Photocrosslinking Kinetics of Polymer Blends Undergoing Spinodal Decomposition Process

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ABSTRACT: Photocrosslinking reaction kinetics of poly(2-chlorostyrene) performed inside the spinodal region of poly(2-chlorostyrene)/poly(vinyl methyl ether) (P2CS/PVME) blends was investigated by means of ultraviolet (UV)-visible absorption spectroscopy. The reaction was performed via photodimerization of anthracene moieties chemically labeled on the P2CS chains. The crosslinking kinetics of (P2CS/PVME) blends submitted to a temperature jump from the one-phase into the spinodal regions was observed by monitoring the irradiation time dependence of the absorbances of anthracene as well as of the blend in two regions of wavelengths. One is inside and the other is outside the absorption range of anthracene. The contribution of the sample cloudiness to the absorbance of anthracene was subtracted from the absorption data by using an empirical power law experimentally established between the incident wavelengths and the absorption of the blends. It was found that the reaction kinetics approximately follows the mean-field kinetics inside the spinodal region, resembling the behavior of the crosslinking reaction performed in the miscible region at relatively low crosslinking densities. On the other hand, the method described here fails to estimate the crosslinking densities when the phase separation proceeds rapidly, overcoming the reaction. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 885–893, 1998

Key words: poly(2-chlorostyrene); poly(vinyl methyl ether); polymer blends; photocrosslinking; spinodal decomposition; crosslinking density; mean-field kinetics

INTRODUCTION

It is well known that the phase behavior of interpenetrating polymer networks (IPNs) is determined by the competition between the kinetics of the crosslinking processes and the phase separation induced by these chemical reactions.[1] In the past decades, a number of experimental methods have been widely used to determine the crosslinking density of homogeneous polymer systems.

From the static aspects, the Mooney–Rivlin equation proposed for the stress–strain relationship of vulcanized rubbers can be used to estimate the average crosslinking densities of homopolymer systems.[2–4] Alternatively, the swelling-to-equilibrium method can also be employed for the same purpose provided that the binary interaction parameter χ between the polymer and solvent is known.[5,6] From the dynamical point of view, the crosslinking density can be estimated from the equilibrium shear modulus in dynamic mechanical experiments.[7] To apply these methods, the samples need to be homogeneous and their crosslinking densities (γ) are required to exceed the percolation threshold. For slightly crosslinked samples, that is, those obtained at the early stage of the curing process, the most suitable candidate would be some *in situ* spectroscopic techniques

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such as infrared or UV-visible absorption which enables one to directly monitor the consumption of photocrosslinkers during the course of the reaction.[8,9] More recently, methods to determine the crosslinking densities of phase-separated IPNs have been developed and are described in detail.[10]

In the past few years, we have carried out photocrosslinking of binary polymer blends undergoing spinodal decomposition processing.[11,12] From these experimental results, it has been known that the morphology of the reacted blends strongly depends on the competition between the crosslinking reactions and the phase separation kinetics. Therefore, quantitative analysis of the extent of the crosslinking reactions during phase separation is indispensible for elucidating the relationship between the reaction and the resulting morphology. For this purpose, it is necessary to develop a method to observe the photochemical reaction kinetics in polymer mixtures undergoing phase separation as well as to measure the crosslinking density of the sample, particularly the extent of the reaction after the blend starts phase-separating. In this work, a spectroscopic method is developed to estimate the crosslinking density in photocrosslinked polymer blends undergoing spinodal decomposition. The advantage of the method is that the kinetics can be directly monitored during the course of the reaction. First, the principle of the determination of these crosslinking densities is described. Subsequently, the kinetic data are constructed and analyzed from the dependence of the absorbance of photocrosslinkers on irradiation time. Finally, the limitation of the method will be discussed in relation to the competition between the crosslinking reactions and phase separation.

EXPERIMENTAL

Materials

Polymer blends used in this work are the mixtures of poly(2-chlorostyrene) (P2CS, radical polymerization) and poly(vinyl methyl ether) (PVME, aldrich). P2CS ($M_w = 2.1 \times 10^5$, $M_w/M_n = 1.8$) was chemically labeled with the photocrosslinker anthracene by the method described previously.[11,12] The label content is ~ 1 anthracene per 150 repeating monomer units of P2CS chains. PVME ($M_w = 9.6 \times 10^4$, $M_w/M_n = 2.1$, Aldrich) was purified by reprecipitation using methanol as good solvent and n-heptane as poor solvent. The
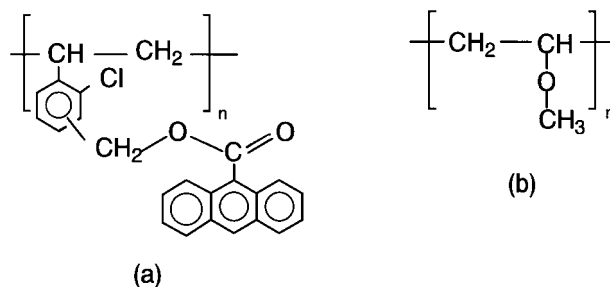
Figure 1 Chemical structures of polymers used in this article: (a) anthracene-labeled poly(2-chlorostyrene)(P2CS); (b) poly(vinyl methyl ether)(PVME).

