Effects of Critical Concentration Fluctuations on the Photocyclization of a Bichromophoric Molecule in the One-Phase Region of Polystyrene/Poly(vinyl methyl ether) Blends

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ABSTRACT: Photocyclization kinetics of a bichromophoric molecule, 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA), was investigated in the one-phase region of polystyrene/poly(vinyl methyl ether) (PS/PVME) blends. Upon irradiation with UV light at 365 nm, the time dependence of absorbance of HNMA does not follow the first-order kinetics. An attempt to fit the decay of absorbance to the Kohlrausch–Williams–Watts relaxation mechanism was unsuccessful. However, the reaction kinetics can be well represented by the sum of two exponential functions of time. The fast decay rate (k_1) strongly depends on both temperature and composition, whereas the slow process (k_2) is almost independent of irradiation time within the experimental time scale. The temperature dependence of k_1 obeys the Williams–Landel–Ferry (WLF) relationship, indicating that the photocyclization process of HNMA in these blends is controlled by polymer segmental free volumes. On the other hand, for $T-T_g$ = constant, where T_g is the glass transition temperature of PS/PVME blends, it was found that the reaction rates are strongly affected by the concentration fluctuation in the blends and drastically change upon approaching the phase boundary. At temperatures and compositions where the reaction rate reflects the critical fluctuations in the blends, the correlation length ξ obtained by small-angle neutron scattering (SANS) is close to the diameter of HNMA, suggesting that the critical fluctuations in PS/PVME blends can be monitored by the photocyclization process of HNMA.

I. Introduction

The polymer blend has been a growing research field in recent years due to its practical importance as well as its unique thermodynamic interactions that can provide a typical system to study slow critical phenomena.[1] For conditionally compatible blends, the physical properties of materials in the one-phase region cannot be described, in most cases, by the linear additivity of the property of individual components. Typical examples for the breakdown of linear additivity can be found in the composition dependence of the glass transition temperatures of binary polymer blends. The deviation from the linear additivity has been ascribed to the thermodynamic interactions between different polymer segments. The information on thermodynamic interactions can be obtained from small-angle neutron scattering (SANS) by fitting experimental data to appropriate scattering functions.[2]

Recently, molecular probe techniques such as fluorescence excimer[3] and fluorescence quenching[4a] have been demonstrated to be a useful tool to study phase-separation kinetics of polymer blends at the scale beyond the radius of gyration R_g of polymer chains. Segmental mobilities in the one-phase region of binary polymer blends were also investigated by fluorescence depolarization.[4b] However, few experiments are devoted to the understanding of the coupling between thermodynamic interactions and mobilities for the transport processes of probe molecules in miscible polymer mixtures. In general, the transport coefficients in a mixture of two different chemical substances depend not only on the frictional properties but are also affected by the thermodynamic interactions between different components of the system. The effect of thermodynamic interactions on the transport properties has been examined for liquid mixtures of small molecules in the past decades.[5] For polymer blends, these couplings have been observed via mutual diffusion by light scattering techniques.[6] However, for the scale less than R_g, this information has been lacking. Therefore, it is of great interest in understanding the correlation between the diffusional process of a small molecule and the onset of the concentration fluctuations in the miscible region of binary polymer blends. To achieve this purpose, it is necessary to separate experimentally the effects of frictional properties from those of thermodynamic interactions on the transport process of probe molecules in the blends. The main contribution of thermodynamic interactions to the transport process of a probe molecule can be approximately estimated by carrying out experiments at temperatures which are at the same distance from the glass transition temperature T_g of the blends while varying the blend composition. Alternatively, the net effects of frictional properties of the blends on the probe molecule can be investigated, on the other hand, by undertaking experiments in the region far away from the phase boundary in order to reduce the interference from thermodynamic interactions.

