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Further evidence for the effects of critical concentration fluctuations on the diffusion-controlled reaction kinetics in binary polymer mixtures

Q. Tran-Cong*, Y. Ishida, A. Tanaka, and T. Soen

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

SUMMARY

Kinetics of the intramolecular photodimerization reaction of a molecular probe, 9-(hydroxymethyl)-10-[(Naphthylmethoxy)methyl] anthracene (HNMA) was studied in the miscible region of binary polymer mixtures. Poly(ethylene oxide)/poly(methyl methacrylate)(PEO/PMMA), polystyrene/poly(vinyl methyl ether) (PSH/PVME) and deuterated polystyrene/poly(vinyl methyl ether) (PSD/PVME) mixtures were used as binary polymer blends. It was found that the reaction kinetics is strongly affected by the concentration fluctuations in the vicinity of the coexistence curve. These behavior are consistent with the magnitude of the binary interaction parameters χ estimated from the small-angle neutron-scattering and the melting point depression data. These experimental results confirm the fact that the reaction kinetics of HNMA reflects the concentration fluctuations with the wavelength comparable to the dimension of the probe.

INTRODUCTION

The transport process in binary mixtures depends, in general, on the frictional properties as well as the thermodynamic interactions of the system[1)]. The frictional properties are determined by viscosity whereas the thermodynamic interactions are described by the free energy of the mixing process. For homopolymers, the diffusional process is dictated by the temperature difference between the glass transition and the experiment temperature. In polymer binary mixtures, the χ parameter is a measure for the thermodynamic interactions between monomer pairs[2)]. In the previous report[3)], we have shown that the intramolecular photodimerization of the molecular probe 9-(hydroxymethyl)-10-[(Naphthylmethoxy)methyl] anthracene (HNMA, **Figure 1**) is strongly affected by the critical concentration fluctuations

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*Corresponding author

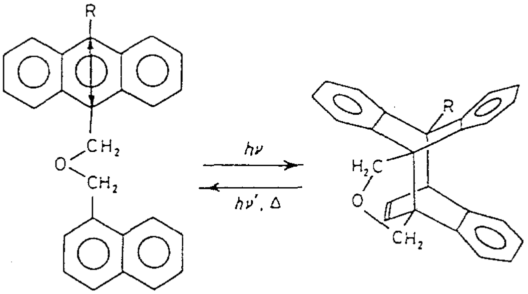

Figure 1. Intramolecular photodimerization of HNMA. R = $-CH_2OH$

upon approaching the coexistence curve of polystyrene/ poly(vinyl methyl ether) (PS/PVME) blends. This photodimerization is a diffusion-controlled reaction and its reaction rate is inversely proportional to the relaxation time of the intramolecular conformational transition. The net effects of the critical concentration fluctuations were examined by following the reaction kinetics in the one-phase region of PSH/PVME blends under the condition (T-Tg) = constant. Tg is the glass transition temperature of the miscible blends. By comparing these results with small-angle neutron-scattering (SANS) data, we have found that the intramolecular photodimerization of HNMA reflects the concentration fluctuations with the wavelength comparable to the dimension of the probe.

In this communication, further experimental evidence is shown for the correlation between the reaction kinetics and the concentration fluctuations. The reaction kinetics of HNMA in another two blends is studied. One is poly(ethylene oxide)/poly(methyl methacrylate)(PEO/PMMA) which is known to be miscible at temperatures higher than 200°C4). The other is deuterated polystyrene/poly(vinyl methyl ether)(PSD/PVME) blend which was chosen to compare with the previous results3) since the isotopic effects are well known to strongly modify the thermodynamic interactions between two polymer components5). The experimental results are discussed in conjunction with the binary interaction parameter χ which is estimated from the SANS data for PSD/PVME and from the melting point depression data for PEO/ PMMA blends.

