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Holographic Grating Relaxation Studies of Probe Diffusion in a Polymer Blend

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ABSTRACT: Probe diffusion of camphorquinone (CQ) in a polystyrene (PS)/poly(2,6-dimethyl-1, 4-phenylene oxide) (PPO) blend is studied by using the laser-induced holographic grating relaxation technique. The probe diffusion coefficient is measured as a function of temperature and composition. Above the glass transition temperature, the temperature dependence of the diffusion coefficient fits well to the Vogel−Fulcher equation. At a fixed temperature above T_g, it is found that the logarithm of the probe diffusion coefficient varies linearly with the weight fraction of PS or PPO.

Introduction

Diffusion of small molecules in a polymer host has been a topic of active investigation for several decades. Many techniques such as sorption, radioactive isotope tracer, and pulsed field gradient nuclear magnetic resonance (NMR) have been employed for the diffusion measurement.[1] In recent years, additional techniques including fluorescence photobleaching recovery (FPR),[2−4] laser-induced holographic grating relaxation (HGR) or forced Rayleigh scattering (FRS),[5−14] elastic recoil detection (ERD), forward recoil spectrometry (FRES),[15] and small angle neutron scattering (SANS)[16] have also been developed to study probe diffusion that is too slow for ordinary techniques. Among these modern techniques, HGR and FPR have been extensively used because they are able to detect slow diffusion coefficients down to the order of 10^{-15} cm^2/s without expensive instrumentation.[17]

Using HGR, Wang and co-workers have studied probe diffusion of camphorquinone and azo dye molecules in various polymer matrices in the vicinity of the glass transition.[18−21] They interpreted the diffusion coefficient data of these probes in the polymer using free volume theory[22] with success. Similar findings are also reported by Sillescu and co-workers,[6] Lodge and co-workers,[9] and others.[23] Johnson and co-workers[24] and more recently Bloomfield and co-workers[3] have studied the diffusion of chromophore-labeled biological molecules in polymer systems using HGR and FPR. Their studies show the potential of applying these techniques to investigate biological and controlled drug release systems.[25] There are also reports using the HGR technique on the probe diffusion of polymer chains in polymer solutions and in a melt[14] as well as in polymer gels.[10] Recently, Ehlich et al. have reported FRS studies of a dye-labeled lamella PS−polyisotrene block copolymer melt.[26]

Despite extensive activities, only very few probe diffusion studies have been carried out in polymer blends. Relevant to the present work is the study of Stallings and co-workers[27] using a conventional high vacuum time-lag technique, who have investigated the diffusion of noble gases in a blend of poly(2,6-dimethyl-1, 4-phenylene oxide) (PPO) and polystyrene (PS) in the temperature range 25−50 °C. The PPO/PS blend system is completely compatible over the entire composition range. Stallings et al. found that the diffusion coefficient data in these blends follow an Arrhenius temperature dependence. This is not surprising. Considering the small size of these inert gas molecules diffusing below T_g, one expects only a small coupling between the translational motion and the polymer segments. It is rather interesting to note that, even in these small inert gas penetrant, one finds in pure PPO and in a PPO/PS (50/50) blend that the diffusivity decreases with increasing penetrant size. The diffusion coefficients measured at 25 °C plotted vs blend compositions show a minimum at the 50/50 composition. The magnitude of this minimum increases with decreasing penetrant size. Shur and Ranby[28] have reported results of gas permeability studies of semi-compatible polymer blends of poly(vinyl chloride) (PVC) and ethylene−vinyl acetate copolymer (EVA). They found that the gas diffusion coefficient decreases monotonically with the increase of vinyl acetate (VAc) content. This was interpreted as due to the denser packing of polymer molecules as the VAc content is increased.

While the effect of polymer structure in the glassy state on penetrant transport behavior is important, large scale chain motion above T_g is expected to strongly couple to the transport property of probe molecules. Most of the previous studies of probe translational diffusion above T_g are made in the homopolymer system. In this paper, using the HRS technique, we have studied the probe diffusion of camphorquinone in compatible PPO/PS polymer blends. This paper reports the result of the probe diffusion coefficient as a function of temperature and PPO/PS blend composition.

