# Phase dissolution in polymer blends. Kinetics of dissolution and related problems in rubber technology*

**Yasushi Takagi, Toshiaki Ougizawa and Takashi Inoue**†
*Tokyo Institute of Technology, Department of Textile and Polymeric Materials, Ookayama, Meguro-ku, Tokyo 152, Japan*
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For a blend of *cis*-1,4-polybutadiene and poly(styrene-*co*-butadiene), which has been found to exhibit upper critical solution temperature (*UCST*) behaviour, the kinetics of phase dissolution in the single-phase region above the *UCST* was investigated by light scattering, using novel specimens with regularly phase-separated structure having a periodic distance of a few micrometres. The apparent diffusion constant for the dissolution was estimated to be of the order of $10^{-13}$–$10^{-12}$ cm$^2$ s$^{-1}$. The rate of phase dissolution was much increased by the presence of a small amount of organic peroxide. The results give a new viewpoint on understanding the mixing and curing process in elastomer blends.

**(Keywords: polymer blend; upper critical solution temperature; phase dissolution; diffusion constant; cure; butadiene rubber/styrene–butadiene rubber)**

## INTRODUCTION

It is well known that most pairs of high molecular weight polymers are immiscible. If the molecular weight is very low, they are miscible at elevated temperatures and tend to phase separate at lower temperatures. This upper critical solution temperature (*UCST*) behaviour has been observed in a mixture of oligomers. Some dissimilar polymers with specific interaction between them are miscible even if their molecular weights are high. The miscible polymers tend to phase separate at elevated temperatures. This lower critical solution temperature (*LCST*) behaviour is typical for miscible polymer blends[1–3].

Quite recently, we found that some dissimilar polymers with high molecular weights exhibit both *UCST* and *LCST*[4]. Two phase diagrams are reproduced in *Figure 1*. One of the interesting subjects related to this phase behaviour is the thermodynamic interpretation of the coexistence of *UCST* and *LCST*[5]. Another interesting subject is the kinetics of phase dissolution in the single-phase region above the *UCST*.

In this paper, we will describe the results of light scattering studies on the kinetics of phase dissolution after the temperature jump from the two-phase region to the single-phase region above the *UCST*. The polymer pairs in this study are familiar ones in the rubber industry. So, one item of technological interest is to investigate the effect of curing agent on the kinetics of phase dissolution. This was also undertaken. From these results, we will discuss the problems in rubber technology, such as mixing and curing processes.

## EXPERIMENTAL

Polymer specimens (BR, SBR-23 and SBR-45) are commercial ones supplied by the Japan Synthetic Rubber Co. Ltd. Their characteristics are shown in *Table 1*. The BR is a *cis*-1,4-polybutadiene prepared by solution polymerization with Ti catalyst. The SBR is poly(styrene-*co*-butadiene) prepared by emulsion polymerization.

Equal amounts of BR and SBR were dissolved at 8 wt % of total polymer in toluene. The solution was cast onto a cover glass (for microscopy) placed in a flat dish with a flat glass cover. The rate of solvent evaporation was controlled by adjusting the gap between the cover and dish. After the polymer concentration had passed ~95 wt %, the concentrated solution was further dried under vacuum of $10^{-4}$ mmHg for 10 h.

We also prepared the blend films loaded with organic peroxide (PO). In this case, we added 3 phr (parts per hundred polymer) of PO to the 8 wt % solution, then cast and dried in the same way. Thus we prepared the cast film with a simple formulation (BR/SBR/PO = 50/50/3).

The blend film on the cover glass was inserted in a hot chamber (*Figure 2a*) kept at a constant temperature and was annealed. The chamber was set horizontally on the light scattering stage as in *Figure 2b*. Radiation from a He–Ne gas laser of 632.8 nm wavelength was applied vertically to the film specimen. The goniometer trace of the intensity of the scattered light from the film was given. Thus, the change of the light scattering profile was observed during the isothermal annealing.

Glass transition and melting temperatures were estimated by d.s.c. (du Pont, model 910).