We have shown that the photocyclization process of bis-(9-anthrylmethyl) ether (BAME) in bulk polymer matrices is a diffusion-controlled reaction and its conformational transitions are governed by polymer segmental free volumes.[7] In this work, in order to improve the solubility of the probe in the polymer matrix, 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) was synthesized[8] and used as a probe to monitor the local mobilities in polystyrene/poly(vinyl methyl ether) (PS/PVME) blends. At first, the photocyclization kinetics of HNMA was investigated in the one-phase (miscible) region of (PS/PVME) blends with various compositions. The temperature dependence of the reaction rates is analyzed in terms of free volume theory. Subsequently, the contribution of thermodynamic interactions to the reaction kinetics is elucidated by examining the dependence of reaction rates on the blend compositions at temperatures which have the same distance from the glass transition temperatures of the blends. Finally, by comparison of these results with the data of correlation lengths obtained

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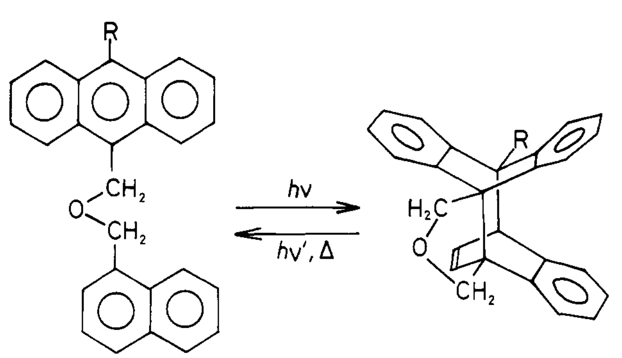

Figure 1. Photocyclization of 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA; R = $-CH_2OH$).

from SANS data, the possibility for the detection of the concentration fluctuations in the one-phase region of polymer blends by using molecular probe techniques will be discussed.

II. Experimental Section

(1) Materials. Polystyrene (PS; $M_w = 1.4 \times 10^5$, $M_w/M_n = 1.3$) used in this experiment was obtained by fractionating a commercial available sample (Wako Chemical Industries, Japan) using benzene and methanol mixtures. Poly(vinyl methyl ether) (PVME; Aldrich, $M_w = 8.8 \times 10^4$, $M_w/M_n = 2.5$) was used after twice precipitating with n-heptane and methanol mixtures. The weight-average molecular weight, M_w, of PVME was obtained from measurements of the intrinsic viscosity, $[\eta]$, with methanol as solvent.[9] The molecular weight distribution of these polymers was obtained by GPC with polystyrenes as standard references. The bichromophoric molecule 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene was prepared according to the procedure described previously[8] and was purified by gel filtration with successive recrystallizations in toluene. Samples with thickness 0.3 mm were obtained by casting benzene solutions of PS/PVME mixtures containing HNMA. All the concentrations of HNMA in PS/PVME blends were kept at 10^{-4} mol/L, which corresponds to an absorbance of ca. 0.1 at 393.5 nm. PS/PVME blends doped with HNMA were carefully dried under vacuum at 90 °C to remove solvent as well as oxygen and were sealed between two glass plates with a spacer which is used to adjust the sample thickness. For experiments carried out at temperatures close to T_g of the blends, PS/PVME samples are annealed at these temperatures at least one night prior to irradiation experiments. Without annealing, it was found that the decay of absorbance of HNMA exhibits oscillative behavior which probably originates from the thermal history of the samples.

(2) Irradiation Experiments and Data Analysis. PS/PVME blends doped with HNMA were irradiated at 365 nm by using a high-pressure mercury lamp (250 W; Model USH-35, Ushio Co., Japan). The change with time in absorbance at 393.5 nm of anthracene moieties of HNMA was monitored after irradiation over different time intervals by using a UV-visible spectrophotometer (Shimadzu Model UV-160). All other experimental procedures were the same as those described in the previous work.[8] In order to analyze the photocyclization kinetics, the temporal decay of absorbance was fit to appropriate model functions by using the nonlinear least-squares method (Fortran program SALS with the modified Marquardt algorithm developed by Fletchert[10]). Details of data analysis as well as justification will be described later.

(3) Characterization of Photocyclization of HNMA. Upon irradiation with UV light at 365 nm, anthracene moieties of HNMA are excited. During its excited lifetime, photocyclization takes place when anthracene encounters naphthalene via conformational transitions of the ether linkage –COC–. This reaction is schematically shown in Figure 1.