Experimental Section

1. Sample Preparation. Camphorquinone (CQ) purchased from Aldrich Chemical Co. was used as the diffusion probe in the HRS experiment. To prepare the PPO and PS blend, a proper amount of PPO powder (from Aldrich) and PS pellets (Aldrich) were dissolved in tetrahyrofuran to form a solution. The solution was filtered with a 0.2 μm Teflon filter to remove dust. After filtration, methanol was added to the solution to precipitate both PPO and PS. The PPO/PS powder mixture

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Table 1. Glass Transition Temperature and Molecular Weight of Polymers Used

sample	name	T_g (°C)	MW	source
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)	210	2.4×10^5	Aldrich
PS	polystyrene	100	2.8×10^5	Aldrich

Table 2. Polymer Blends and Glass Transition Temperatures

sample	composition	T_g (°C)
PPO/PS(22/78)	22% PPO	122
PPO/PS(40/60)	40% PPO	141
PPO/PS(50/50)	50% PPO	148
PPO/PS(60/40)	60% PPO	167
PPO/PS(78/22)	78% PPO	182

obtained was dried at 90 °C in a vacuum oven. To make blend samples for HGR measurements, 0.6% (by weight) of CQ was mechanically mixed with the PPO/PS polymer powder. The mixture was melted and pressed into films in a temperature-controlled presser. Films were controlled to have a thickness of about 0.08 mm. Films obtained were checked to ensure uniformity and optically clarity.

Glass transition temperatures of the blend samples were determined by a Perkin-Elmer (Delta series) differential scanning calorimeter (DSC). The samples were first heated above T_g to reduce stress and also ensure similar thermal history; they were then cooled and reheated at a rate of 20 °C/min. Each blend was found to exhibits only one glass transition temperature. The glass transition temperature was also found to vary monotonically with the weight percent of PPO in the blend. This indicates that the blend is compatible. The T_g values of all PPO/PS blends are negligibly affected by the addition of 0.6% CQ. The T_g data are summarized in Table 2. The data show that T_g^{-1} (K^{-1}) increases linearly with increasing weight percent of PS.

The uniformity of CQ in the PS/PPO blend was checked by measuring the UV/vis absorption spectrum at various positions of the sample. The solution spectrum of CQ in PS/PPS blend dissolved in dioxane was also found to be similar to the film spectrum without dioxane. These results clearly indicate that CQ molecules do not aggregate at this low concentration.

2. Laser-Induced Holographic Grating Relaxation Measurements. The optical setup employed in the present study is similar to that used in the previous work.[5] The PPO/PS film was mounted in a specially designed copper holder, which was then placed in a temperature controlled chamber with glass windows to permit transmission of laser beams. A holographic grating was induced by crossing two equal intensity coherent beams from an Ar^+ laser (Spectra Physics 2000) operating at 488.0 nm wavelength and at a power of 40 mW. The beams were attenuated by an appropriate factor (2 to 10) before incident on the sample. The writing time was 1−5 s, controlled by an electronically actuated shutter. The crossing angle θ was varied from 3.6 to 15°. At $\theta = 3.6°$, it corresponds to a grid spacing of 8.26 μm. Gratings were generated as a result of a photochemical reaction involving hydrogen abstraction of CQ.[29] After the gratings were formed, one of the writing beams was shuttered and the other was attenuated by a factor of 100−10 000 immediately. The attenuated beam served as a reading beam that was diffracted by the induced gratings to the photodetector, which was positioned to satisfy the Braggs condition.

The HGR curve exhibits either a monotonic decay or a decay−growth−decay shape and is given by[13,30]

$$I(t) = (a\mathrm{e}^{-t/\tau_1} + b\mathrm{e}^{-t/\tau_2})^2 \tag{1}$$

where a and b are optical constants; these constants are functions of refractive index and the population of molecules in the ground and excited states.[13] When a and b have the same sign, the signal gives rise to a monotonic decay; otherwise, a decay−growth−decay curve is observed. τ_1 and τ_2 are relaxation times, which are, respectively, associated with diffusion coefficients (D_1 and D_2) of CQ and the photoproduct CQP according to