chemical structures of these polymers are illustrated in Figure 1. P2CS/PVME blends with the thickness 50 μm were prepared by casting benzene solutions containing appropriate amounts of the two polymers. These samples were dried under vacuum at 90°C over 2 days prior to the experiments.

Instruments and Procedure

Photocrosslinking reactions were performed by using a Hg–Xe lamp (500 W, Hamamatsu Photonics, Japan). Ultraviolet light with wavelengths mainly at 365 nm was selected from the light source by using a sharp-cut filter (SC-052, Corning). The infrared components of the lamp were eliminated by using a water filter with a 5-cm path length. The light intensity at 365 nm was adjusted at 70 mJ/s cm^2 by using a convex lens. The change in absorbance of the first peak of anthracene at 385 nm was monitored by using a spectrophotometer (UV-160, Shimadzu). The temperature of the sample was thermostated with a precision of ±0.5°C. Both the cloud points and the spinodal temperatures of the blends were determined by small-angle X-ray scattering (National Laboratory of High Energy Physics, Tsukuba). It is known that P2CS/PVME blends possess a lower critical solution temperature (LCST). Since the details of their phase behavior were published elsewhere,[13,14] only the phase diagram of the P2CS/PVME blend used in this article is sketched in Figure 2 to clarify the experimental conditions. The two compositions P2CS/PVME (40 : 60, critical) and (60 : 40, off-critical) were chosen for the studies of the photocrosslinking kinetics.

The sample was first kept at 100°C in the one-phase region for a period of 30 min and was then quickly jumped into a brass heating block set at a temperature inside the spinodal region. For both the compositions, the jump depth, which is the
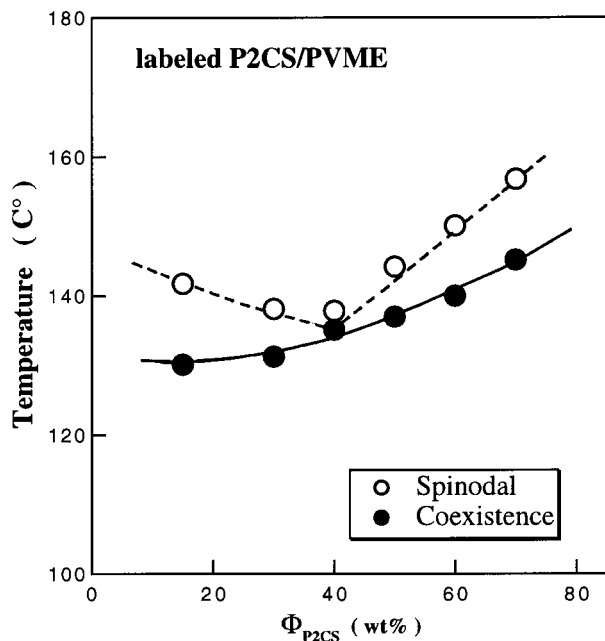
Figure 2 Phase diagram of an anthracene-labeled poly(2-chlorostyrene)/poly(vinyl methyl ether) blend obtained by small-angle X-ray scattering: (●), cloud points; (○), spinodal temperature. The jump depths $\Delta T = 2°C$ for both cases.

gap between the experimental and the spinodal temperatures, was set at 2°C. After reaching thermal equilibrium in 3 min, the blend was irradiated in appropriate time intervals and was then quickly quenched to a temperature below its glass transition temperature (T_g). The temperature-jump diagrams for both the critical (40 : 60) and off-critical (60 : 40) compositions are schematically illustrated in Figure 3. Subsequently, the absorbance as well as the transmittance of the crosslinked blends were measured at several wavelengths located both inside (385 nm) and outside (450, 500, 600 nm) the absorption range

of anthracene. To avoid the interference of the coarsening process taking place during the time required by the already crosslinked blend to reach thermal equilibrium at the destination temperature, one sample was used for one data point. Furthermore, all the blends used in one set of experiments were prepared at the same time under the same conditions in order to unify their thermal histories.

