Macromolecules **1995,** *28,* 1979−1989 **1979**

Tracer Diffusion in the Blends of Polystyrene and Tetramethylbisphenol A Polycarbonate

Eugene Kim†

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853

Edward J. Kramer*

Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, New York 14853

John O. Osby

Dow Chemical USA, Building B-1471, Freeport, Texas 77541

Received April 18, 1994; Revised Manuscript Received November 8, 1994⊗

ABSTRACT: The tracer diffusion coefficients (D^*) of deuterated tetramethylbisphenol A polycarbonate (d-TMPC) and deuterated polystyrene (d-PS) into protonated blends of TMPC/PS were measured in an effort to gain insight into the factors which determine the monomer friction coefficient of the individual components of a miscible polymer blend. Forward recoil spectrometry (FRES) was used to obtain the depth profile of deuterium after diffusion well above the glass transition temperature (T_g). The temperature dependence of the D^*'s was measured for matrices with PS weight fraction w of 0, 0.5, and 1; in all cases the D^* of TMPC was more strongly temperature dependent than that of PS, which is in contrast with the results in blends of PS/poly(xylenyl ether)(PXE) and in disagreement with the simple free volume model of the dynamics of polymer melts. At high molecular weights of the protonated matrix, diffusion of the deuterated tracer molecules was independent of the molecular weight of the matrix and scaled as M^{-2}, where M is the molecular weight of the tracer polymer, strongly suggesting that reptation is the diffusion mechanism in this regime. The reptation model was used to extract monomer friction coefficients for the PS ($\zeta_{o,PS}$) and TMPC ($\zeta_{o,TMPC}$) from their respective D^*'s measured as a function of w at $T = T_g + 45$ °C. The monomer friction coefficient of TMPC was larger than that for PS by more than 100 times. The ζ_o of each species depended strongly on composition at either constant $T - T_g$ or constant fractional free volume. However, $\zeta_{o,PS}/\zeta_{o,TMPC}$ varied only moderately (by about a factor of 3) as a function of w, again in marked contrast with the results in blends of PS:PXE where it varied by about a factor of 10^3.

1. Introduction

Extensive explorations to understand the relaxation processes in polymeric systems have been performed in the last few decades. These processes take place over an extraordinarily broad range of time scales, and predicting their behavior will require a very detailed understanding of the interactions on a molecular level. The dynamics in chemically dissimilar miscible polymer blends provide information about both intermolecular interactions (the influence of interactions with neighboring molecules) and intramolecular constraints (the energy barrier for the conformational transition), which together essentially determine the phenomenological friction experienced by a moving molecule. This information can be obtained by investigating how the individual mobility of each separate chain would be modified by such conditions as composition and temperature. However, only a limited number of systems have been studied so far and more efforts are still needed for the overall picture to be drawn. Recently, a significant amount of experimental work in blends has been accumulated by measuring tracer diffusion,[1−4] by analyzing the frequency dependence of loss moduli,[5−7] by studying local dynamics by dielectric relaxation measurements[8−11] and by nuclear magnetic resonance (NMR),[12−15] and by investigating the orientation of different species when subjected to a uniaxial strain.[16−18] The studies of tracer diffusion have been carried out on blends of PS/poly(xylenyl ether)(PXE),[1,2] PS/poly(vinyl methyl ether),[3] and PS/poly(methylstyrene),[4] where the influence of excess free energy of mixing (as represented by the Flory segment−segment interaction parameter χ) is negligible and only the combinatorial entropy of mixing drives the diffusion.

In a high molecular weight homopolymer matrix where the matrix chains are sufficiently entangled, the relaxation and diffusion of labeled tracer chains are well described by the reptation model which was proposed by de Gennes[19] and later quantified by Doi and Edwards.[20] The essential aspect of the model is that the entanglements in the matrix provide a "tube like" contour through which the tracer chain makes a curvilinear motion. A chain is composed of segments which are connected by hypothetical springs and the mobility arises from random forces due to thermal noise. The reptation model has been shown to agree well with experiments for various polymer melts, although the model still lacks microscopic theoretical justification. The pros and cons of reptation are summarized in depth in the recent review paper by Lodge et al.[21] From the reptation model, Graessley derived the following expression for the tracer diffusion coefficient:[22]

$$D^*_{\mathrm{rep}} = \left[\frac{4}{15}\,\frac{M_o M_e k_B T}{\zeta_o}\right]\frac{1}{M^2} \qquad (1)$$

where D^*_{rep} is the reptation tracer diffusion coefficient, M_e is the entanglement molecular weight of the matrix

---

* To whom correspondence should be addressed.

† Present address: Department of Chemical Engineering, Princeton University, Princeton, NJ 08544

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1995.

0024-9297/95/2228-1979$09.00/0

chain, M is the molecular weight of the diffusing chain, M_o is the molecular weight of the monomer unit, k_B is Boltzmann's constant, and T is the absolute temperature. The monomer friction coefficient, ζ_o, is a measure of the local resistance arising from the dragging force exerted during the relaxation process. The value of the well-defined monomer friction coefficient determined from D^* measurements has been shown to be in good agreement with that determined from zero shear rate viscosity.[23-26] From eq 1 diffusion can be nicely viewed in terms of only one parameter, i.e. ζ_o. In blends the monomer friction coefficients of both species, $\zeta_{o,PS}$ and $\zeta_{o,TMPC}$, can be extracted as follows (with i indexing the species), by assuming that the blend system is characterized by a single entanglement molecular weight which can be obtained from one value of the plateau modulus (G_N^0):

$$\zeta_{o,i} = \left[\frac{4}{15}\frac{M_{o,i}M_{e,blend}k_BT}{D^*_{rep,i}}\right]\frac{1}{M_i^2} \quad (2)$$

In eq 2 we assume that the motion of both types of chains (PS and TMPC) occurs in a common tube whose diameter is characteristic of the blend as a whole and thus we use a single M_e to represent the blend of a given composition. This assumption, which has been justified previously,[2] is consistent with the phenomenological theory of M_e due to Graessley and Edwards.[27]

In this paper, we examine tracer diffusion in high molecular weight PS/TMPC blends where reptation is the dominant mechanism in order to address the following questions: How would the friction factor vary as a function of temperature for each chain? Also, how does it change as a function of blend composition? The activation barrier for the tracer diffusion can be monitored from the temperature dependence. Composition dependence of the tracer diffusion coefficients can be thought to come from the influence of the intermolecular interaction, if the intramolecular constraints are kept constant. We attempted to approach this condition by monitoring the composition dependence of D^* both at a constant temperature interval above T_g, i.e. at a constant $T - T_g$, and at a temperature corresponding to constant free volume.