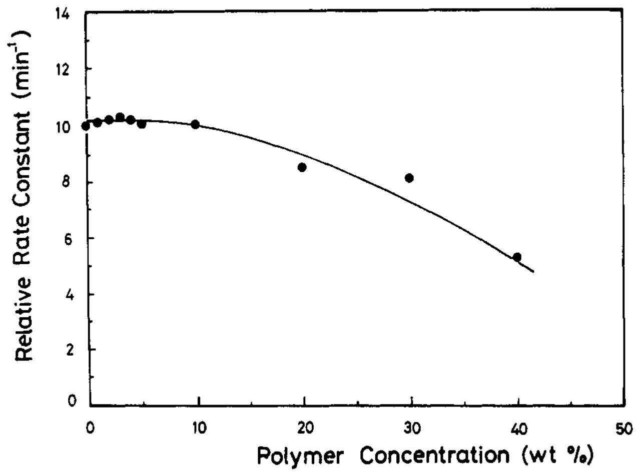

Figure 2. Effect of polystyrene concentration on the rate of photocyclization reaction of HNMA in p-dioxane at 18 °C.

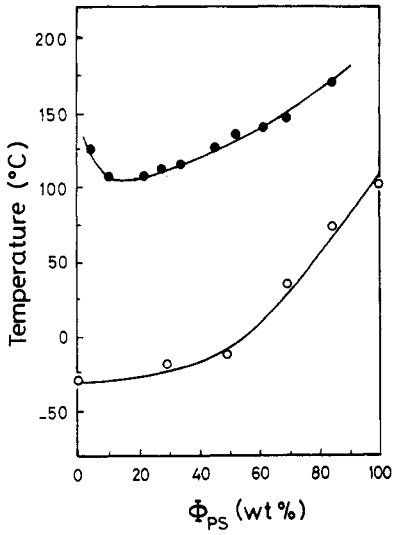

Figure 3. Cloud-point curve and glass transition temperature of PS/PVME blends: (●) 0.2 °C/min; (○) 5 °C/min.

Photophysical properties of bichromophoric molecules including HNMA in liquids have been carefully investigated.[11] To confirm that the photocyclization of HNMA in polymers is a diffusion-controlled reaction, the reaction kinetics of this molecule was followed in concentrated polymer solutions. In Figure 2 is shown the dependence of reaction rates (k) of this reaction on the concentration of polystyrene in p-dioxane. For polymer concentrations less than 10 wt %, k is almost the same as that in pure solvent. However, as the polymer concentration exceeds 10 wt %, k starts dropping quickly, indicating that conformational transitions of HNMA are restricted by the viscosity of polymer solutions. Therefore, photocyclization of HNMA is a diffusion-controlled reaction. This result is consistent with those obtained previously with bis(9-anthrylmethyl) ether (BAME), a homologue of HNMA, in a series of cellosolve homologues.[7]

(4) Characterization of PS/PVME Blends. The cloud-point curve of PS/PVME blends was obtained by measuring the light scattering intensity from samples at a fixed angle as described previously.[12] In Figure 3 is shown the cloud-point curve of PS/PVME blends obtained with a heating rate of 0.2 °C/min. On the other hand, the glass transition temperatures of PS/PVME blends were measured by using differential scanning calorimetry (DSC; Mac Science Model 3100) with the heating rate 5 °C/min. All the blends exhibit a single glass transition temperature. The dependence of T_g on the blend compositions is also shown in Figure 3. In this work, the photocyclization kinetics of HNMA was measured in the one-phase region of PS/PVME blends, i.e. the regime between the phase boundary and the glass transition curve.

III. Results and Discussion

(A) Reaction Kinetics of Photocyclization of HNMA in PS/PVME Blends. Photocyclization of HNMA in PS/PVME blends does not follow the first-

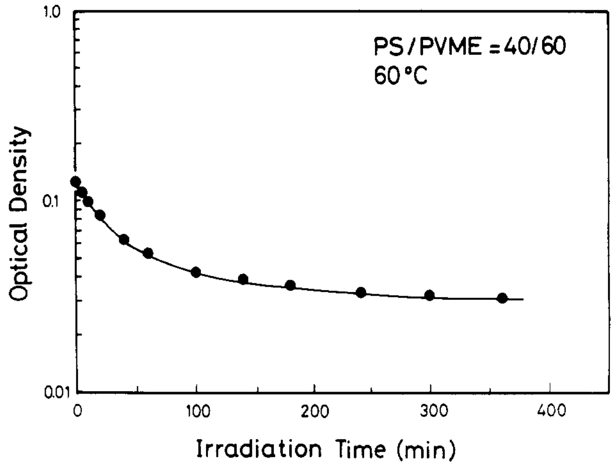

Figure 4. Dependence on irradiation time of the absorbance at 393.5 nm of HNMA in PS/PVME (40/60) blend at 60 °C: (●) experiment; (—) curve fitting based on eq 2 by using a nonlinear least-squares method [$OD_0 = 0.125$; $F_1 = 8.07 \times 10^{-2}$; $k_1 = 3.28 \times 10^{-2}$ min^{-1}; $F_2 = 4.33 \times 10^{-2}$; $k_2 = 1.01 \times 10^{-3}$ min^{-1}].