RESULTS AND DISCUSSION

Estimation of the Crosslink Density (γ) from Spectroscopic Data

The crosslink density γ used in this work is defined as the average number of crosslinking junctions per a P2CS chain in the blend under irradiation. For P2CS/PVME blends photocrosslinked by photodimerization of anthracene, γ can be defined as the ratio between the molar concentrations C_D of reacted anthracene molecules and C_{P2CS} of P2CS chains in the irradiated blend. Thus, the crosslink density $\gamma(t)$ obtained after an irradiation time t can be written as

$$\gamma(t) = \frac{1}{2} \frac{C_D}{C_{P2CS}} = \frac{1}{2} \frac{[C_A(0) - C_A(t)]}{C_{P2CS}} \quad (1)$$

The numerical factor $\frac{1}{2}$ in the r.h.s. of eq. (1) is due to the fact that 2 anthracene molecules form one crosslinking junction. Furthermore, $C_A(0)$ and $C_A(t)$ are, respectively, the molar concentrations of anthracene in the blend at the irradiation time $t = 0$ and t.

By definition, the label content α, which is the average number of anthracenes per one P2CS chain, can be expressed as
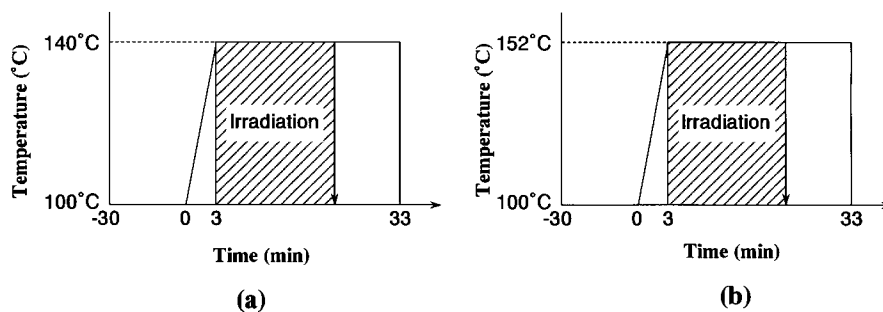

Figure 3 Temperature-jump diagrams and irradiation conditions for P2CS/PVME blends: (a) critical composition (40 : 60) and (b) off-critical composition (60 : 40).

$$\alpha = \frac{C_A(0)}{C_{\text{P2CS}}}$$

From the above-defined α, the crosslinking density $\gamma(t)$ in eq. (1) can be expressed in terms of measurable quantities such as absorbance (OD) or transmittance (T) as

$$\gamma(t) = \frac{\alpha}{2} \frac{[C_A(0) - C_A(t)]}{C_A(0)}$$

or

$$\gamma(t) = \frac{\alpha}{2} \frac{OD(0, \lambda_o) - OD(t, \lambda_o)}{OD(0, \lambda_o)}$$

$$= \frac{\alpha}{2} \left[1 - \frac{\log_{10} \dfrac{10^2}{T(t, \lambda_o)}}{\log_{10} \dfrac{10^2}{T(0, \lambda_o)}} \right] \quad (2)$$

Here λ_o and t represent, respectively, the absorption wavelength of anthracene and irradiation time. In this article, λ_o was taken as 385 nm, which is the wavelength of the first maximum of the absorption spectra of anthracenes in the blend. In general, when the coexistence curve of the reacted sample does not reach the experimental temperature during the reaction time, the crosslink density $\lambda(t)$ can be calculated by using eq. (2) with the absorbance or transmission data directly obtained from experiments. However, for the blend crosslinked inside the spinodal region, the cloudiness arising from the phase separation greatly distorts the spectroscopic data. As a consequence, it is necessary to eliminate the effects of the cloudiness from the absorption data when applying eq. (2) to the estimation of $\gamma(t)$.

In general, compared to a miscible sample, the transmission of a phase-separating blend decreases due to the scattering of the incident light. Though the initial transmittance $T(0, \lambda_o)$ of anthracene at a wavelength λ_o actually increases to $T(t, \lambda_o)$ after crosslinking in t(min), it apparently decreases to $T_s(t, \lambda_o)$ due to the influence of the loss $S(t, \lambda_o)$. The latter quantity arises mainly from the scattering at the wavelength λ_o as schematically shown in Figure 4. Therefore, $T(t, \lambda_o)$ can be expressed as