2. Free Volume Theory

Free volume theory has been shown to be a simple but useful tool for explaining the processes occurring in glass-forming materials at temperatures not far above the glass transition temperature.[28] The free volume is assumed to expand linearly with temperature T above T_g,

$$f = \Delta\alpha(T - T_\infty) = f_g + \Delta\alpha(T - T_g) \qquad T > T_g \quad (3)$$

where f is fractional free volume, $\Delta\alpha$ is the expansion coefficient of the free volume, T_∞ is the "Vogel" temperature at which the free volume vanishes, and f_g is f at T_g. We first assume for the sake of simplicity that each chain in a given miscible blend will have the same T_∞, corresponding to the single glass transition temperature of the blend. In section 5.2, we will also consider the alternative assumption that each chain has its own T_g which is different from that of the pure polymer. The Vogel–Fulcher equations for the tracer diffusion coefficient and the monomer friction coefficient can be derived:[29]

$$\log\frac{D^*}{T} = A - \frac{B}{T - T_\infty} \quad (4)$$

$$\ln \xi_o = A' + \frac{B}{T - T_\infty} \quad (5)$$

with

$$B \propto v^*/\Delta\alpha \quad (6)$$

where A and A' are constants for a given polymer and v^* is the critical void size to allow a jump.

The WLF equation is also obtained,

$$\log\frac{\xi_o(T)}{\xi_o(T_{ref})} = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}} \quad (7)$$

with

$$c_1 = B/c_2 \quad (8)$$

$$c_2 = T_{ref} - T_\infty \quad (9)$$

Nearly universal coefficients of the WLF equation were found for various materials when T_g was taken as T_{ref}, and this finding has been interpreted as signifying that the free volume expansion governs molecular motion in a variety of materials ranging from low molecular weight organic liquids to polymers in such a way that the detailed chemical structure may not be very important except in that it determines T_g.[28]

The above simple free volume theory states that as the temperature is increased from T_∞, D^* is accordingly increased solely by the expansion of the free volume with a rate, B, which is proportional to the critical void size to allow the tracer chain to jump and inversely proportional to the expansion coefficient of free volume of the matrix molecules. When two chemically different chains are microscopically in contact, as in the PS/TMPC blend,[30,31] and the blend system has a single glass transition temperature, the most simple interpretation of free volume theory is that there is only one v^* associated with the long range cooperative motions near the glass transition temperature. Therefore if we simply assume that v^* is the same for each chain, the slope, B, in the plot of $\log(D^*/T)$ vs $1/(T - T_\infty)$ is also predicted to be same. When Composto et al. examined the tracer diffusion of d-PS and d-PXE into a PS/PXE blend (55 vol % PS) at a temperature well above T_g, they found nearly the same value of B for both components, in agreement with this prediction.[32] For polymer blends, however, the major modes of local motion for each component—which are responsible for the mobility of the polymer liquid—do not, in general, have the same relaxation rate. The internal barrier for rotational isomerization about main-chain bonds and the unit size for that motion, as well as the intermolecular interaction, combine to determine the value of B. Thus in miscible polymer blends, different critical void sizes can be expected for each polymer species, and such blends may manifest complex thermorheological behavior even if the assumption of a single T_g were correct. These arguments lead one to question the simplicity of the conventional free volume model and the generality of the result of Composto et al.

On the other hand, at temperatures well above T_g, the temperature dependence of the relaxation of polymeric molecules becomes nearly Arrhenius and a single

Table 1. Weight-Average Molecular Weight and Polydispersity Indices of Deuterated Polymers

	M_w	M_w/M_n
d-PS	9.0×10^4	1.02
d-PS	1.1×10^5	1.1
d-PS	$1.2_3 \times 10^5$	1.05
d-PS	$1.9_6 \times 10^5$	1.03
d-PS	$3.0_3 \times 10^5$	1.05
d-PS	$4.8_9 \times 10^5$	1.1
d3-PS	$1.1_2 \times 10^5$	1.04
d5-PS	$9.8_9 \times 10^4$	1.05
d-TMPC	$1.6_5 \times 10^4$	2.35
d-TMPC	$2.2_8 \times 10^4$	2.50

Table 2. Weight-Average Molecular Weight and Polydispersity Indices of Protonated Polymers

	M_w	M_w/M_n
PS	$2.5_3 \times 10^5$	~2
PS	3.9×10^5	1.06
PS	6.7×10^5	1.07
PS	$1.8_6 \times 10^6$	1.12
TMPC	1.8×10^4	2.33
TMPC	$2.3_4 \times 10^4$	2.59
TMPC	$4.2_2 \times 10^4$	2.88
TMPC	7.6×10^4	5.88

activation enthalpy describes the motion.[28] In this range of temperature free volume no longer determines the rate of diffusion. For the range of temperature where free volume is thought to play a major role, however, the activation enthalpy can be approximated as follows:[28]

$$E_a = 2.303RB\left(\frac{T}{T - T_\infty}\right)^2 \qquad (10)$$

As T increases, the apparent activation enthalpy, E_a, decreases, asymptotically approaching $2.303RB$, and a constant activation energy is not achieved until a high enough temperature is reached. In this temperature range, the above equation says that there are two factors which determine the apparent activation energy: the value of B and the distance from T_∞. It was recently reported by Lomellini[33] that the temperature dependence of the melt viscosity of PS and PC obeyed the free volume model well over a range of temperatures which was much wider than the one studied in this report. We have estimated E_a for both species from our data as a function of both temperature and composition.