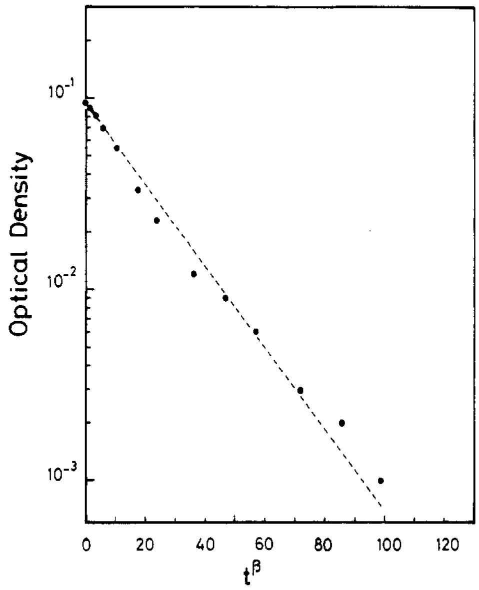

Figure 5. Computer simulation for the data shown in Figure 4 by using the Williams–Watts relaxation mechanism with $\beta = 0.78$ as a floating parameter. Data points are shown after subtraction of the base line.

order kinetics. As an example, the time dependence of the optical density (OD) at 393.5 nm in PS/PVME (40/60) measured at 60 °C is shown in Figure 4. Obviously, the logarithm of the optical density does not linearly vary with irradiation time. In order to analyze these data, the Kohlrauch–Williams–Watts (KWW) kinetics[13] was used for the curve-fitting process

$$OD(t) = OD_0 \exp\{-(kt)^{\beta}\} \qquad (1)$$

where OD_0 is initial optical density of HNMA at 393.5 nm in the as-cast film before irradiation, k the average reaction rate of the photocyclization process, and β the exponent describing the distribution of reaction rates in polymer blends.

However, an attempt to fit the experimental results with eq 1 was unsuccessful for any chosen exponent β. As an example, the temporal decay of the absorbance measured at 393.5 nm was plotted against t^{β} in Figure 5 with $\beta = 0.78$. This value is obtained by a nonlinear least-squares method. The curve-fitting process shows a systematic deviation from the experimental results. Therefore, we conclude that the photocyclization kinetics of HNMA in PS/PVME blends does not obey the KWW relaxation mechanism. On the other hand, the OD decay curves can be well represented by the sum of two exponentials

$$OD(t) = OD_0\{F_1 \exp(-k_1 t) + F_2 \exp(-k_2 t)\} \qquad (2)$$

where k_1 and k_2 are the rate constants of the fast and slow processes and F_1 and F_2 are the corresponding fractions.

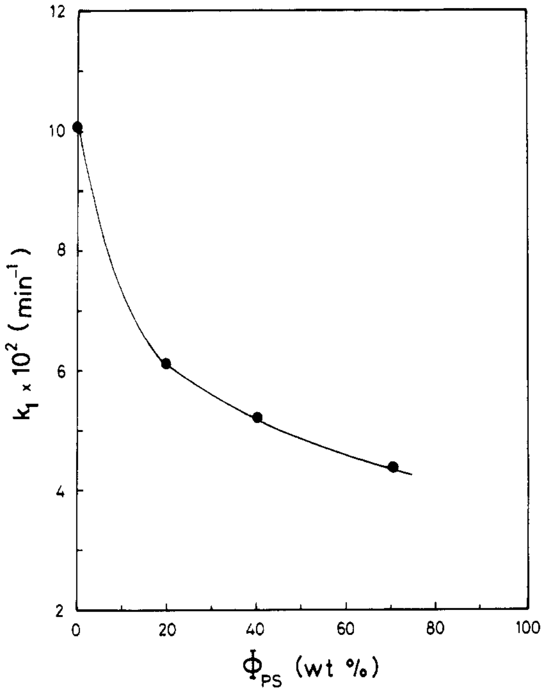

Figure 6. Dependence of reaction rate k_1 on the composition of polystyrene at 70 °C.