$$T(t, \lambda_o) = T_s(t, \lambda_o) + S(t, \lambda_o) \quad (3)$$
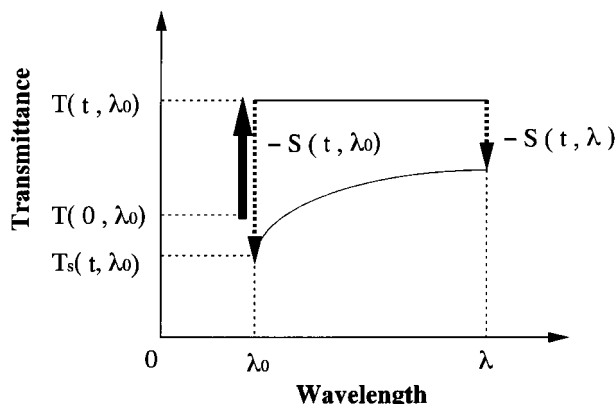

Figure 4 Procedure of correction for the effect of phase separation on the transmission of photocrosslinked blends.

Since $S(t, \lambda_o)$ cannot be obtained independently at the absorption wavelength λ_o of anthracene, the loss $S(t, \lambda)$ at several wavelengths λ outside the absorption range of anthracene was measured first. Then, the influence of the cloudiness $S(t, \lambda_o)$ on the transmission of the blend at the wavelength λ_o is estimated from the empirical relationship between the loss $S(t, \lambda)$ and the incident wavelength λ:

$$S(t, \lambda) \propto \frac{1}{\lambda^n} \quad (4)$$

The exponent n, defined as the calibration index, can be determined experimentally from the relation between $S(t, \lambda)$ and λ. Subsequently, the contribution of the loss $S(t, \lambda_o)$ at the absorption wavelength λ_o of anthracene is estimated from the following relationship provided that the prefactor on the r.h.s. of eq. (4) does not depend on wavelength for a narrow range around λ_o:

$$\frac{S(t, \lambda_o)}{S(t, \lambda)} = \left[\frac{\lambda_o}{\lambda} \right]^n \quad (5)$$

In practice, the normalized loss $s(t, \lambda)$ defined below was used instead of $S(t, \lambda)$:

$$s(t, \lambda) = \frac{S(t, \lambda)}{T(0, \lambda)} \quad (6)$$

Here $T(0, \lambda)$ is the transmittance of a sample measured at the wavelength λ before irradiation. This normalization is to compensate for the small difference in thickness between different samples

since one sample was used for each irradiation time interval. By definition in this way, the normalized loss $s(t, \lambda)$ will be in the range between 0 and 1. The former is obtained before irradiation, whereas the latter corresponds to the situation where the blend is completely opaque and has no transmission. The value of the index n is thus determined from the plot of $\ln s(t, \lambda)$ versus $\ln \lambda$. Subsequently, $S(t, \lambda_o)$ was calculated from eq. (5) with λ, λ_o, and $S(t, \lambda)$ obtained from experiments. In this work, the data of $S(t, \lambda)$ at $\lambda = 450$ nm, which is the wavelength closest to λ_o, were used in eq. (5). The transmission $T(t, \lambda_o)$ at 385 nm of anthracene after correction for the effects of cloudiness is thus calculated from eq. (3), and the crosslink density $\gamma(t)$ was finally obtained from eq. (2).

EXPERIMENTAL RESULTS

Normalized Loss $s(t, \lambda)$ of Transmission Due to Phase Separation

The irradiation time dependence of the normalized loss $s(t, \lambda)$ of a P2CS/PVME (60 : 40) blend measured at 450, 500, and 600 nm after a temperature jump (T-jump) is shown in Figure 5(a). For the same irradiation time, the loss increases with decreasing the detection wavelength λ, reflecting the influence of light scattering on the transmission of the sample. Furthermore, this loss increases with irradiation time due to the coarsening process of the phase-separated structures. Above 20 min of irradiation, the increase of $s(t, \lambda)$ with irradiation time becomes insignificant because the coarsening of the spinodal decomposition process of the blend is frozen by the photodimerization of anthracene. As shown in Figure 6, the morphology observed by a phase-contrast optical microscope under this irradiation condition is the interconnecting structures which are frozen by the crosslinking reaction during the spinodal decomposition of the blend. It is worth noting that without irradiation, the P2CS/PVME (60 : 40) blend reaches the phase equilibrium under the same experimental condition.