3. Experimental Section

The samples for the tracer diffusion measurement were prepared as follows. The mixtures of PS and TMPC were dissolved using anisole (methoxybenzene) as a common solvent and the solutions were spun cast onto a silicon wafer to prepare the base films. The deuterated tracer polymers were spun onto a glass slide, floated onto deionized water, and then picked up on the base layer. After drying, the samples were annealed at a temperature above T_g for a time t, sufficient for $(4D^*t)^{1/2}$ to reach about 200−300 nm. The blend under consideration is known to show lower critical solution temperature (LCST) behavior with a critical temperature of about 240 °C;[31,34,35] all our diffusion measurements were performed in the one phase region. After the samples were annealed, they were then quenched to room temperature to stop the diffusion. The tracer layer was rapidly diluted during the diffusion process so that the volume fraction of the deuterated polymer becomes less than 10%. Nearly the same value of the diffusion coefficient was observed for any tracer layer thickness below about 20 nm. The weight-average molecular weight M_w and polydispersity index of each of the polymers used in this study are shown in Tables 1 and 2. Three different deuterium-labeled PS's were used: fully deuterated PS (d-PS), which is the one used throughout these studies; one with only the phenyl ring deuterated, thus having 5 deuterium atoms on the monomer unit (d5-PS); and one with only the backbone deuterated, thus having 3 deuterium atoms on the monomer unit (d3-PS). On a repeating unit of d-TMPC, hydrogen atoms on the isopropylidene portion were replaced by deuterium, therefore only 6 out of 22 hydrogens were replaced. Forward recoil spectrometry was used to establish the concentration vs depth profiles. D^*'s were extracted by matching the data and a simulated depth profile which is a solution to Fick's second law. The details of this procedure were described elsewhere.[32,36,37] For the polydisperse d-TMPC, D^* for the weight-average molecular weight could be obtained.[38] For d-PS diffusion measurements a profile slightly different from the Fickian one was observed in the immediate vicinity of the surface, which is thought to be due to the lower surface energy of d-PS.[39] This portion of the spectrum was disregarded for measuring D^*. The problem could be overcome by preparing a trilayered film so that the tracer layer is sandwiched by two matrix layers, which results in the same D^* as the above procedure.

The glass transition temperature, T_g(DSC), was measured by differential scanning calorimetry (DSC-2, Perkin-Elmer). For reproducible results, a similar thermal history was given to each blend. First the blend was heated to about 20 °C above T_g and then allowed to equilibrate for 10 min. It was then cooled to about 70 °C below T_g at the rate of 5 °C/min. Lastly, the heat absorbed was monitored as it was reheated to above T_g at the rate of 20 °C/min. The transition was determined from the inflection point. One T_g was observed at each composition of the blend with the transition becoming broader for the mixture than for the pure components (the transition breadth of pure components was 12−13 °C and that of the blend was 20−31 °C). A broadening of the transition similar to what we observe was also reported by Illers et al.[40] The values of T_g as a function of composition were in good agreement with the ones measured by Illers et al.,[40] which lie between the measurements by Wisniewsky et al.[41] and the ones by Kim and Paul[35] (Figure 1). The scatter probably results from different methods of determining T_g (i.e. from the inflection point or the onset of the transition), the different rates of heating, the different thermal histories, and the different molecular weights of the components. The T_g's from DSC were about 10 °C higher than the ones determined by PVT measurements on the same polymers, a difference that can be attributed to the very different rates of the two sets of measurements. The entanglement molecular weight (M_e) of the blend was calculated ($M_e = \varrho RT/G_N^0$) from the plateau modulus data of the two homopolymers and seven blends measured by Wisniewsky et al.[41] and then fitted to the polynomial equation: $\log M_e = 3.57 + 0.0151w + 0.499w^2 + 0.135w^3$.

The pressure−volume−temperature (PVT) relation was measured for the hydrogenated blends of PS with $M_w = 2.5_3 \times 10^5$ and TMPC with $M_w = 4.2 \times 10^4$ at $w = 0, {}^1/_3, {}^2/_3$, and 1. The details of measurement were discussed elsewhere.[31] The above PS is of sufficiently high molecular weight that the PVT properties will not be molecular weight dependent and will not be affected by polydispersity (it was seen that very little effect of molecular weight is present above $M_w = 10\ 000$[42]). A linear dependence of the logarithm of the specific volume (v_s) on T at atmospheric pressure was found both below and above T_g (Figure 2). The corresponding expansion coefficients ($\alpha = \mathrm{d} \log v_s/\mathrm{d}T$) in the glassy and melt states (α_g and α_l, respectively) were determined (Figure 3). Interestingly, α_l and α_g changed in opposite ways as a function of composition. The expansion coefficient of the free volume, $\Delta\alpha$, was calculated from the difference between α_l and α_g, which, strictly speaking, ignores the expansion of free volume in the glassy state. To estimate $\Delta\alpha$ for compositions other than those in Figure 3, the data in this figure were interpolated.