The physical meaning of eq 2 can be explained as follows. HNMA can exist in PS/PVME under various conformations. For those conformations under which anthracene and naphthalene rings are close to each other, photocyclization could take place on a short time scale since both molecules are not required to diffuse over a long distance in order to achieve the intramolecular photodimerization. On the other hand, for HNMA with anthracene and naphthalene in conformations unfavorable to the reaction, it could take a longer time for these two molecules to encounter each other prior to the photocyclization process. Namely, the distribution of the reaction rates is determined by the conformational distribution of HNMA in these blends.

As an example, a result of the analysis using eq 2 for the time dependence of absorbance measured at 60 °C in a PS/PVME (40/60) blend is shown by the solid line in Figure 4. The nonlinear least square fitting gives $k_1 = 3.28 \times 10^{-2}$ min^{-1} and $k_2 = 1.01 \times 10^{-3}$ min^{-1}. Therefore, k_2 is almost negligibly small in comparison with k_1. Actually, the decay process which is characterized by k_2 is almost independent of irradiation time. Further examination of the analysis results obtained by the curve-fitting process shows that the rate constant k_2 and the fraction F_2 are almot unchanged with temperature and blend composition within the time scale of this experiment (ca. 7 h). The insensitivity of the fraction F_2 and the reaction rate k_2 to the blend compositions as well as temperature is mainly due to the low absorbance of HNMA in these blends. In order to avoid the existence of a light intensity gradient (internal filter effect) caused by the high concentration of HNMA in the samples, the initial absorbance was adjusted to ca. 0.1. As a result, the magnitude of absorbance becomes very small for irradiation over a long time and might result in the inaccuracy in data anlaysis. Consequently, only the rate constant k_1 is used for further investigation of the photocyclization process of HNMA in PS/PVME blends.

(B) Temperature and Composition Dependence of Photocyclization Kinetics in PS/PVME Blends. At constant temperature, k_1 decreases with increasing composition of PS as shown in Figure 6. This fact can be ascribed to the enhancement of T_g of PS/PVME blends upon increasing PS compositions. On the other hand, the temperature dependence of k_1 does not show the Arrhenius behavior for all the blend compositions used in this work (PS/PVME: 20/80, 40/60, and 70/30). As depicted in Figure 7 for PS/PVME (40/60), as temperature decreases, k_1 decreases and apparently tends to reach a limiting value upon approaching T_g of the blend. A similar behavior has been observed for bis(9-anthrylmethyl) ether, a homologue of HNMA, in bulk polystyrene and poly(vinyl acetate) matrices.[7] Therefore, the temperature dependence of the reaction rate k_1 is analyzed in terms of free volume theory based on the Williams–Landel–Ferry (WLF) relationship. Since the photocyclization of HNMA is a diffusion-controlled reaction, the reaction rate k_1 can be related to the relaxation time of conformational transitions τ via

$$k_1(T) \sim 1/\tau(T) \qquad (3)$$

The shift factor a_T, i.e., a normalized relaxation time at an arbitrary temperature T, can be defined in terms of the reaction rate k_1 as

$$a_T = k_1(T_0)/k_1(T) \qquad (4)$$

Note that the ratio $T\rho/T_0\rho_0$ is approximately equal to unity since the temperature range is narrow in these experiments. Here T_0 is a reference temperature and ρ and ρ_0 are the densities of the blend at temperatures T and T_0.

The temperature dependence of k_1 in the context of the WLF relationship can be written as

$$\log a_T(T) = -\{C_1(T - T_0)/[C_2 + (T - T_0)]\} \qquad (5)$$

where C_1 and C_2 are the WLF constants which are related to the fractional free volume f_0 and the thermal expansion coefficient α_f at the reference temperature T_0 by[14]

$$C_1 = B/2.303f_0$$

and

$$C_2 = f_0/\alpha_f \qquad (6)$$

where B is a constant approximately equal to 1.