EXPERIMENTAL

Sample

9-(hydroxymethyl)-10-[(Naphthylmethoxy)methyl]anthracene (HNMA) was synthesized and purified according to the procedure reported previously6). The concentration of HNMA in these blends is kept at less than 10^{-4}M which corresponds to an absorbance of ca. 0.1 at 393.5nm. Polyethylene oxide (PEO1, M_w= 9.8 x 10^4, Mw/Mn = 1.3, Aldrich; PEO2, M_w = 8.5 x 10^4, Mw/Mn = 1.06, Tosoh), poly(methyl methacrylate) (PMMA, Mw=1.4x10^5, Mw/Mn = 1.7, Wako), and poly(vinyl methyl ether) (PVME, M_w = 8.8 x 10^4, Mw/Mn =2.5, Aldrich) were purified by precipitating with appropriate solvent mixtures. Polystyrene (PSH) and deuterated polystyrene (PSD) were prepared by radical polymerization of the corresponding monomer in benzene at 60°C with AIBN as initiator. The molecular weights of these two polymers were adjusted to be 1.4 x 10^5. The procedure to prepare the blends as well as of irradiation was already reported$^{3)}$.

Instrument and Data Analysis

The change with irradiation time of the absorbance of the anthracene moieties was followed by using a UV photometer (Shimadzu UV-160). The decay of absorbance was analyzed by using a nonlinear least square program SALS as described previously$^{3)}$. For all temperatures and compositions, the decay of absorbance of HNMA in these miscible blends cannot be expressed by a single exponential function of irradiation time. However it can be well represented by the sum of two exponentials:

$$OD(t) = OD_0 [F_1 \exp(-k_1 t) + F_2 \exp(-k_2 t)] \quad (1)$$

where OD_0 is the initial absorbance of HNMA at 393.5nm. k_1 and k_2 are the reaction rates of the fast and slow process. F_1 and F_2 are the corresponding fractions.

Since the rate constants k_2 and the corresponding fraction F_2 of the slow decay process are almost unchanged with temperature and the blend composition, only the reaction rates k_1 of the fast process were used for further analysis. For instance, k_1 = 4.4 x 10^{-2} min^{-1}, F_1 = 0.73, k_2 = 6.1 x 10^{-4} min^{-1}, F_2 = 0.27 for HNMA in PSH/PVME (70/30) at 70°C and k_1 = 8.4 x 10^{-2} min^{-1}, F_1 = 0.56, k_2 = 7.2 x 10^{-4} min^{-1}, F_2 = 0.44 for PEO/PMMA(20/80) at 110°C. The possible reason for the behavior of these characteristic constants of the photodimerization kinetics of HNMA in these blends was discussed in the previous report$^{3)}$.

The glass transition temperatures and the melting points of these blends were measured by using a thermal analyzer system (Mac Science, Model 3100). The heating rate is 5°C/min. The cloud points were obtained by a light

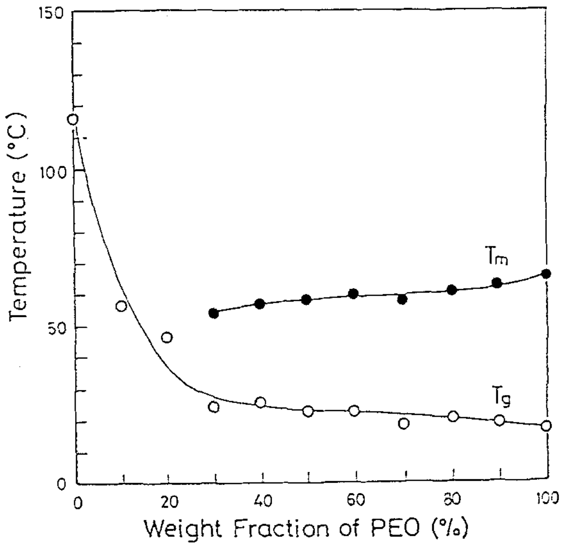

Figure 2. Melting points (●) and glass transition temperatures (○) of PEO/PMMA blends

scattering photometer at a fixed angle$^{7)}$ with a heating rate of 0.2°C/min.