On the other hand, the irradiation time dependence of $s(t, \lambda)$ for a P2CS/PVME blend with the critical composition (40 : 60) exhibits a strong dependence on irradiation time as shown in Figure 5(b). $s(t, \lambda)$ rapidly increases with irradiation time within 5 min and reaches the limit $s(t, \lambda) = 1$ corresponding to the complete reflection of
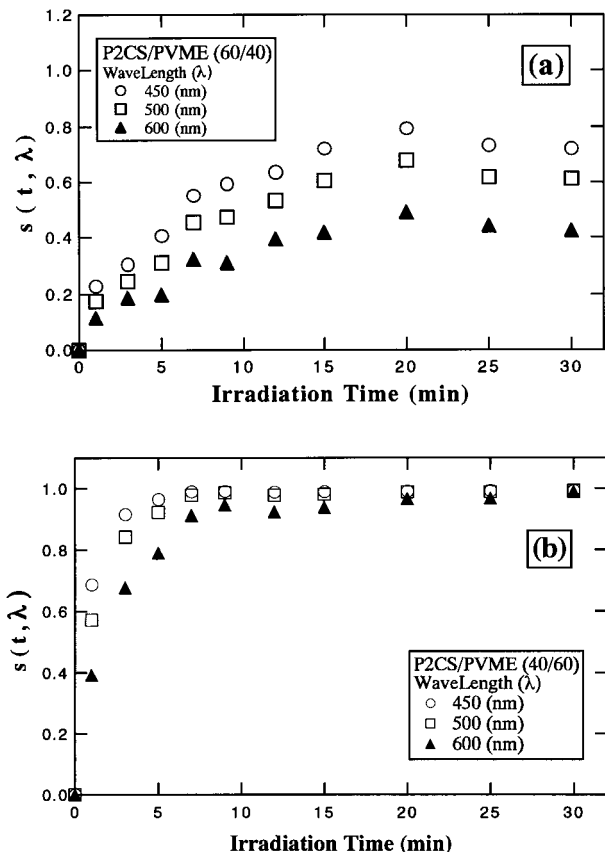

Figure 5 Dependence of the normalized loss on irradiation time obtained at various wavelengths for P2CS/PVME blends: (a) (60 : 40), (b) (40 : 60).

incident light from the sample after 10 min of irradiation. These results indicate that the phase separation process in the irradiated (40 : 60) blend overcomes the photocrosslinking reaction and as a consequence, the sample almost reaches its phase equilibrium after 30 min of irradiation. This conclusion is supported by the fact that the morphology obtained under this experimental condition exhibits random two-phase structures. The reasons responsible for the domination of phase separation under this particular condition is due to the low glass transition temperature (T_g) as well as the low concentration of the crosslinker anthracenes of this composition in comparison to the P2CS/PVME (60 : 40) blend.

Dependence of the Loss $s(t, \lambda)$ on the Incident Wavelength

The relationship between $s(t, \lambda)$ and the incident wavelength λ for P2CS/PVME (60 : 40) and (40 : 60) blends is illustrated in Figure 7. Over 30 min
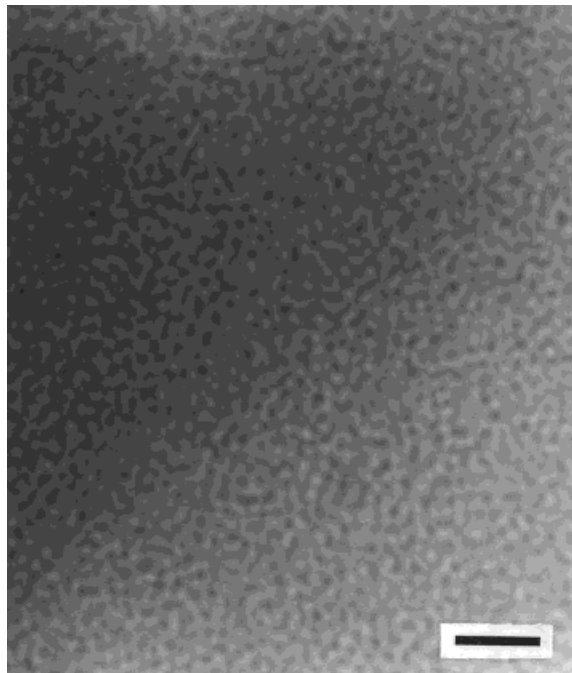
Figure 6 A phase-contrast optical micrograph of a P2CS/PVME (60 : 40) blend photo-crosslinked at 152°C. For clarity, the crosslinked blend was annealed in the dark for 60 min after irradiation for 30 min. The scale corresponds to 5 μm.