As an example, Figure 8 shows the plot of $1/\log a_T$ versus $1/(T - T_0)$ for the photocyclization process of HNMA in PS/PVME (70/30) with T_0 = 60 °C chosen as a reference temperature.

The linearity of this plot implies that the temperature dependence of the photocyclization process of HNMA obeys the WLF relationship. In other words, the conformational transitions of HNMA are controlled by segmental free volumes of polymer chains in the blends. Similar experimental results have been reported previously for the transport processes of small molecules in bulk polymer matrices including miscible binary blends.[7,15,16] The fractional free volume, f_0, and the thermal expansion coefficient, α_f, estimated from the reaction kinetics of HNMA based on eqs 5 and 6 are shown in Figure 9 for the three compositions 20/80, 40/60, and 70/30 (PS/PVME).

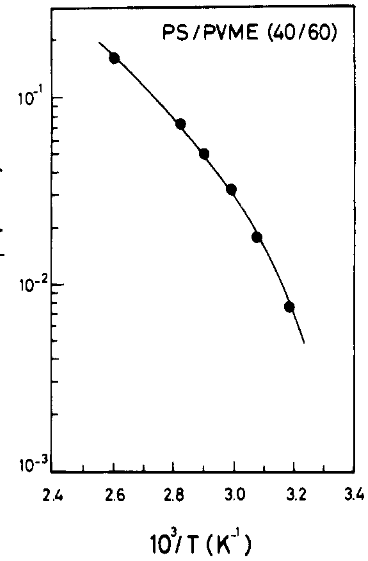

Figure 7. Arrhenius plot of k_1 for a PS/PVME (40/60) blend.

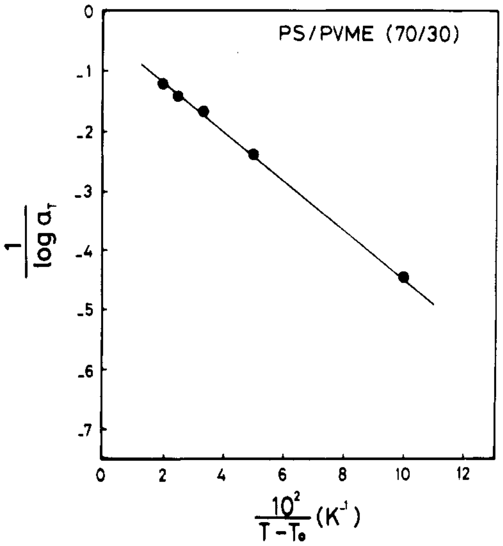

Figure 8. WLF plot for k_1 in a PS/PVME (70/30) blend with T_0 = 60 °C.

It was found that the fractional free volumes as well as the thermal expansion coefficients obtained from eqs 5 and 6 does not depend strongly on the blend composition and their magnitudes are larger than those obtained from rheological experiments. These results seemingly contradict the prediction of the WLF relaxation mechanism. In order to elucidate these problems, experiments were carried out for different compositions at temperatures which have the same distance from T_g's of the blends. The purpose of this procedure is to compensate for the enhancement of the glass transition temperature upon increasing PS composition in an attempt to separate the thermodynamic interactions from the effects of frictional properties on the photocyclization kinetics. To be more specific, the composition dependence of the photocyclization rate constants was measured at different temperatures which satisfy the condition $T - T_g$ = constant where T_g is the glass transition temperature of the blends with different compositions. Experimental results obtained under these specific conditions are shown in Figure 10. For reference, the reaction rates at the two extreme compositions (0/100) and (100/0) (PS/PVME), i.e., pure PS and PVME, are also shown in the same figure. For all blend compositions, though $T - T_g$ values are kept constant, the strong dependence of the reaction rate k_1 on composition was observed. For low compositions of PS, the