4. Results

4.1. Molecular Weight Dependence. The diffusion was examined to see whether it satisfied the

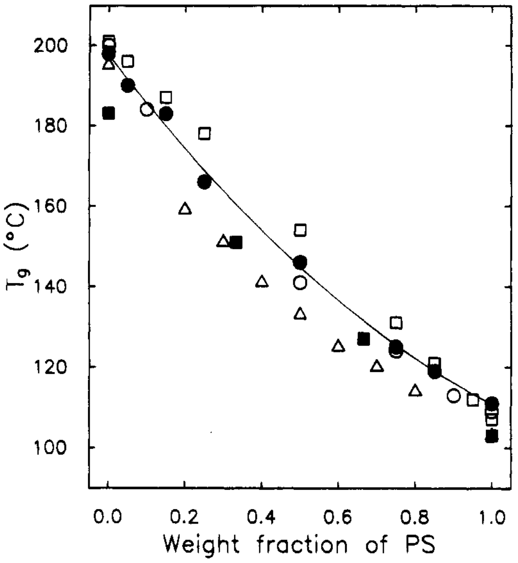

Figure 1. Glass transition temperature versus weight fraction w of PS. ● are the results from DSC work, T_g(DSC), as described in the text when the weight-average molecular weights of the PS and TMPC were 6.7×10^5 and $4.2_2 \times 10^4$, respectively; ■ are the results from *PVT* work when the weight-average molecular weights of the PS and TMPC were $2.5_2 \times 10^5$ and $4.2_2 \times 10^4$, respectively; ○ are the DSC results of Illers et al.[40] (at 20 °C/min, using the inflection point of transition) when the weight-average molecular weights of the PS and TMPC were 3.2×10^5 and 4.1×10^4, respectively; □ are the DSC results of Wisniewsky et al.[41] when the weight-average molecular weights of the PS and TMPC were $2.2_3 \times 10^5$ and $2.7_7 \times 10^4$, respectively; △ are the DSC results of Kim and Paul[35] (at 20 °C/min, using the onset of transition) when the weight-average molecular weights of the PS and TMPC were 3.3×10^5 and 3.3×10^4, respectively. The line represents the polynomial fit to the DSC data obtained by us.

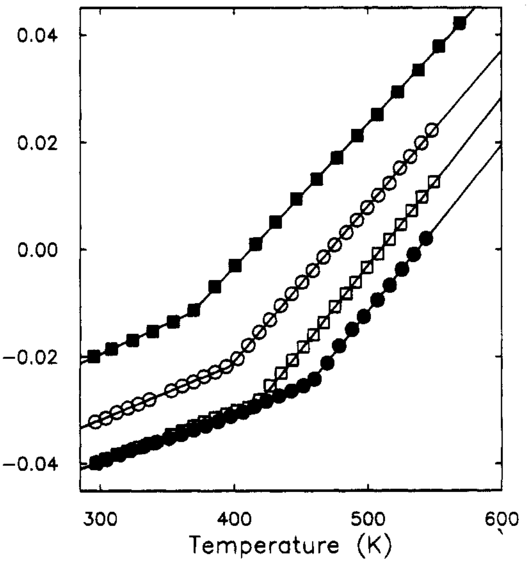

Figure 2. Log of specific volume versus temperature for the blends where weight fraction w of PS is 0 (●), $^1/_3$ (□), $^2/_3$ (○), and 1 (■).

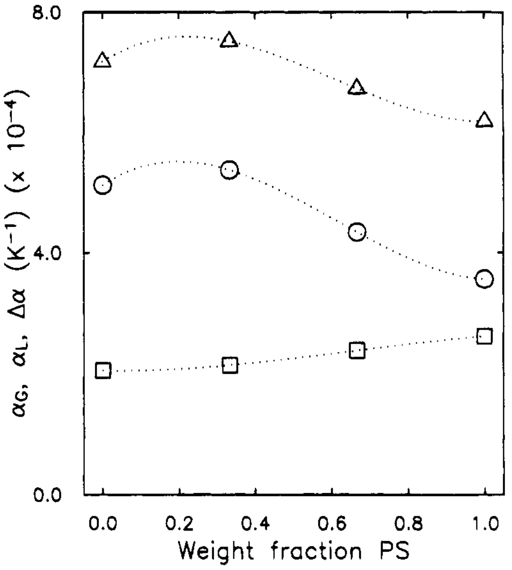

Figure 3. Expansion coefficients α_g of glass (□), α_l of melt (△), and $\Delta\alpha$ of the free volume (○), as a function of weight fraction w of PS.

reptation conditions by checking firstly that D^* was independent of the matrix molecular weight and secondly that it scaled as M^{-2}. The tracer diffusion coefficients were measured in TMPC matrices for both species with various molecular weights as a function of the molecular weight of the matrix. It was shown that D^* did not decrease further when the matrix molecular weight was greater than 4.2×10^4, which is about $10M_e$. From these results we chose the molecular weight of TMPC for the matrix blends (P_{TMPC}) to be 4.2×10^4 or greater. Similar experiments were carried out by using blends with w's of 0.65 and 1 and changing the molecular weight of PS in the matrices (P_{PS}). When P_{PS} was greater than 3.9×10^5, no decrease in D^* was found in all cases for the molecular weights of tracers studied here. The ratio of D^*'s of d-TMPC with $M_w = 1.6_5 \times 10^4$ and that with $M_w = 2.2_8 \times 10^4$ diffusing through TMPC matrices approached the value expected if D^* is proportional to M^{-2} for P_{TMPC} of 4.2×10^4 or greater. A similar ratio was found in the matrices having other compositions when TMPC with $M_w = 4.2 \times 10^4$ and PS with $M_w = 6.7 \times 10^5$ were used. A slope of nearly −2 was found in the log−log plot of D^* versus d-PS molecular weight (ranging from 9.0×10^4 to $4.8_9 \times 10^5$) for w's of 0.5 and 0.75. These molecular weight dependences are consistent with those expected for the reptation mechanism. The detailed results were presented elsewhere.[43] All results reported hereafter are for similar conditions, i.e. where reptation should be valid.

4.2. Temperature Dependence. The temperature dependence of tracer diffusion for the two different species was studied at compositions of w = 0, 0.5, and 1, and the data are shown in Figure 4. We chose the molecular weights of d-PS and d-TMPC so that both D^*'s could be measured at the same temperature. This objective was achieved by choosing a d-PS which has a higher molecular weight than d-TMPC. Data for various molecular weights were combined by multiplying D^* by the square of weight average molecular weight M^2. Tracer PS polymers with different deuterium contents (Table 1) were also allowed to diffuse into a matrix with w of 0.5 at various temperatures. All data were also reduced to a single line (the third line from left in Figure 4), showing that all of them have the same friction coefficient and the same temperature dependence. This result confirms that, as expected, the effect of deuteration on tracer diffusion is negligible. All the data were also plotted at each composition according to the Vogel−Fulcher equation (eq 4) in Figure 5a−c after shifting D^*'s to those of 2×10^5 for d-PS and 2×10^4 for d-TMPC by dividing the values in Figure 4 by the square of 2×10^5 and 2×10^4, respectively. Due to the scatter of the D^* data points and the limited range of