of irradiation, $\ln s(t, \lambda)$ is proportional to $\ln \lambda$ within the range of wavelengths monitored in the experiments. This linear relationship confirms the validity of eq. (4) and as a result, the proportional coefficient in the front of the r.h.s. of eq. (4) is approximately independent with the incident wavelengths. The exponents n obtained from the slopes of these two plots are illustrated versus irradiation time in Figure 8. It was found that for the P2CS/PVME (60 : 40) blend, the exponent n is -2.0 and almost unchanged with irradiation time. From the value $n = -2$ obtained from Figure 7(a), the loss due to scattering $S(t, \lambda_o)$ at the absorption wavelength 385 nm of anthracene was calculated by using eq. (5). The result is substituted into eq. (3) to obtain the transmission $T(t, \lambda_o)$ at 385 nm of anthracene. Finally, the crosslinking density $\gamma(t)$ defined in eq. (1) was calculated from eq. (2) using the two transmittances $T(0, \lambda_o)$ and $T(t, \lambda_o)$ given in eq. (3). The results of the crosslinking kinetics obtained for a P2CS/PVME (60 : 40) blend are shown in Figure 9. It was found that within 20 min of irradiation, $\gamma(t)$ increases rapidly with the reaction time and approaches the average value 5 junctions/chain, indicating that half of the anthracenes labeled on

the P2CS chains photodimerized under this experimental condition. This amount remains almost unchanged after 20 min of irradiation. These kinetic data suggest that after the blend undergoes phase separation, irradiation is still efficient enough to induce the photocrosslinking reactions between P2CS chains. However, it is eventually prevented by the cloudiness of the sample at the late stage of irradiation.

On the other hand, the same procedure was unsuccessfully applied to monitor the crosslinking process of the critical composition P2CS/PVME (40 : 60) submitted to the same jump depth (2°C). As shown in Figure 8(b) for the irradiation-time dependence of the calibration index n, the (40 : 60) blend rapidly turns cloudy just after 9 min of irradiation. In contrast to the case shown in Figure 8(a), the calibration index n is not a constant within a narrow range of wavelengths, and quickly increases from -2 to 0 with irradiation time. This result suggests that the phase separation proceeds very rapidly under this experimen-
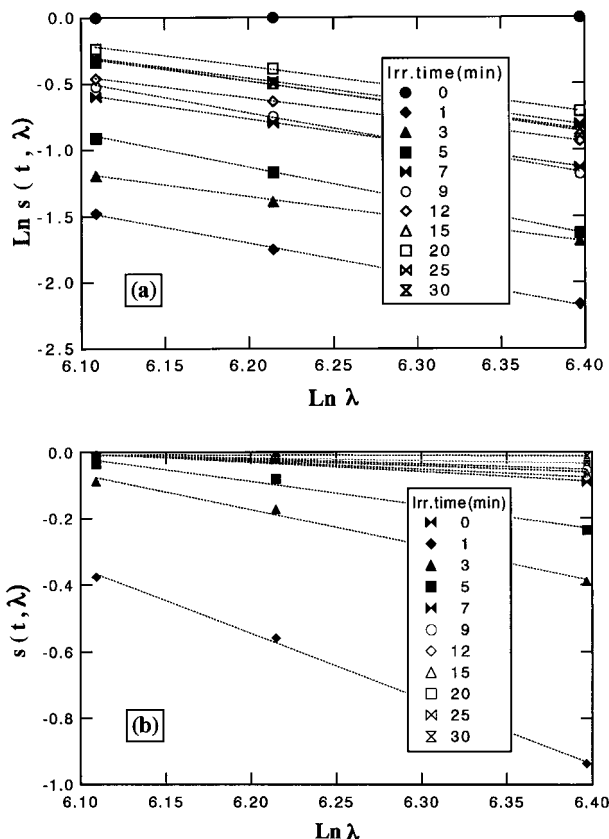

Figure 7 Experimental verification of the wavelength dependence of the normalized loss $s(t, \lambda)$ for P2CS/PVME blends: (a) (60 : 40); (b) (40 : 60). I_n stands for irradiation.
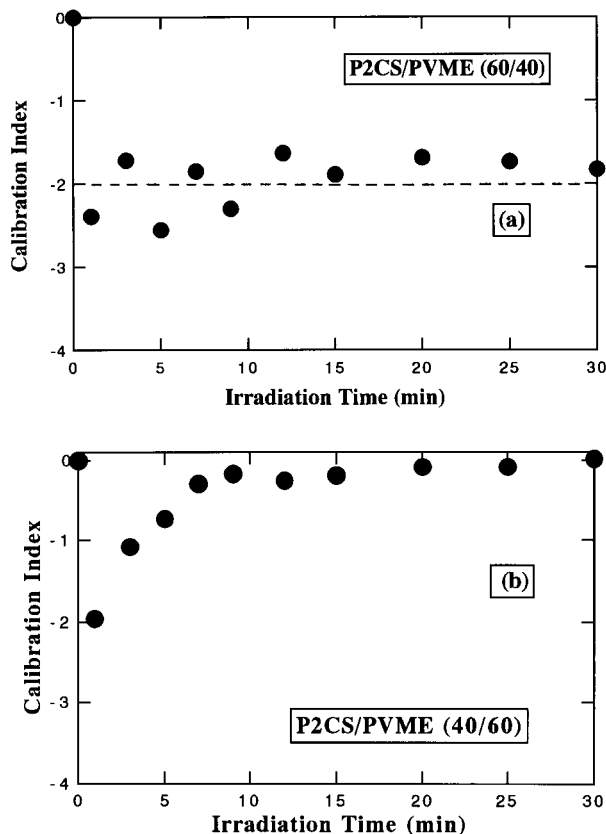
Figure 8 Dependence of the calibration index n on irradiation time in photocrosslinked P2CS/PVME blend: (a) (60 : 40), (b) (40 : 60).