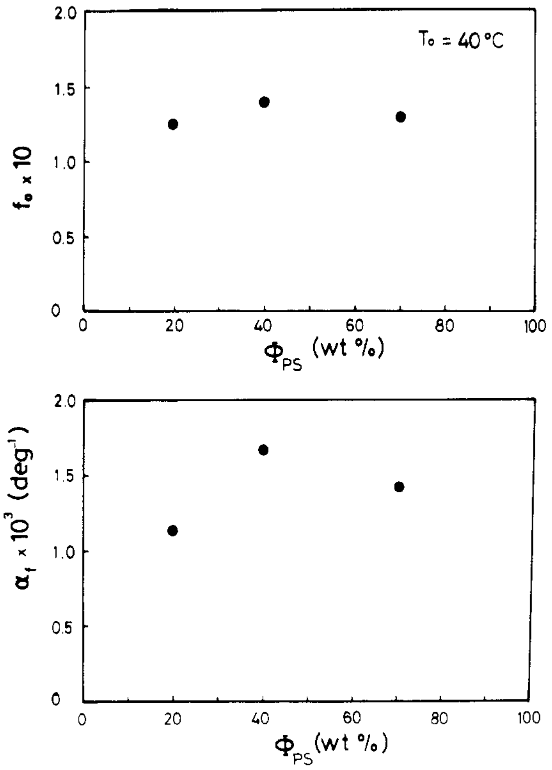

Figure 9. Composition dependence of the fractional free volume and thermal expansion coefficient obtained from a WLF plot with T_0 = 40 °C.

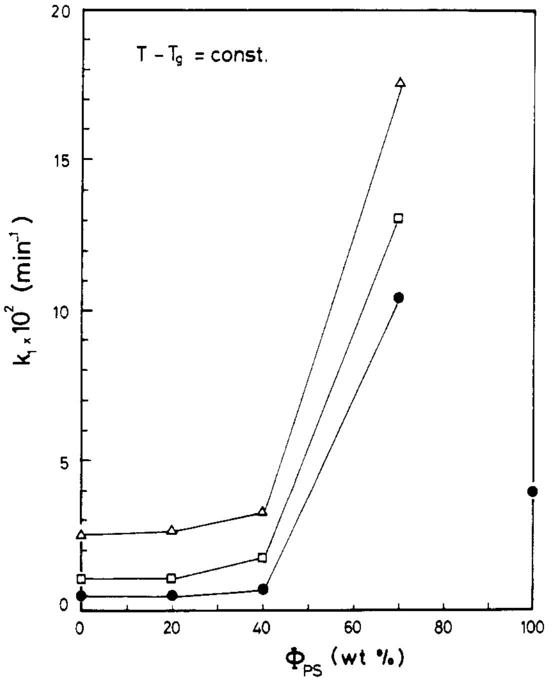

Figure 10. Composition dependence of k_1 obtained under the conditions $T - T_g$ = (△) 75 °C; (□) 65 °C, and (●) 55 °C.