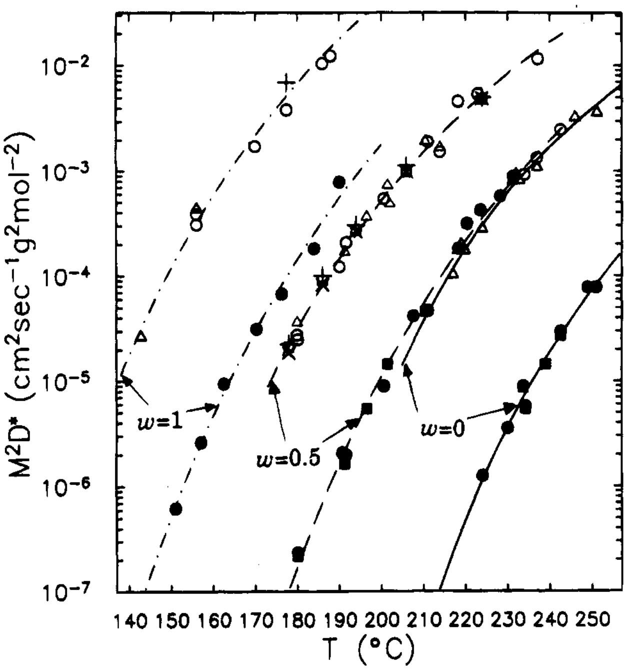

Figure 4. Temperature dependence of tracer diffusion coefficients of d-PS and of d-TMPC multiplied by the square of the respective weight-average molecular weights of tracer chains, M^2D^*, in matrices with different compositions. Weight-average molecular weights used for d-TMPC were 16 500 (■) and 22 800 (●), for d-PS were 110 000 (△), 123 000 (□), 196 000 (○), and 112 000 (+) for d3-PS and 98 900 (×) for d5-PS, respectively. From right to left the data increase in w: in a matrix with $w = 0$, with $w = 0.5$ (D^*'s with different deuterations are also shown), and with $w = 1$. Lines represent the Vogel–Fulcher equation obtained from a linear least squares fit to the data, as explained in the text. Also refer to Figure 5a–c for the plots at individual compositions.

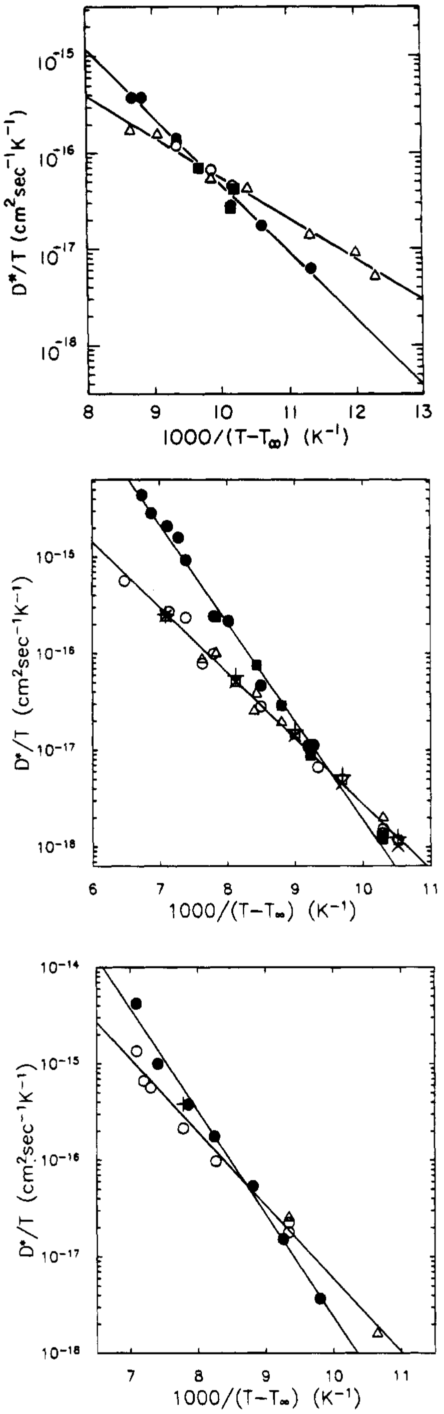

Figure 5. Temperature dependence of tracer diffusion coefficients (Vogel–Fulcher plot; eq 4) of d-PS and of d-TMPC in matrices with different compositions. Data for various molecular weights were shifted to those of 2×10^5 for d-PS and 2×10^4 for d-TMPC, by multiplying the square of weight-average molecular weight divided by the square of 2×10^5 and 2×10^4, respectively. Same symbols were used as in Figure 4. Lines are the first-order fit to the data. T_∞'s used were obtained from T_g(DSC) − T_∞ = 62 °C, as explained in the text. (a, top) In a matrix with $w = 0$. The value used for T_∞ is 136 °C. (b, middle) In a matrix with $w = 0.5$. The value used for T_∞ is 83 °C. (c, bottom) In a matrix with $w = 1$. The value used for T_∞ is 49 °C.

the temperature studied, it was impossible to accurately determine T_∞ using a nonlinear least squares fitting procedure. Instead, $T_\infty = 49$ °C for PS was used which had been obtained by Graessley et al.[44] along with $B = 710$ by fitting η_0 results, and T_∞'s at $w = 0$ and at $w = 0.5$ were estimated by holding T_g(DSC) − T_∞ constant (=62 °C).[45] Wisniewsky et al. reported that $T_g - T_\infty$ was roughly 60 °C over the entire composition range.[46] The slope B in the Vogel–Fulcher plot for each chain was found to be different with a larger slope for d-TMPC for every composition studied. This different temperature dependence means, from eq 10, that d-TMPC has a larger activation energy E_a at any given temperature and composition than does d-PS. The Vogel–Fulcher B for both species is plotted in Figure 6 as a function of composition.

