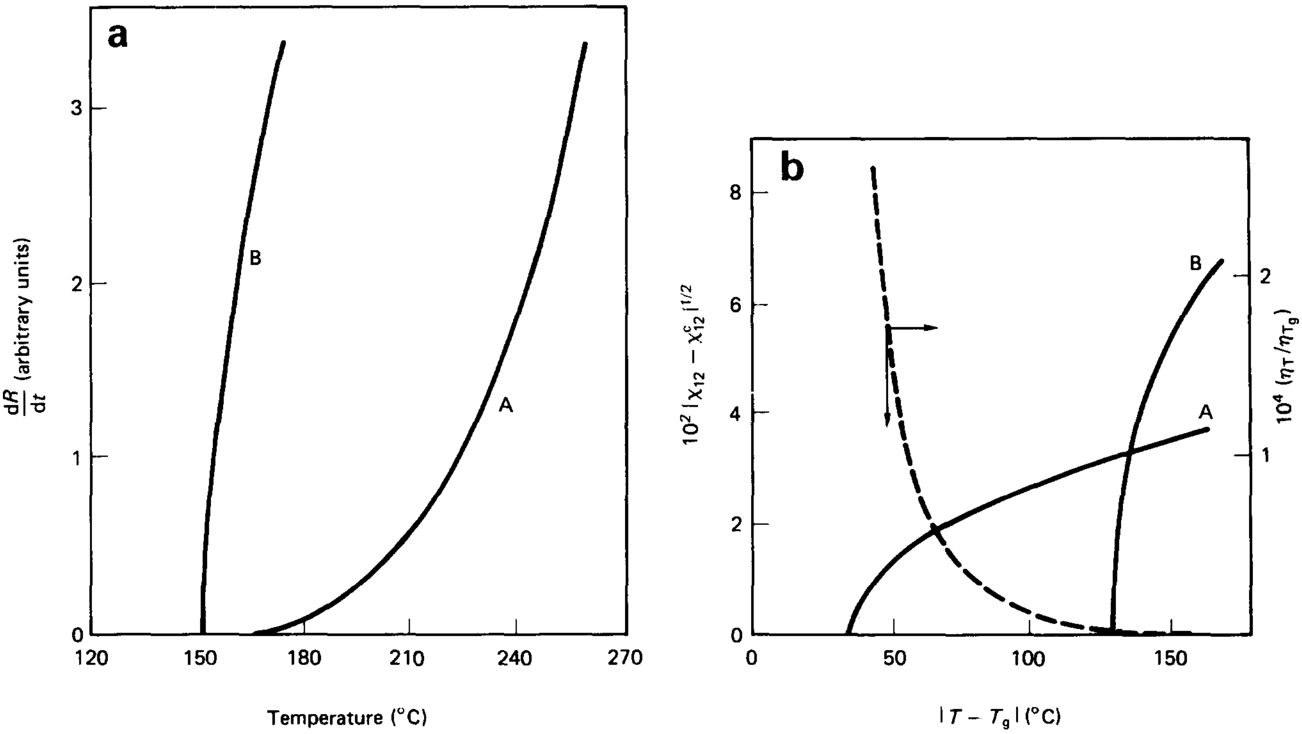

**Figure 8** (a) Temperature dependence of coarsening rate, calculated from equations (3)–(5); (b) thermodynamic and chain mobility contributions as a function of the temperature deviation from $T_g$. Curves A, 50/50 SAN20/SMA; curves B, 30/70 PS/PVME

shifts, if the variables characteristic of the initial stage of demixing were available from light scattering measurements. Unfortunately, the intensity of scattered light was so weak that we could not get reliable data on the early stage of demixing. This may be due to the small difference in refractive index of SAN and SMA. Anyway, these kinetic results indicate that they are on the late stage of demixing.

For the kinetics of demixing at a late stage, the effect of interfacial instability should be taken into account. From Siggia[14], the coarsening rate of the separated phase is given by

$$dR/dt \propto \gamma/\eta \qquad (3)$$

where $\gamma$ is the interfacial tension and $\eta$ is viscosity. The interfacial tension of the demixed system may be given by[15]

$$\gamma \propto |\chi_{12}(T) - \chi_{12}^{c}|^{1/2} \qquad (4)$$

where $\chi_{12}^{c}$ is the interaction parameter at the critical point.

$$\chi_{12}^{c} = \tfrac{1}{2}(m_1^{-1/2} + m_2^{-1/2})^2$$

$m_i$ being the degree of polymerization of polymer *i*. One may express the temperature dependence of $\eta$ in terms of the Williams–Landel–Ferry equation:

$$\log \frac{\eta(T)}{\eta(T_g)} = \frac{-17.4(T-T_g)}{51.6+T-T_g} \qquad (5)$$

Combining equations (3), (4), and (5) and the results in *Figure 5*, one can estimate the temperature dependence of $dR/dt$. The calculated results are shown in *Figure 8a*. The $dR/dt$ of the SAN/SMA system is very small, compared with that of PS/PVME for the same quench depth $|T-T_c|$. That is, *Figure 8a* suggests that the very slow demixing in the SAN/SMA system is caused by an overlap of two effects: first, the weak temperature dependence of $\chi_{12}$, i.e. the driving force for demixing is not as large as expected apparently from the quench depth in the phase diagram, and, secondly, low chain mobility, in other words, the small deviation of $T_c$ from $T_g$. This situation may be understood more easily by plotting $|\chi_{12} - \chi_{12}^{c}|^{1/2}$ and $\eta$, separately, as a function of $|T-T_g|$, as in *Figure 8b*.

## CONCLUSION

The LCST type phase behaviour has been revealed by cloud point measurements employing very long isothermal annealing. The extremely slow demixing phenomenon at the two-phase region above LCST may be interpreted in terms of the very weak temperature dependence of $\chi_{12}$ and the low chain mobility. This slow demixing is not specific to the particular blend SAN/SMA but seems to be general for polymer blends including random copolymer[16]. It should be noted that, to obtain a proper estimation of the phase diagram in such polymer blends, attention should be paid to the time scale of annealing; it may not be rare to require observation over several days.

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