## RESULTS AND DISCUSSION

### *Modulated structure in the cast film*

*Figure 3* is a typical example of the light micrograph of the cast film of BR/SBR-45 (50/50). A highly

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†To whom correspondence should be addressed.

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interconnected two-phase morphology with uniform domain size is seen. We have interpreted the development of this characteristic morphology in terms of spinodal decomposition during the solution casting of ternary polymer solution[6,7]. We will call the regular structure a 'modulated structure', as has been done in the fields of inorganic glasses and metals[8]. The goniometer trace of the scattered light results in a light scattering profile with a peak (see *Figure 4*). The Bragg spacing from the peak corresponds to the periodic distance in the micrograph. Solution casting of the ternary system, BR/SBR/PO, also yields the modulated structure. That is, the presence of a small amount of the peroxide did not disturb the formation of the modulated structure.

### *Phase dissolution*

First, we will be concerned with the phase dissolution in the neat blend (unloaded with PO). The film specimen with modulated structure underwent a rapid temperature jump from room temperature to the various higher temperatures set isothermally below and above the *UCST* in *Figure 1*. Below the *UCST*, no appreciable change in the scattering profile with time of isothermal annealing could be detected in a timescale of 2 h. This means that no appreciable change in the two-phase structure took place. On the other hand, above the *UCST* (but below the *LCST* for the BR/SBR-45 system), the scattered intensity decreased with time of annealing, keeping the peak angle almost constant. A typical example is shown in *Figure 4*.

This type of decay in the scattered intensity has already been discussed for the case of small-angle X-ray scattering studies on the order-to-disorder transition of block copolymers by Hashimoto *et al.*[9] They have formulated the decay in the scattered intensity with the variation of the concentration profile in the microdomain structure from a regular two-phase structure with sharp interface to that with a broad interface, eventually resulting in a uniform concentration distribution. Based upon their formulation, the intensity decay in *Figure 4* corresponds to the phase dissolution of the modulated structure, keeping the periodic distance constant, when the thermodynamic driving force for the phase separation is removed by the temperature jump to the single-phase region above the *UCST*.

The single-phase nature after the phase dissolution was confirmed by d.s.c studies. Curve A in *Figure 5* is a d.s.c. thermogram of the as-cast film of BR/SBR-45 (50/50) blend having a modulated structure. We see two glass transitions at the glass transition points of BR and SBR-45, respectively, and also a crystallization exotherm peak and a melting endotherm peak of BR. These transition features are nothing but an indication of the two-phase nature in the as-cast film. After the d.s.c. run to get the thermogram A, the film specimen was further heated up to 155°C in the d.s.c. pan and was annealed at that temperature for 30 min, then rapidly quenched to liquid-nitrogen temperature. The d.s.c. thermogram of the annealed and quenched specimen is shown as curve B in