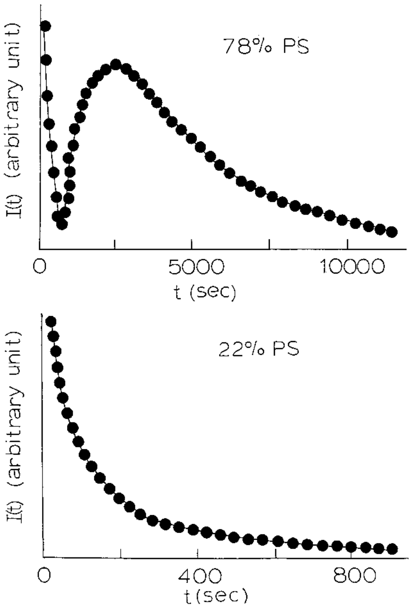

Figure 1. Two types of HGR curves of PPO/PS blends observed. (Top): 78% PS at 142 °C observed with $\theta = 4.8°$. Line is the fit to eq 1, with $\tau_1 = 2.7 \times 10^3$ s and $\tau_2 = 1.3 \times 10^4$ s; $a = 18.9$; $b = -43.1$. (Bottom): 78% PPO at 242 °C, observed with $\theta = 14.2°$. Line is the fit to eq 1, with $\tau_1 = 95$ s and $\tau_2 = 600$ s; $a = 13.05$; $b = 12.62$.

$$D_i = \frac{\lambda^2}{16\pi^2 \sin^2\left(\frac{\theta}{2}\right)\tau_i} \tag{2}$$

Here λ is the wavelength of the laser beam; subscripts of $i = 1$ and $i = 2$ refer to the dye molecule (CQ) and its photoproduct (CQP), respectively. Knowing λ and θ, the diffusion coefficient D_i can be deduced from the measured τ_i value via eq 2.

Depending on the relative PPO/PS concentration in the blend, both types of the HGR curve were observed. Shown in Figure 1 are the decay−growth−decay HRS curve (top), obtained for 78% PS at 142 °C, and the monotonic decay (bottom), obtained for 22% PS at 242 °C. The observed HGR curves fit rather well to eq 1. The fitting parameters are given in the caption of Figure 1. From the curve fitting we obtain relaxation times τ_1 and τ_2. The temperature and composition dependence of τ_1 and τ_2 are similar. In the present paper, only D_2 values associated with τ_2 (corresponding to the photoproduct, CQP) were reported. A detailed discussion of HGR curves and the curve fitting procedure can be found in ref 13.

Results and Discussion

Figure 2 shows the temperature dependence of the diffusion coefficients of CQP in pure PPO at temperatures above and below T_g. For $T > T_g$, the diffusion coefficient data fit well to the Vogel−Fulcher equation, given by

$$\log D = \log D_o - \frac{B}{T - T_o} \tag{3}$$

where D_o, B, and T_o are characteristic parameters. Values of B and T_o are related to the WLF coefficients C_1^D and C_2^D by $B = C_1^D C_2^D$ and $T_o = T_g - C_2^D$. By fitting the diffusion data to eq 3, we obtain $\log D_o = -9.5$, $B = 268.5$, and $C_2^D = 84.6$. This C_2^D value agrees well with the C_2 (82.4) parameter obtained from the dynamic modulus data for PPO,[31] thus suggesting that probe

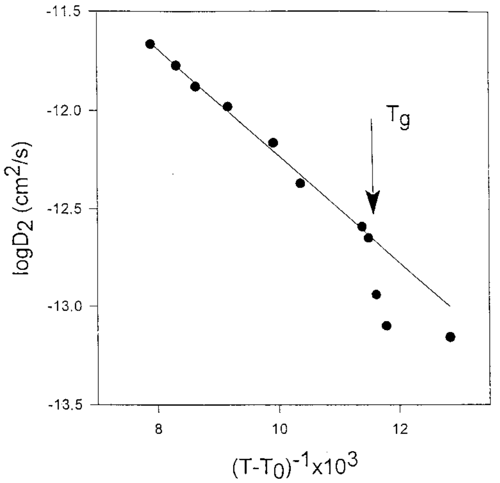

Figure 2. Temperature dependence of the diffusion coefficient of CQP in PPO. Dots are experimental points, and the line is the fit to the Vogel−Fulcher equation.

diffusion above T_g is predominantly affected by the viscoelastic response of the polymer. As the temperature of the sample is brought to the vicinity of T_g, the diffusion coefficient decreases with the decrease of temperature. Clearly the temperature dependence of the diffusion coefficient above T_g is coupled to the α-process of polymer chains. The diffusion coefficient follows the viscoelastic response of the polymer. However, as the temperature is brought below T_g, one notes a distinctive drop of the diffusion coefficient. The result is consistent with several polymer systems that have been studied,[32,33] but has not been noted by Ehlich and Sillescu[6] and by Deppe et al.[34] These authors have reported a smooth variation of the diffusion as the glass transition temperature is traversed. The rapid decrease reflects the "freezing-in" of chain motion associated with the α-relaxation process of the amorphous polymer. However, as shown in a careful study reported in ref 32, such a decrease in the diffusion coefficient is suppressed if the dye concentration is large or if the polymer is plasticized by a small amount of very low molecular weight additives in the polymer. The drop of probe diffusion coefficients at temperatures near T_g is also observed in other polymer systems.[20,32,33,35] For pure PPO, since only two diffusion coefficients are determined for $T < T_g$, the temperature dependence behavior below T_g is not discussed.