4.3. Composition Dependence. Considering the range of diffusion coefficients which are measurable with FRES (ca. 10^{-11}–10^{-16} cm^2 s^{-1}), 45 °C was chosen as the temperature increment above T_g(DSC) where the diffusion coefficients for each species over all compositions could be measured, and these data are shown in Figure 7a. Using eq 2, monomer friction coefficients were calculated and are displayed in Figure 7b. It was found that $\zeta_{0,\mathrm{PS}}$ was more than 100 times smaller than $\zeta_{0,\mathrm{TMPC}}$ at all compositions. Both $\zeta_{0,\mathrm{PS}}$ and $\zeta_{0,\mathrm{TMPC}}$ varied by nearly a factor of 50, but in a roughly similar fashion as the composition was varied: they increase with w of the matrix until a w of ~0.5 is reached and then remain roughly constant. A rough estimate of the temperature at which the free volume is same ($f = 0.049$) for various compositions was made using eq 3, which assumes that the free volume at T_g(DSC), f_g is the same (=0.028[47]) for all compositions.[48] The $T - T_g$(DSC) where the free volume fraction is 0.049 is plotted as a function of w in Figure 8a. After correcting to this constant free volume where $f = 0.049$ using the measured temperature dependence, both chains showed a maximum in ζ_0 with composition (Figure 8b).

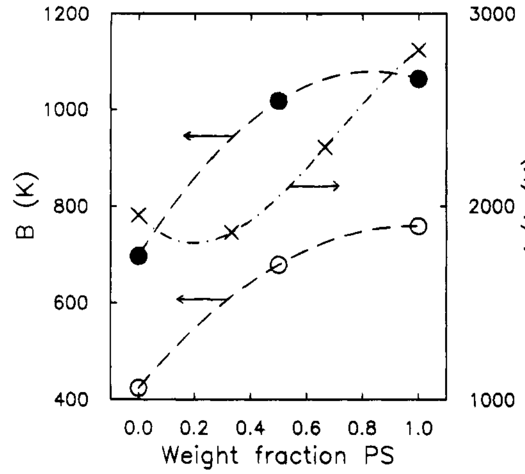

Figure 6. Slope of the Vogel–Fulcher plot B versus weight fraction w of PS in the matrix. The open and filled symbols (○ and ●) represent the values for d-PS and d-TMPC, respectively, using T_∞ obtained assuming T_g(DSC) − T_∞ = 62 °C. $1/\Delta\alpha$ is also plotted (+) for comparison. The lines are drawn to serve as a guide to the eye.

5. Discussion

5.1. Implications for the Free Volume Model. As discussed above the simple free volume model predicts the following: (1) A single T_∞ for both species in the miscible blend. (2) A single value of the Vogel–Fulcher parameter B for both species which should vary inversely with $\Delta\alpha$ as the weight fraction w of PS is changed.

Figure 6 shows that the second prediction is not obeyed by the PS/TMPC system, since B for TMPC is about 50% larger than B for PS at all compositions (the filled symbols in Figure 9). It shows furthermore that B does not vary as $1/\Delta\alpha$. While one might try to generalize the free volume model from eq 6 by asserting that $v^*_{\mathrm{TMPC}} = 1.5v^*_{\mathrm{PS}}$ and while such an assertion seems reasonable in light of the size of the stiff substituted phenyl rings in the TMPC main chain, the fact that the composition dependence of B does not reflect the composition dependence of $1/\Delta\alpha$ means that ultimately even a generalized free volume model fails to account for our observations.

5.2. Comparison with Other Experiments. A major result of our work is that the monomer friction coefficients of PS and TMPC are of quite different magnitudes, with ζ_0 of TMPC exceeding that of PS over the entire composition and temperature range. This general result is in qualitative agreement with the observation of Composto et al.[1] on the PS/PXE system. We find also however major differences in behavior between the two systems. In the PS/PXE system the ratio of $\zeta_{0,\mathrm{PS}}/\zeta_{0,\mathrm{PXE}}$ is profoundly composition dependent, varying from 5×10^{-5} for $w = 0$ to 5×10^{-2} for $w = 0.85$, as shown in Figure 10. In contrast the changes in this ratio for PS/TMPC at $T - T_g$(DSC) = 45 °C are much more modest. The ratio varies from a minimum of 3×10^{-3} at $w = 1$ to a maximum of 9×10^{-3} at $w = 0.65$. Another difference between the two systems is apparent as well. While the temperature dependence of D^*_{PS} and D^*_{PXE} in a PS/PXE blend with $w = 0.55$ is nearly identical[32] (the B in eq 4 is the same), D^*_{PS} and D^*_{TMPC} depend on temperature quite differently for all compositions investigated ($w = 0$, $w = 0.5$, and $w = 1$). In all cases $B_{\mathrm{TMPC}}/B_{\mathrm{PS}} \cong 1.5$, as shown in Figure 9.

The PS/TMPC data support the recent results found in dynamic mechanical measurements,[5–7] NMR measurements,[12,13] and dielectric relaxation measurements[8–11] on miscible polymer blends. Colby[5] and Roovers and Toporowski[6,7] observed the relaxation processes of the individual components of the blends from the frequency dependence of the loss moduli, and Chung et al.[12] and Le Menestrel et al.[13] could also observe the local dynamic processes of individual species near T_g using ^{2}H and ^{13}C NMR, respectively. The associated relaxation times of both species should, in principle, have the same temperature dependence as the ζ_0's in eq 2. What they found was that not only did the two components have different relaxation times, but also they changed differently with temperature. As a consequence, these blends did not show time–temperature superposition. Experimental evidence supporting separate relaxations of various phosphate ester diluents from those of PS (and PXE) in miscible diluent–polymer blends has also been reported using ^{31}P NMR by Cauley et al.[49]