reaction rate k_1 is almost unchanged. However, as the PS composition exceeds 40 wt %, k_1 markedly increases with increasing PS composition. This behavior was observed for several distances $T - T_g$ = 55, 65, and 75 °C. The composition dependence of k_1 becomes more pronounced upon approaching the phase boundary. In opposition to this behavior, as the PS composition reaches 100%, k_1 decreases and becomes close to the value obtained in pure PVME as shown in Figure 10 for $T - T_g$ = 55 °C. These experimental results clearly indicate that the concentration fluctuations in the blend that become pronounced in the vicinity of the phase boundary do affect the photocyclization process of HNMA. To confirm this conclusion, the behavior of k_1 in these experiments is compared to the temperature and composition dependence of the correlation lengths ξ, i.e., the average wavelength of the concentration fluctuations, of PS/PVME blends which were recently obtained by small-angle neutron scattering (SANS).[2,17] A good qualitative agreement was found between the temperature and composition dependence of k_1 and those of the correlation lengths ξ. Namely, at $T - T_g$ = 55, 65, and 75 °C, for the compositions and temperatures where SANS critical scattering intensity is almost unobservable, the reaction rate k_1 does not clearly depend on the blend composition. This is the case of 20/80 and 40/60 (PS/PVME) blends as shown in Figure 10. On the other hand, for the composition 70/30 (PS/PVME) where the critical scattering begins to be observable by SANS experiments in the range 100–120 °C[17] (equivalent to $T - T_g$ = 65–85 °C in our experiments), k_1 markedly increases with increasing PS composition. The correlation lengths ξ for the onset of concentration fluctuations estimated from SANS data in these cases are in the range 20 Å which is close to the size of the probe HNMA used in this work. At this moment, it is difficult to compare quantitatively the experimental results obtained in this work with the SANS data because of the difference in molecular weights as well as in the thermodynamic interactions between hydrogenated PS/PVME and deuterated PS/PVME blends.[18] However, the qualitative consistency between the temperature and composition dependence of the correlation lengths obtained from SANS data and of the rate constant k_1 suggests, at least, that the photocyclization of HNMA in PS/PVME blends reflects the concentration fluctuations with the wavelengths comparable to the probe size. As a consequence, it may be necessary to take into account the effects of concentration fluctuations with the wavelengths comparable to the size of HNMA in order to interpret the composition dependence of the fractional free volume, f_0, and the thermal expansion coefficient, α_f, shown in Figure 9. The fact that the reaction rate k_1 steeply increases as the concentration fluctuations grow to the wavelengths comparable to the probe size can be explained as follows. Upon approaching the phase boundary, both the wavelengths and the amplitudes of the concentration fluctuations become larger. For those wavelengths which are much smaller than the size of HNMA, the reaction rates measured at $T - T_g$ = constant do not depend on the blend composition. In other words, the blend is still homogeneous as "seen" from the probe HNMA. However, as these wavelengths become larger than the probe size, there exist the PVME-rich and the PS-rich regions in the blend during the excited lifetime of anthracene. Under this circumstance, photocyclization of HNMA in the PVME-rich regions will contribute to the fast decay process of absorbance (k_1), whereas the reaction taking place in the PS-rich regions is much slower and contributes to the slower part of the decay. As the wavelengths of concentration fluctuations become larger, the photocyclization process of HNMA in the PVME-rich regions becomes faster, whereas it becomes slower in the PS-rich regions. This explains why the reaction rate k_1 increases upon approaching the phase boundary. On the other hand, since there are no thermodynamic interactions for pure PVME and pure PS, the k_1's for these two cases are not much different from each other as shown in Figure 10. Probably there are two reasons which are responsible for the difference in the magnitude of k_1 obtained in pure PVME and pure PS. One is that the compositional dependence of HNMA mobilities is not completely compensated under the experimental condition $T - T_g$ = constant. The other reason involves the compositional dependence of the fluorescence quenching process of anthracene moieties by PVME.[19] In this work, under the condition $T - T_g$ = constant, the change of k_1 upon approaching the phase boundary is much larger than the magnitude difference of k_1 obtained in these two homopolymers. We think that it is reasonable to conclude that the concentration fluctuations in the one-phase region of PS/PVME blends do affect the photocyclization process of HNMA. It should be noted that these concentration fluctuations give rise to a change in the frictional coefficients of HNMA in its environment and consequently affect the reaction rate via modification of the frictional coefficients. Therefore, the steep increase in the reaction rate k_1 shown in Figure 10 is not a critical slowing down phenomenon.[20]

In conclusion, the photocyclization kinetics of HNMA in PS/PVME blends is affected by the concentration fluctuation with the wavelengths comparable to the probe size. These effects can be examined under the condition $T - T_g$ = constant. This is the case we try to show in this work. On the other hand, in the region far from the phase boundary, the reaction kinetics is probably independent of these thermodynamic interactions. Recently, it is found that the reaction rate of the photocyclization process of HNMA in the one-phase region of poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA) blends is almost unchanged with the blend compositions under the condition $T - T_g$ = constant.[21] Further quantitative investigation of the correlation between the reaction rate and the χ parameter of these blends under these experimental conditions is currently in progress.

IV. Summary

Photocyclization of 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene in the miscible region of polystyrene/poly(vinyl methyl ether) blends was investigated for the three compositions 20/80, 40/60, and 70/30 (PS/PVME). The following results were obtained:

(1) The reaction kinetics can be well represented by the sum of two exponential functions of time. The fast decay process strongly depends on both temperature and composition whereas the slow process is almost unchanged in the time scale of experiments (ca. 7 h).

(2) The temperature dependence of the reaction rates obeys the Williams–Landel–Ferry (WLF) relaxation mechanism, indicating that conformational transitions of HNMA are controlled by the segmental free-volumes of polymer chains in the blends.

(3) For $T - T_g$ = constant, upon approaching the phase boundary, it was found that photocyclization kinetics reflects the concentration fluctuations with the correlation length comparable to the size of HNMA. These results imply that the thermodynamic interactions of the blend should be taken into account for the interpretation of the reaction kinetics of HNMA.

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