Figure 3 shows the temperature dependence of the diffusion coefficient of CQP in pure PS and in the PPO/PS blend with different PS compositions. All diffusion coefficient data are above T_g. The data fit well to the Vogel−Fulcher equation. Fitting parameters for CQP in various PPO/PS blends are summarized in Table 3. While the $C_1{}^D$ data have an irregular pattern (see below for additional discussion), the $C_2{}^D$ data decrease with increasing PS content, yielding a value of 47.0 for pure PS. This value is consistent with the C_2 value (50.0) obtained from the dynamic modulus of the polymer.[32] This result again confirms that PPO and PS are compatible in all compositions.

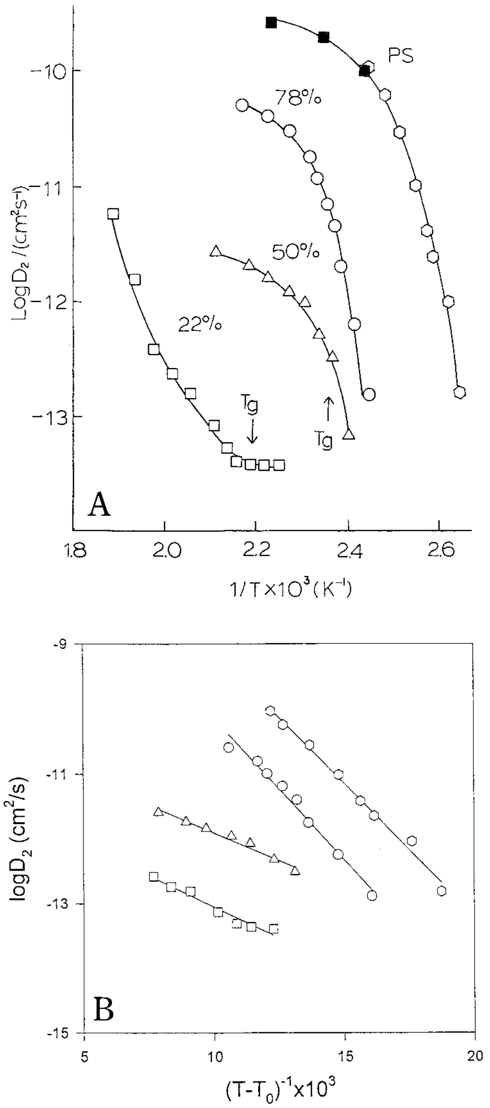

Figure 3. (A) Diffusion coefficients of CQP in PPO/PS (78/22) (□), PPO/PS (50/50) (△), PPO/PS (22/78) (○), and pure PS (⬡) plotted vs T. Dots are experimental points, and lines are drawn to guide the eye. ■ are data from previous work.[18] (B) Diffusion coefficients of CQP in the PPO/PS blend fitted to the Vogel−Fulcher equation. Dots are experimental points, and lines are the fit. The symbol caption is the same as that of part A.

Table 3. Vogel−Fulcher and WLF Fitting Parameters for PPO, PS, and PPO/PS Blends

sample	log D_o	B	$C_2{}^D$	$C_1{}^D$
PPO	−9.5	270.7	84.6	3.2
PPO/PS(78/22)	−11.1	195.8	80.0	2.4
PPO/PS(50/50)	−10.1	173.5	73.0	2.4
PPO/PS(22/78)	−5.5	450.9	46.6	9.6
PS	−5.4	385.0	47.0	8.3

The probe diffusion measurement carried out at a fixed temperature above T_g for the blend with varying composition should yield information about the effect the glass transition. The result of such study is given in Figure 4, which shows the diffusion coefficient of CQP in PPO/PS blends at 175 °C as a function of the blend composition. Within experimental uncertainty, the diffusion coefficient linearly increases with the increase of the PS weight fraction in the blend. The increase of the diffusion coefficient is easily understood. PS has a lower T_g, and upon blending with PPO, it has a plasticizing effect on PPO, thereby resulting in a decrease of T_g. In this case, the diffusion coefficient increase correlates with the increasing temperature distance from the T_g of the blend. This present result is, however, in contrast to that of inert gas molecules diffusing in the PPO/PS blend, which show a minimum in the diffusion coefficient at the 50/50 PPO/PS compo-