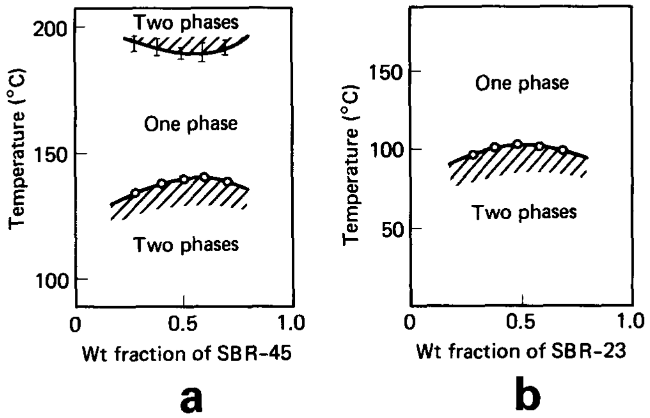

**Figure 1** Phase diagrams: (a) BR/SBR-45 system; (b) BR/SBR-23 system

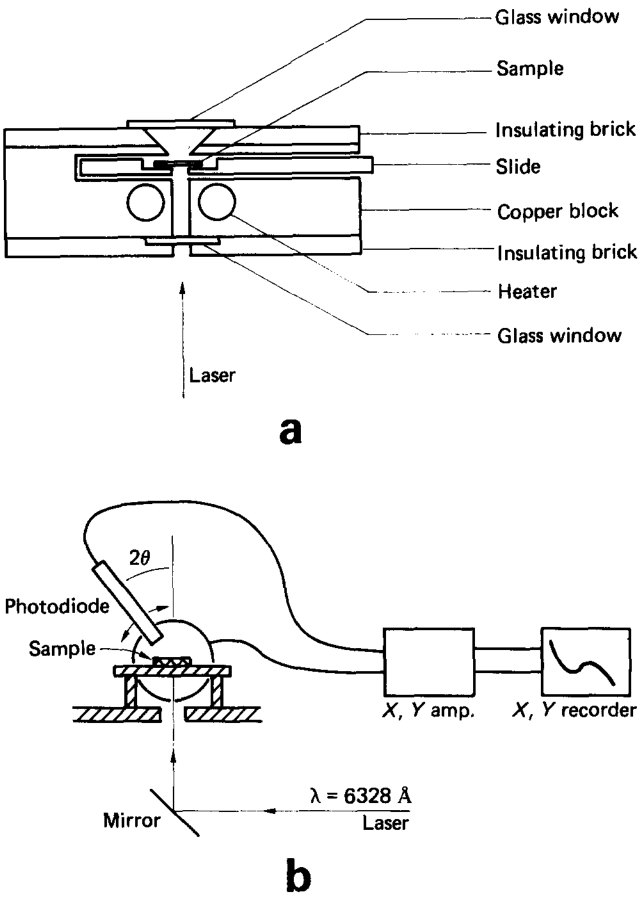

**Figure 2** (a) Hot chamber; (b) light scattering apparatus

**Table 1** Polymer specimens

| Code | Polymer | Grade | $\bar{M}_w \times 10^{-4}$ | $\bar{M}_n \times 10^{-4}$ |
|---|---|---|---|---|
| BR | polybutadiene[a] | JSR BR02 | 39 | 18 |
| SBR-23 | poly(styrene-*co*-butadiene) (23/77)[b] | JSR 1500 | 51 | 16 |
| SBR-45 | poly(styrene-*co*-butadiene) (45/55)[b] | JSR 0202 | 48 | 16 |