RESULTS AND DISCUSSION

The composition dependence of the glass transition temperatures and of the melting points of PEO/PVME blends is shown in **Figure 2**. For the blends with the PEO composition larger than 30wt%, PEO partially crystallizes. However below 20wt%, PEO forms a miscible blend with PMMA. Furthermore, no evidence of the phase separation in PEO/PMMA blends were found by light scattering up to 200°C. These experimental results are consistent with those reported previously$^{8)}$. On the other hand, the cloud points and the glass transition temperatures of PSH/PVME and PSD/PVME blends with the same PS molecular weight are shown in **Figure 3**. The isotopic effects on the miscibility of these blends can be confirmed by the fact that PSD is much more miscible with PVME than PSH. The glass transition temperatures of these two blends are almost the same over the whole range of composition. This feature enables us to elucidate the effects of thermodynamic interactions on the reaction kinetics of HNMA in these particular blends. In order to compensate the variation of the glass transition temperature with the blend composition, the reaction kinetics was followed at temperatures satisfying the condition (T-Tg) =

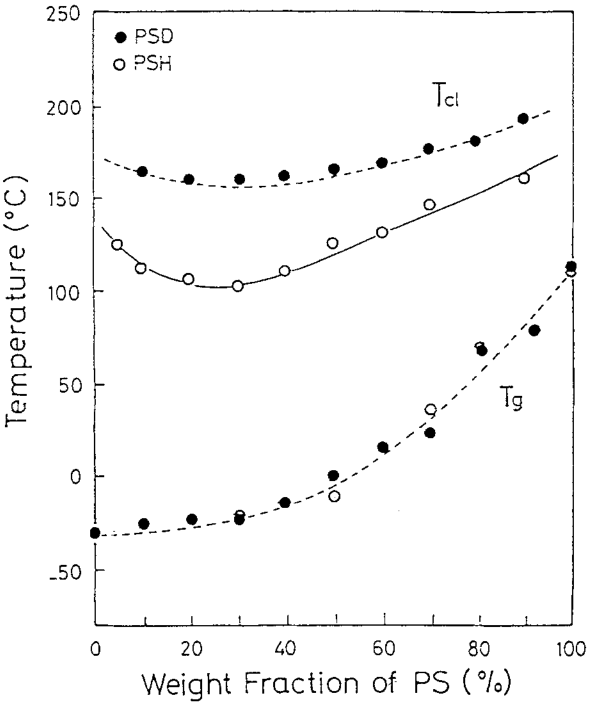

Figure 3. Cloud points (upper part) and glass transition temperatures (lower part) of PSH/PVME (○) and PSD/PVME (●) blends.

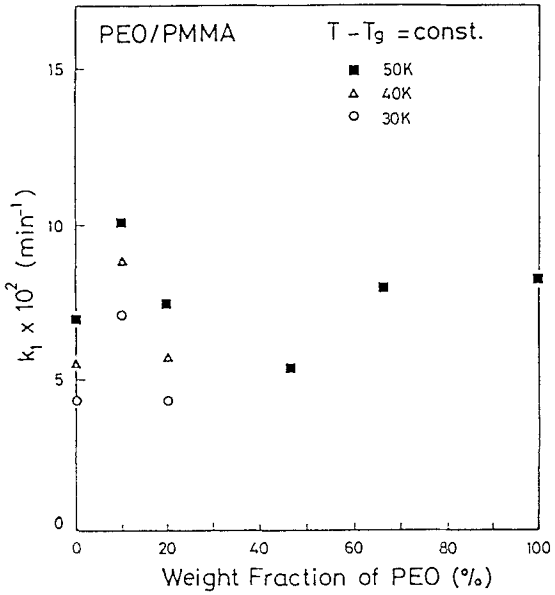

Figure 4. Composition dependence of k_1 in PEO/PMMA blends under the condition T-Tg = constant. (■), PEO2; otherwise PEO1