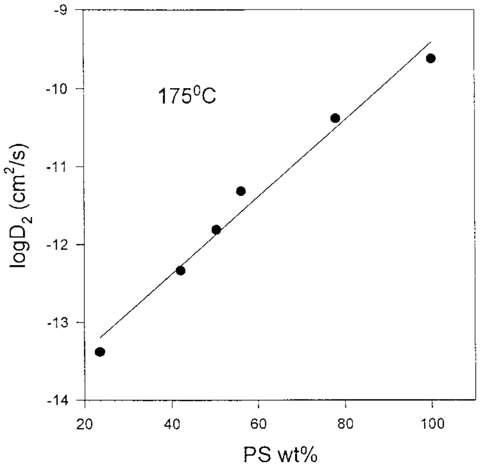

Figure 4. Composition dependence of the diffusion coefficient of CQP in the PPO/PS blend at 175 °C.

sition,[27] as mentioned above. In the present case, the CQP diffusion data exhibit a monotonic increase with the PS concentration. Nevertheless, one should note that the diffusivity data of ref 27 correspond to the PS/PPO blend in the glass state at 25 °C. The mechanism for diffusion below T_g is probably different from that above T_g. The diffusion data shown in Figure 4 correspond to the result at 175 °C, and except for the 20% PS blend (which has a T_g of 182 °C), the T_g values of the rest of samples are below 175 °C (Table 2).

The T_g dependence can be understood by using free volume theory.[34] Above glass transition, the probe diffusion coefficient is related to the free volume fraction, f, by

$$D_{\mathrm{blend}} = \alpha RT\mathrm{e}^{-\beta/f} \tag{4}$$

where α and β are constants, T is the absolute temperature, and R is the gas constant. For the compatible blend of PPO and PS, the free volume fraction f of the blend (f) is a function of the weight (or volume) fraction of pure PPO and PS. For simplicity, one could assume the free volume fraction of the blend to be equal to an algebraic sum of the free volume fraction of PS and PPO. However, this assumption leads to a large curvature in the composition dependence in the log D_{blend} vs x_{ps} plot shown in Figure 4, and is thus inconsistent with the experimental data. Instead, if one assumes a geometric mean for the volume fraction of the blend by

$$\frac{1}{f} = \frac{w_{\mathrm{PPO}}}{f_{\mathrm{PPO}}} + \frac{w_{\mathrm{PS}}}{f_{\mathrm{PS}}} \tag{5}$$

where w_i is the weight fraction of component i in the blend, then using eq 5 and also assuming the parameters α and β are independent of composition, one can readily obtain from eq 4

$$\log D_{\mathrm{blend}} = w_{\mathrm{PPO}} \log D_{\mathrm{PPO}} + w_{\mathrm{PS}} \log D_{\mathrm{PS}} \tag{6}$$

This result is clearly borne out by the data given in Figure 4. However, as mentioned above, while one would generally assume f to be a weighted algebraic rather than a weighted geometric sum of the fractional free volumes of component polymers, the resulting composition dependence of D_{blend} could also be due to the fact that the β parameter of eq 4 actually depends on composition. The composition dependence of the β parameter could give rise to the irregularity of the $C_1{}^D$ parameter obtained above (Table 3) because according to free volume theory $C_1{}^D = \beta/f_g$, where f_g is the fractional free volume at T_g, in contrast to the parameter $C_2{}^D$, which is associated with the temperature dependence of the fractional free volume f. Nevertheless, one should note that free volume theory is a heuristic one, and despite the interesting simplicity of eq 5, there is no microscopic derivation of this equation. Without the justification of a microscopic theory, we can only consider eq 5 as an empirical result at present.

In summary, we have studied the diffusion coefficient of camphorquinone in a PS/PPO polymer blend. We have shown that above T_g, the temperature dependence of the diffusion coefficient fits well to the WLF equation. The probe diffusion coefficient is correlated with the viscoelasticity of the component polymers in the blend. We have shown that the probe diffusion coefficient also strongly depends on the copolymer composition. In the present PPO/PS blend, we find that above T_g the logarithm of the probe diffusion coefficient, log D_{blend}, linearly varies with the weight fraction of the component polymers.

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