[a] B unit: all *cis*-1,4
[b] B unit: *cis*/*trans*/vinyl = 13/69/18

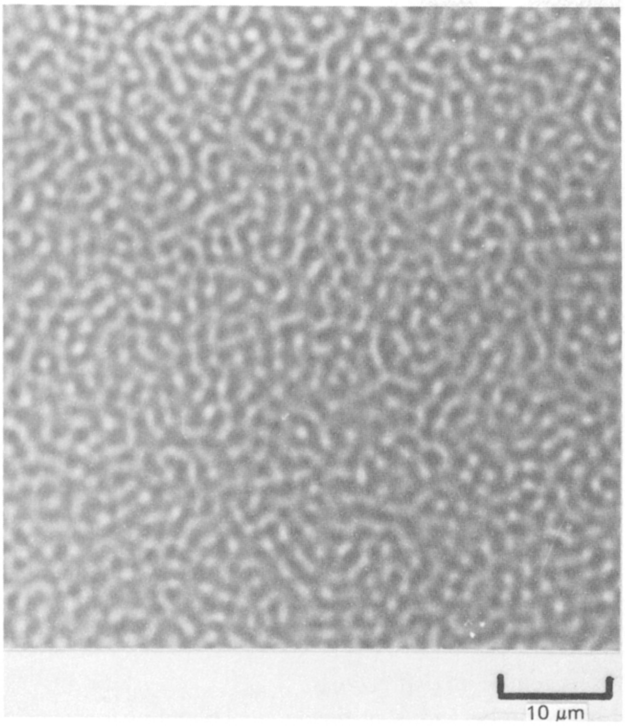

**Figure 3** Light micrograph of BR/SBR-45 (50/50) system

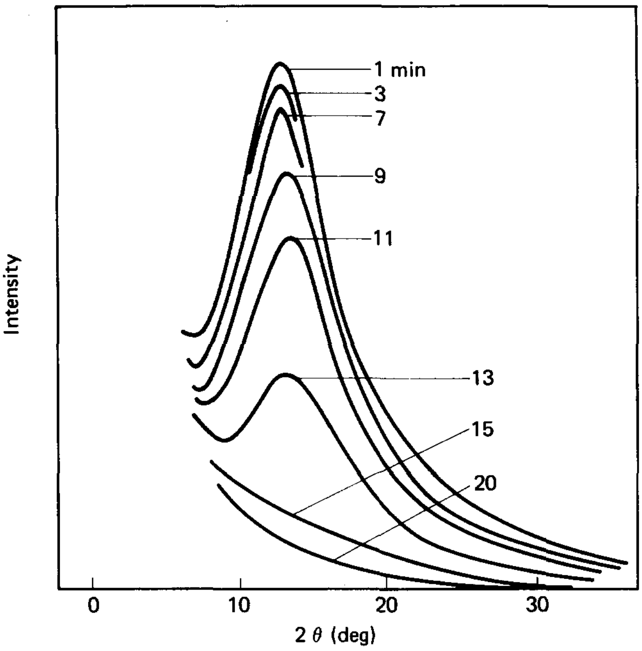

**Figure 4** Change of light scattering profile of BR/SBR-45 (50/50) system during annealing at 155°C

*Figure 5*. All of the transitions in the as-cast film have disappeared. A broad single glass transition is seen between the glass transition temperatures of BR and SBR-45. This implies that the two-phase structure has transformed to an almost homogeneous mixture; in other words, phase dissolution took place by annealing above the *UCST*.

The structural change depicted from the results by light scattering and d.s.c. is the broadening of the polymer–polymer interface, eventually resulting in phase dissolution into an almost homogeneous system.

*Kinetics of phase dissolution*

In *Figure 6* is shown the change in peak intensity of the scattered light, $I$, with annealing time after the temperature jump to above the *UCST*. The peak intensity initially remains constant for a certain time, and then decreases exponentially with time. There seems to be a kind of induction period. The reason why an induction period exists for the phase dissolution is not obvious at present. In this work, we will discuss the kinetics of phase dissolution from the later stage of the intensity change, i.e. by the linear decay of $\ln(I/I_0)$ vs. time plots in *Figure 6*, where $I_0$ is the peak intensity at zero annealing time. From the slope of the intensity decay, one can estimate the apparent diffusion constant $\tilde{D}$ for the phase dissolution using:

$$\ln(I/I_0) = -2\tilde{D}[(4\pi/\lambda)\sin(\theta_m/2)]^2 t$$

where $t$ is the time, $\lambda$ is the wavelength of the light in specimen, and $\theta_m$ is the scattering peak angle[9,10]. Similarly we estimated the value of $\tilde{D}$ for the BR/SBR-23

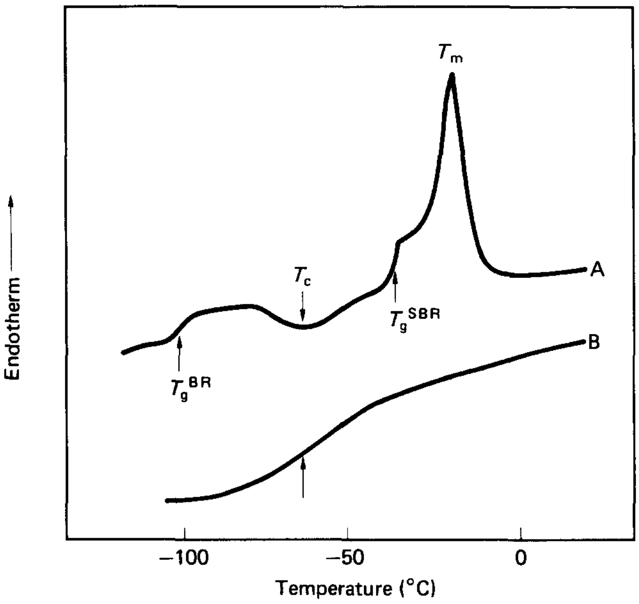

**Figure 5** D.s.c. thermograms of BR/SBR-45 (50/50) systems: curve A, as-cast film; curve B, film annealed at 155°C for 30 min