constant as described in the previous work. As shown in **Figure 4**, for PEO/PMMA blends, the reaction rate k_1 does not show any systematical changes with the blend composition for (T-Tg) = 30°C, 40°C and 50°C. This behavior is completely in contrast with those shown in **Figure 5** for PSH/PVME and PSD/PVME. Namely, under the condition (T-Tg)= 55°C and 75°C, the reaction rate k_1 in these two blends exhibits a strong dependence on the blend composition. In the previous work[3], this peculiar dependence of the photodimerization kinetics of HNMA in PSH/PVME blends was assigned to the contribution of the critical concentration fluctuations in the vicinity of the coexistence curve. To clarify this point, the binary interaction parameters χ for both PSD/PVME and PEO/PMMA are estimated from the small-angle neutron-scattering (SANS) and the melting point depression data. The

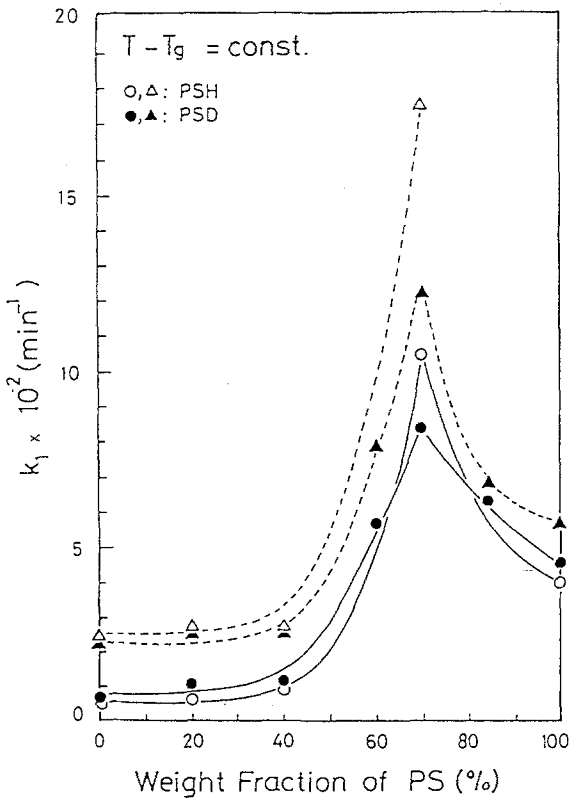

Figure 5. Composition dependence of k_1 in PSH/PVME and PSD/PVME blends. (-----): T-Tg = 75°C; (———): T-Tg = 55°C

former was obtained from the existing SANS data[9]. The later is calculated from the melting point data obtained directly by differential scanning calorimetry[10]. It was found that $\chi = -0.017$ at 105 ℃ (equivalent to T-Tg = 65K) for PSD/PVME (70/30) whereas $\chi = -0.15$ at 100 ℃ for PEO/PMMA blends used in this work. Furthermore, as shown in **Figure 5** the composition dependence of the reaction rate k_1 is weaker in PSD/PVME than that for PSH/PVME blends. Taking into account that the isotopic effects have increased the miscibility of the blends, we think that the weak dependence of k_1 on the PSD/PVME blend composition is due to the fact that the experiment temperatures are far from the coexistence curve. In this range of temperature, the critical concentration fluctuations of PSD/PVME are not significant in comparison to those of PSH/PVME blends. This explanation is also supported by the data of k_1 obtained for PEO/PMMA blends as shown in Figure 4.

In conclusion, from the experimental results described above, it is obvious that the photodimerization kinetics of HNMA in binary polymer blends does reflect the concentration fluctuations with the wavelength comparable to the dimension of the probe.

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