tal condition and almost overcomes the crosslinking reaction. For this particular case, the spectroscopic method described in this article fails to monitor the crosslinking kinetics of the blends.

Photocrosslinking Kinetics in the Spinodal Region

From the transmission data of anthracene obtained for the P2CS/PVME (60 : 40) blend irradiated inside the spinodal region, the crosslinking kinetics data were constructed. Provided that the photodimerization of anthracene proceeds homogeneously in the irradiated blend, the corresponding rate equation for the mean-field kinetics is

$$\frac{dC_A(t)}{dt} = -kC_A^2(t) \qquad (7)$$

where $C_A(t)$ is the concentration of the photocrosslinker anthracene at $t(\min)$ after irradiation and k is the mean-field reaction rate.

With the initial condition $C_A(t = 0) = C_A(0)$,

the solution of the rate equation can be obtained by solving eq. (7) in the conventional way:

$$C_A(t) = \frac{1}{[kt + C_A^{-1}(0)]} \qquad (8)$$

Experimentally, the concentration $C_A(t)$ can be directly obtained from the absorbance (or the transmission) of anthracenes after correction for the cloudiness by using eqs. (3) and (2). To relate eq. (8) to the spectroscopic data, the reaction yield $p(t)$ defined below is used instead of $C_A(t)$:

$$p(t) = \frac{[C_A(0) - C_A(t)]}{C_A(0)} = \frac{[OD_o - OD(t)]}{OD_o} \qquad (9)$$

where OD_o and $OD(t)$ are the absorbances at 385 nm of anthracenes obtained before and after $t(\min)$ of irradiation.

The final expression for the crosslinking kinetics on the basis of the mean-field approximation is obtained by incorporating eq. (8) into (9):

$$\frac{1}{[1 - p(t)]} = kC_A(0)t + 1 \qquad (10)$$

Thus, the validity of eq. (10) can be examined by plotting $1/[1 - p(t)]$ versus the irradiation time t. The result is shown in Figure 10 for a P2CS/PVME (60 : 40) blend photocrosslinked at 152°C over 30 min inside the spinodal region. The linear relationship between $1/[1 - p(t)]$ and the irradiation time t is in good agreement with the prediction given in eq. (10). Therefore, it can be con-
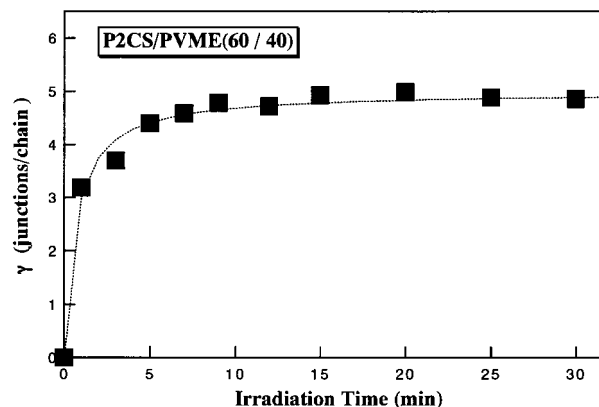