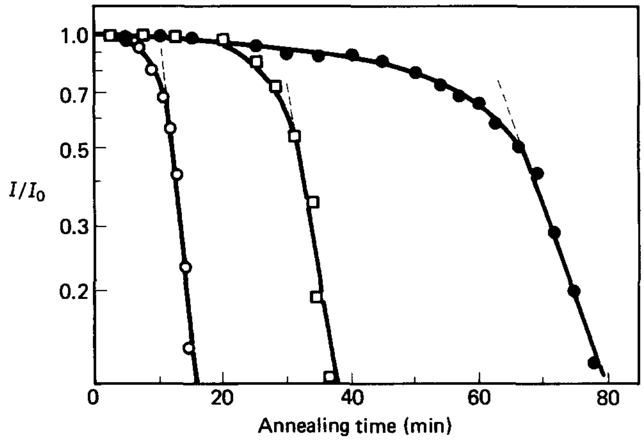

**Figure 6** Change of scattered intensity of BR/SBR-45 (50/50) system during annealing at various temperatures: ●, 135°C (1.51 µm); □, 145°C (1.65 µm); ○, 155°C (1.84 µm). Figures in parentheses are the periodic distance of modulated structure

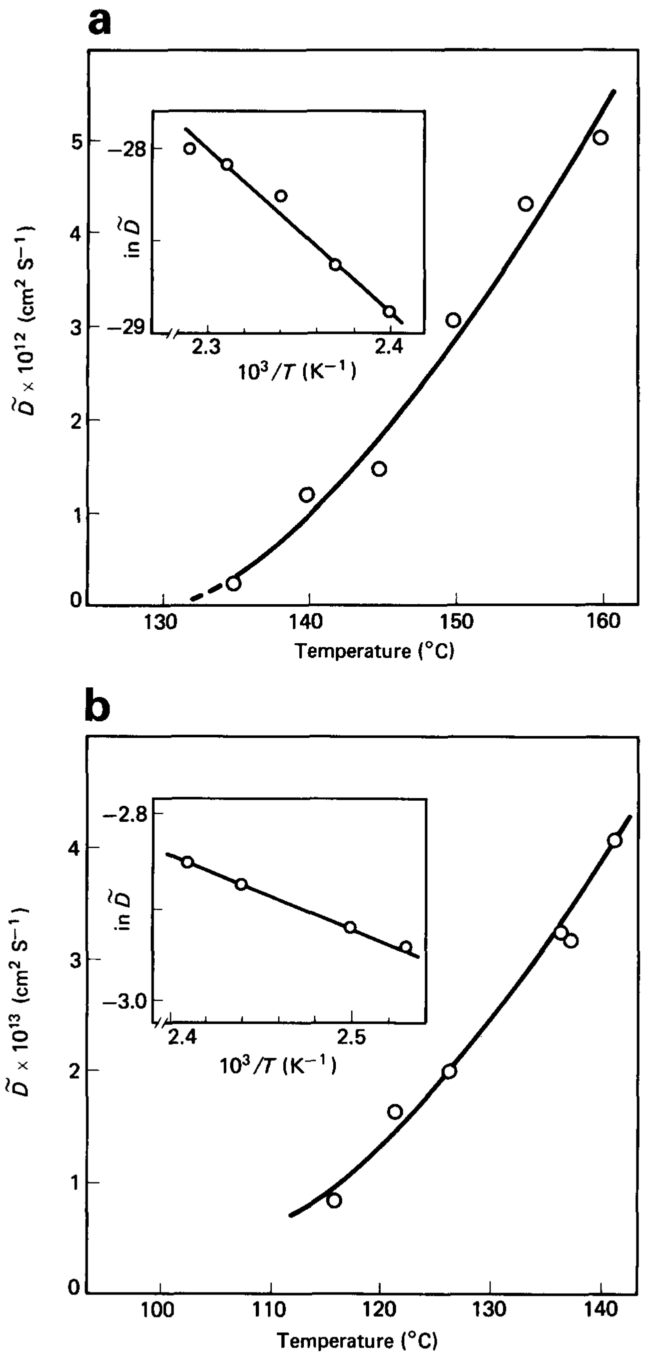

**Figure 7** Temperature dependence of apparent diffusion constant $\tilde{D}$ and its Arrhenius plot: (a) BR/SBR-45 (50/50) system; (b) BR/SBR-23 (50/50) system

(50/50) system at various temperatures above the *UCST*. The temperature dependence of $\tilde{D}$ is shown in *Figure 7*. The values of $\tilde{D}$ are in the range of $10^{-13}$–$10^{-12}$ cm$^2$ s$^{-1}$.