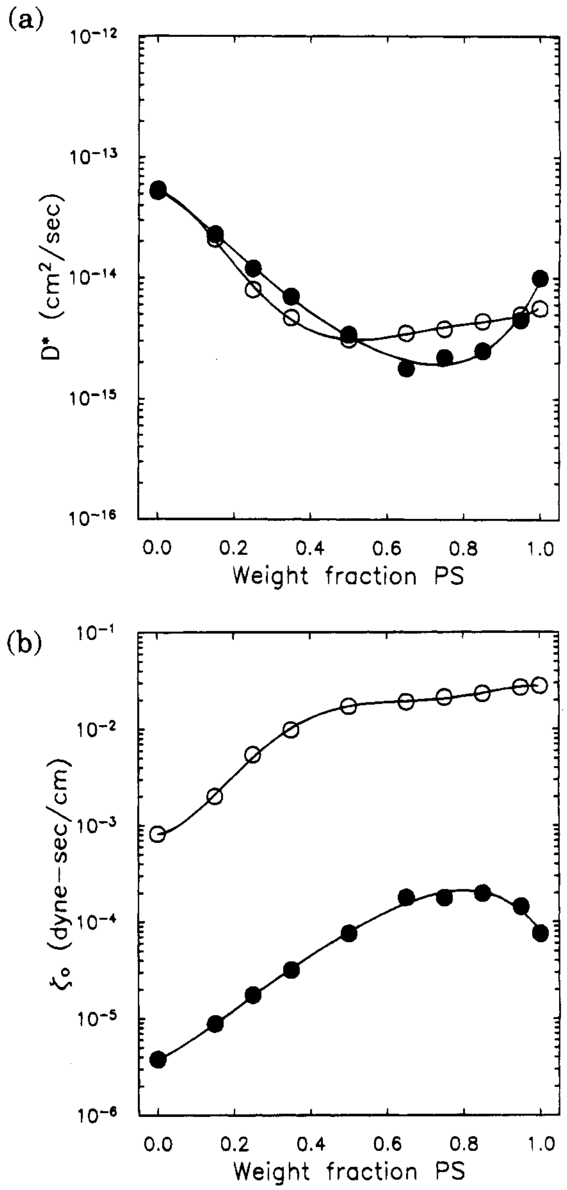

Figure 7. (a, top) Tracer diffusion coefficients D^*_{PS} (●) and D^*_{TMPC} (○) of d-PS with $M_w = 1.9_6 \times 10^5$ and d-TMPC with $M_w = 2.2_8 \times 10^4$, respectively, and (b, bottom) monomer friction coefficients $\zeta_{0,\mathrm{PS}}$ (●) and $\zeta_{0,\mathrm{TMPC}}$ (○) of d-PS and d-TMPC, respectively, as a function of weight fraction w of PS in the matrix at $T = T_g$(DSC) + 45 °C. The lines are drawn to serve as a guide to the eye.

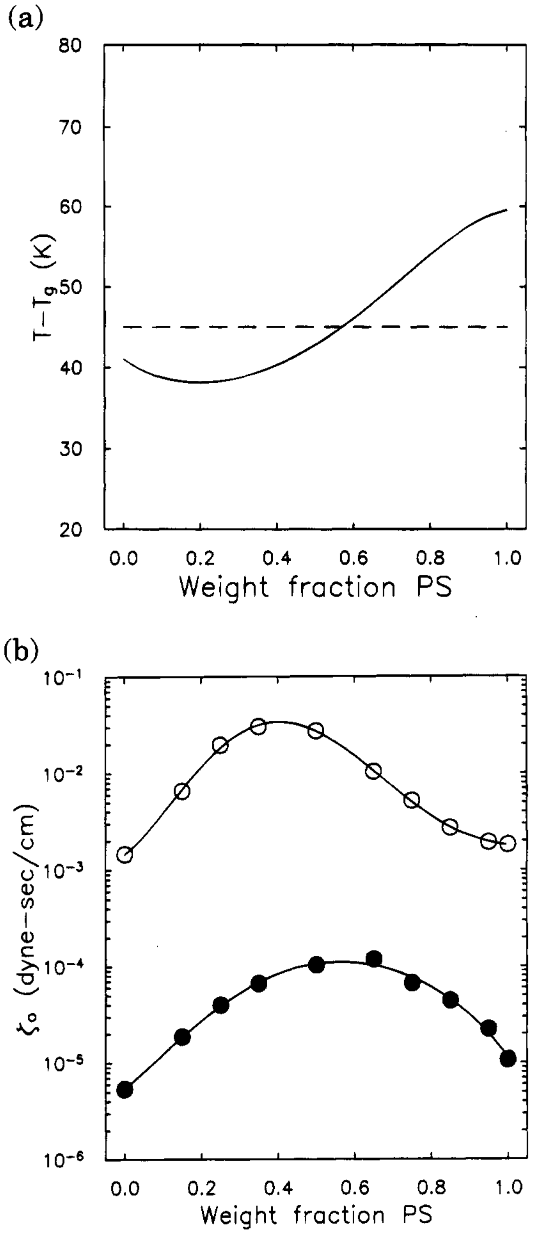

Figure 8. (a, top) Distance from T_g(DSC) to the temperatures where the free volume becomes 0.049 is plotted as a function of weight fraction w of PS in the matrix (solid line). Dashed line represents $T - T_g$(DSC) = 45 °C, the condition under which the data in Figure 7 were obtained. (b, bottom) Monomer friction coefficients $\zeta_{o,PS}$ (●) and $\zeta_{o,TMPC}$ (○) of d-PS and d-TMPC, respectively, versus weight fraction w of PS in the matrix shifted to a temperature corresponding to a constant free volume f = 0.049. The lines are drawn to serve as a guide to the eye.