Figure 9 Irradiation time dependence of the crosslinking density γ defined in eq. (1) for a P2CS/PVME (60 : 40) blend photocrosslinked at 152°C.
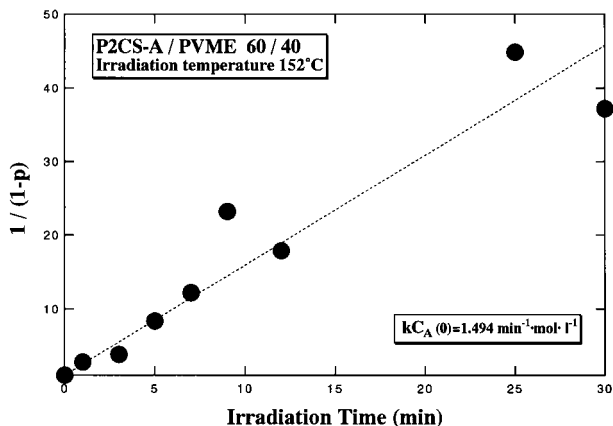
Figure 10 Photocrosslinking kinetics of a P2CS/PVME (60 : 40) blend obtained inside the spinodal region at 152°C.

cluded that the photocrosslinking reactions of the P2CS/PVME (60 : 40) blend performed inside the spinodal region under this particular condition proceed homogenously during irradiation. From the slope of Figure 10, it was found that $kC_A(0) = 1.49 \min^{-1} \text{mol L}^{-1}$. Since $C_A(0)$ is approximately fixed at $1.0 \times 10^{-5} \text{ mol L}^{-1}$ for all the samples used in this work, the apparent rate constant of the crosslinking reaction is $1.49 \times 10^5 \min^{-1}$. It is worth noting that this rate constant explicitly depends on the intensity of the exciting light.

Comparison with the Photocrosslinking Reaction Performed in the One-Phase Region

For comparison, a P2CS/PVME (60 : 40) blend was photocrosslinked at 55°C in the miscible region. Since the experimental temperature ($T_{\exp}$) is located at 85°C below the cloud point, the newly formed coexistence curve of the reacted blend does not reach $T_{\exp}$ upon irradiation and, as a consequence, phase separation did not occur during the crosslinking process. Therefore, the kinetics can be directly obtained from eq. (2) by measuring the irradiation time dependence of the absorbance of anthracene at 385 nm. $1/[1 - p(t)]$ was calculated from eq. (9) and is plotted versus irradiation time t in Figure 11. Obviously, within the first 100 min of irradiation, the kinetics is well expressed by the mean-field kinetics and subsequently deviates from this approximation at longer time. Namely, the reaction proceeds homogenously in the blend at the beginning of the crosslinking process. However, because the average concentration of anthracenes decreases and

the mean distances between the photocrosslinkers become larger at the late stage, the reaction is slowed down and deviates from the mean-field prediction. The kinetics at this stage of crosslinking can be well described by the stretched exponential, i.e. Kohlrausch–Williams–Watts (KWW) function.[15,16] The discussion on the kinetics in the miscible region is beyond the scope of this paper and the detailed investigation is reported elsewhere.[17]

SUMMARY AND CONCLUSION

A spectroscopic method using UV-visible absorption data was developed to monitor the photocrosslinking reaction kinetics performed inside the spinodal region of anthracene-labeled P2CS/PVME polymer blends. It was found that

1. The applicability of the method depends on the competitions between the growth rates of the phase separation and the crosslinking reaction. The method is useful for the case where the reaction is dominating, whereas it is not successfully applied when the phase separation proceeds so rapidly.
2. For the blend with relatively low crosslinking densities, it was found that the reaction in the spinodal region approximately follows the mean-field kinetics and proceeds almost homogeneously.
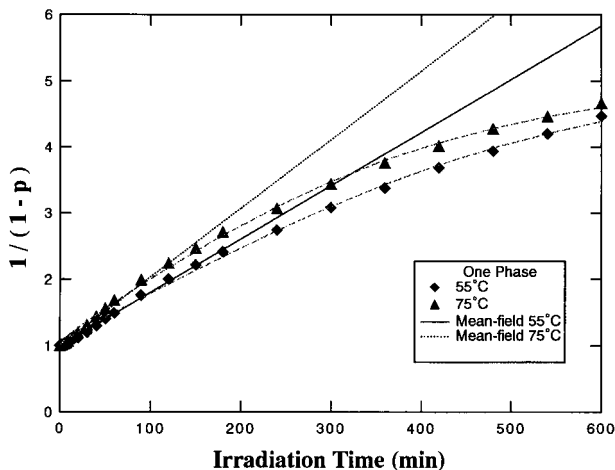
The experimental results obtained in this work

Figure 11 Photocrosslinking kinetics in the miscible region of a P2CS/PVME (60 : 40) blend obtained at 55°C (♦) and 75°C (▲).

indicate that even after the sample undergoes phase separation and becomes cloudy, irradiation is still efficient enough to induce crosslinking reaction to an extent. These results might be useful for the interpretation of the correlations between the crosslinking conditions and the resulting morphology in polymers cured with UV light.

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