Phase dissolution is the reverse of phase separation. However, the basic formulation of the dynamics may be formally common for the two phenomena. The only difference is the sign of $\tilde{D}$. So, the theory of spinodal decomposition[11] may be applicable for the phase dissolution with modulated structure. Hence, the temperature at which $\tilde{D}$ becomes zero corresponds to the spinodal temperature. The spinodal temperature estimated from the results in *Figure 7** locates reasonably within the *UCST* curve in *Figure 1*.

By employing an Arrhenius-type expression for the apparent diffusion constant:

$$\tilde{D} = D_0 \exp(-Q/RT)$$

the apparent activation energy for diffusion, $Q$, is estimated from the inset of *Figure 7*. The values of $Q$ estimated are 17.6 kcal mol$^{-1}$ and 33.8 kcal mol$^{-1}$ for BR/SBR-23 and BR/SBR-45 systems, respectively. To our knowledge, there exists only one result of $Q$ for phase dissolution. It is 11.7 kcal mol$^{-1}$ for the poly(vinyl chloride)/poly($\varepsilon$-caprolactone) system by Gilmore *et al.*[12] They estimated $Q$ by a different but more direct method: combination of scanning electron microscopy and energy-dispersive analysis of X-ray fluorescence. Our results are of the same order as theirs, and thus our experimental procedure results in a proper estimation of $Q$.

Based upon the above results on the phase diagram and the dynamics of phase dissolution, we are able to proceed with arguments on the problems in rubber technology, such as mixing and curing process of elastomer blends.

### *Discussion on mixing process*

In the rubber industry, mechanical blending is the most widely used method for mixing blends. The high shearing forces in heavy equipment, such as Banbury mixer and screw extruder, evolve heat during mixing. The temperature of polymers increases with mixing time. Sometimes it exceeds 100°C in a mixing time less than 10 min. So, the BR/SBR-23 system with low *UCST* (*Figure 1*) might experience high temperatures above the *UCST* at a late stage of mixing. Hence, phase dissolution could be expected. However, homogeneous blends or molecular solutions in elastomer blends were never obtained by mechanical mixing[13]. This is not surprising: the time for dissolution is too short, even if the temperature goes up above the *UCST* after a fine dispersion (say, order of micrometres) has been obtained by mechanical mixing. For example, if one estimates the diffusion distance in terms of root-mean-square displacement $\overline{(x^2)}^{1/2}$ by Einstein's equation, $\overline{(x^2)} = 2\tilde{D}t$, $\overline{(x^2)}^{1/2}$ is 0.077 $\mu$m for $\tilde{D} = 10^{-13}$ cm$^2$ s$^{-1}$ and is 0.245 $\mu$m for $\tilde{D} = 10^{-12}$ cm$^2$ s$^{-1}$, when $t$ is 5 min. These distances are far less than the domain size obtained by mechanical mixing. So, no appreciable degree of phase dissolution can be expected during the mixing process.

If the mixing is further continued or the mixed blend is annealed at temperatures above the *UCST* for much longer times, one can expect a homogeneous blend. We can find such a result in the literature. Böhm *et al.*[14] prepared a 50/50 blend of polybutadiene (*cis*/*trans*/vinyl = 54/35/11) and poly(styrene-*co*-butadiene) (25 wt% styrene, emulsion SBR) by mixing in a Brandender Plasticorder. The as-mixed blend was a two-phase system. After annealing the mixed specimen at 150°C in vacuum for 26 h, a single glass transition peak was observed between the glass transition temperatures of the component polymers. This implies that phase dissolution took place during the annealing after the mechanical mixing.

### *Curing and phase dissolution*

In the rubber industry, curing is usually carried out at around 150°C. This means that for the BR/SBR-23

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* The spinodal temperature is given by extrapolating a linear relation between $\tilde{D}/T$ and $T$. The linear relation is expected theoretically. Its detail will be presented in a forthcoming paper

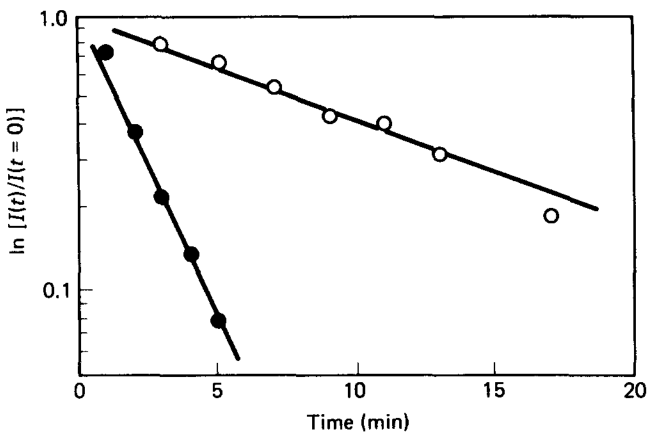

**Figure 8** Effect of the presence of peroxide for BR/SBR-23 (50/50) system on the decay of scattered intensity at 150°C: ●, loaded with dicumyl peroxide; ○, unloaded

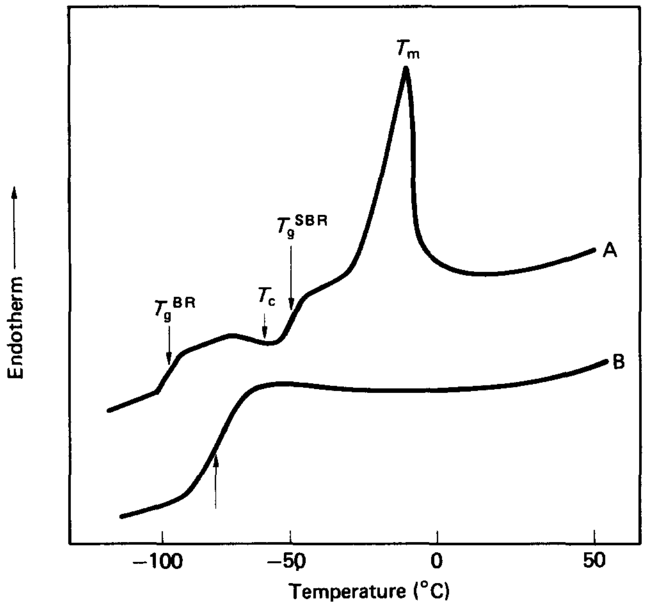

**Figure 9** D.s.c. thermograms of BR/SBR-23/BPO (50/50/3) system: curve A, before annealing; curve B, after annealing at 110°C for 200 min

system, for instance, the curing process corresponds to a temperature jump from room temperature in the two-phase region to a higher temperature in the single-phase region and isothermal annealing at a temperature above the *UCST*. So, phase dissolution is expected during curing. In the case of curing, however, the system is a ternary one consisting of two polymers and the curing agent. The problem is, what is the effect of the curing agent on phase dissolution?

*Figure 8* shows a typical example demonstrating the effect of the peroxide loading, in terms of the change in peak intensity of scattered light with time of annealing. The peroxide-loaded blend shows a much faster decay of the peak intensity than the unloaded one. This implies that the phase dissolution takes place much faster than that in the unloaded system.

The single-phase nature in the cured blend (after long annealing) was confirmed by the d.s.c. studies shown in *Figure 9*. From the results by light scattering and d.s.c. studies, the structural change depicted is same as in the case of the unloaded blend and its rate is much increased by the presence of peroxide. This is nothing but the point suggested in our recent article[15]. Here, we will describe the more quantitative and extensive results.

The values of $\tilde{D}$ were estimated by the same procedure described above. These are shown as a function of temperature in *Figures 10* and *11*. The $\tilde{D}$ values for the unloaded system are reproduced from *Figure 7* for comparison.

For the unloaded BR/SBR-23 system at 100°C, for instance, the value of $\tilde{D}$ is about $10^{-14}\,\text{cm}^2\,\text{s}^{-1}$. By loading benzoyl peroxide, it increases to $5\times10^{-13}\,\text{cm}^2\,\text{s}^{-1}$, about 50 times larger than that of the unloaded blend. Also, at higher temperatures, the values of $\tilde{D}$ in the loaded systems are much larger than those in the unloaded systems. It is evident that the rate of phase

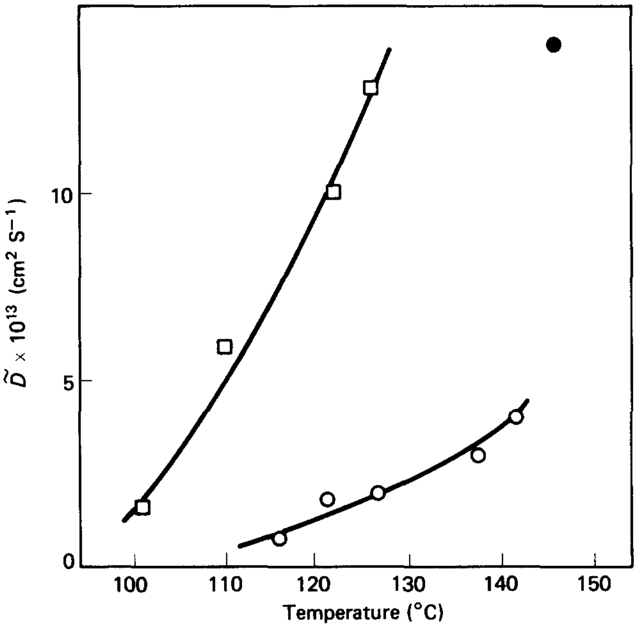

**Figure 10** Temperature dependence of apparent diffusion constant $\tilde{D}$ of BR/SBR-23 system: ○, unloaded; ●, dicumyl peroxide loaded; □, benzoyl peroxide loaded

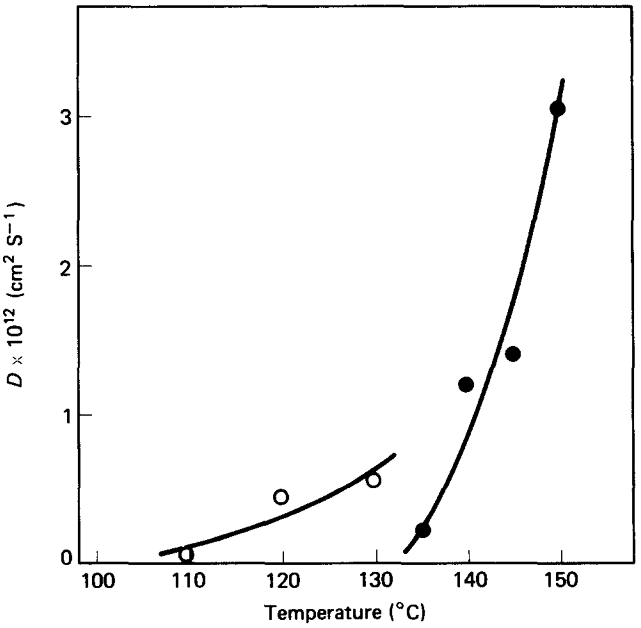

**Figure 11** Temperature dependence of apparent diffusion constant $\tilde{D}$ of BR/SBR-45 system: ●, unloaded; ○, loaded with benzoyl peroxide

dissolution is promoted by the presence of peroxide at various temperatures.

It should be noted that the $\tilde{D}$ value in the loaded system is not zero even below the *UCST*. In other words, phase dissolution proceeds even in the two-phase region if peroxide is present. At present, we do not have a clear interpretation of this behaviour. However, it may be plausible that the *UCST* in the BR/SBR system shifts downwards due to the presence of the BR–SBR block or graft copolymer[16] generated by chemical reaction during curing, especially at the early stage of curing.

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