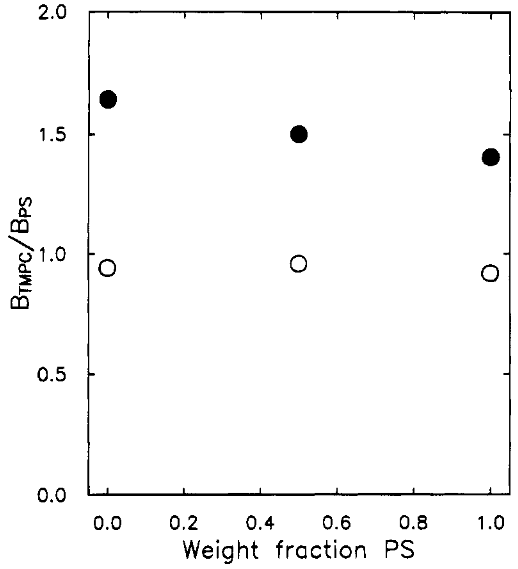

Figure 9. Ratio of B for d-TMPC to that for d-PS, B_{TMPC}/B_{PS}, was plotted as a function of composition. The filled symbol (●) represents the values obtained when the same T_∞ was used for each species at a given composition by holding T_g(DSC) − T_∞ constant (=62 °C).[45] The open symbol (○) represents the values when the T_∞'s used were obtained from $T_g - T_\infty$ = 62 °C where T_g's for each species used are given in Table 3. Refer to the text for the details.

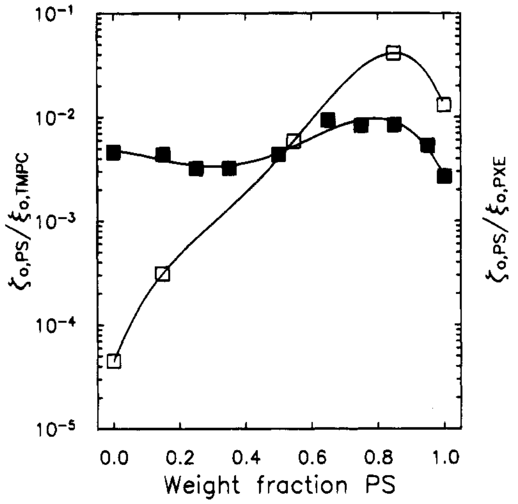

Figure 10. Ratio of monomer friction coefficients $\zeta_{o,PS}/\zeta_{o,TMPC}$ of d-PS and d-TMPC (■) versus the weight fraction w of PS in the PS:TMPC matrix blends measured at $T = T_g$(DSC) + 45 °C and those $\zeta_{o,PS}/\zeta_{o,PXE}$ of d-PS and d-PXE versus weight fraction w of PS in the PS:PXE matrix blends measured at T = T_g(DSC) + 66 °C (□). The lines are drawn to serve as a guide to the eye.

Chung et al.[12] proposed a model based on local compositional heterogeneity for their blends of 1,4-polyisoprene (PI) and poly(vinylethylene) (PVE) for which the Flory parameter χ is nearly equal to 0. The model was invoked to explain why they measured different log mean correlation times for the two species as well as why the distribution of correlation time was broader than that measured in the pure components. This heterogeneity would become larger as the temperature increased from T_g because the size of a cooperative rearranging region becomes smaller and, as a statistical consequence, a given chain would experience more heterogeneous surroundings within that region. Colby ascribed the breakdown of time−temperature superposition to a large correlation length for concentration fluctuations,[5] which causes each chain to see very heterogeneous surroundings. Following the ideas above, the two monomer friction coefficients for a given composition in the PS/TMPC system would be expected to become more different as the temperature is increased. In our system the Flory parameter χ is strongly negative at low temperatures for w = 0.5 (e.g. χ = −0.05 at T = 195 °C[50]) but decreases to zero and becomes positive as the temperature is increased, leading to phase separation (LCST behavior). The magnitude of composition fluctuations will diverge as $(\chi_s - \chi)^{-1}$ as temperature approaches the spinodal (χ_s = the value of χ at the spinodal; the molecular weights used for PS and TMPC were 6.7 × 10^5 and 4.2 × 10^4, respectively). Thus besides the statistical increase in heterogeneity due to

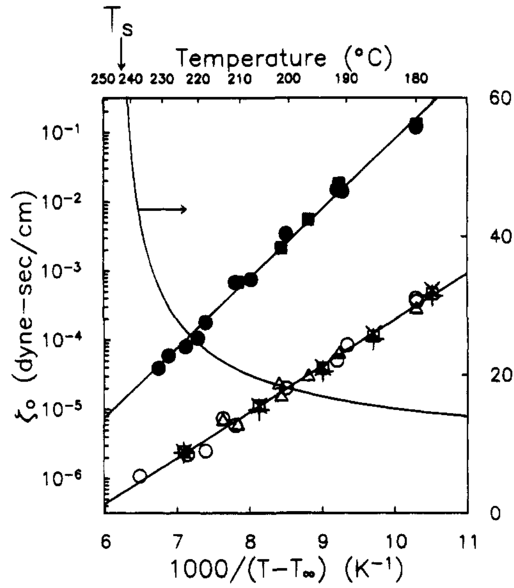

Figure 11. Temperature dependence of monomer friction coefficients $\zeta_{o,PS}$ and $\zeta_{o,TMPC}$ of d-PS and d-TMPC in a matrix with $w = 0.5$. Same symbols were used as in Figure 4. The value used for T_∞ was 83 °C. Lines represent the Vogel–Fulcher plot obtained from a linear least squares fit to the data. The correlation length given approximately as $(a/6)(\phi(1 - \phi)(\chi_s - \chi))^{-1/2}$ where ϕ is a volume fraction of PS (=0.49) and a is the statistical segment length of a blend as a whole (taken to be 11.7 Å[30]) is also plotted. T_s is the spinodal temperature at $w = 0.5$ and the molecular weights used for PS and TMPC are 6.7×10^5 and 4.2×10^4, respectively.

the decrease in size of the cooperatively rearranging region for $\chi = 0$ considered by Chung et al., our system should experience an extra increase in heterogeneity at higher temperatures due to the incipient phase separation into TMPC-rich and PS-rich phases. On the contrary, rather than the monomer friction coefficients of TMPC and PS becoming more different as the temperature is increased, they become more similar, as shown in Figure 11. The monomer friction coefficients (derived from D^*) follow the same Vogel–Fulcher relationship established at low temperatures right up to temperatures where phase separation begins. One must conclude, at least at the temperatures well above T_g where we can measure D^*, that the origin of the differences in magnitude and temperature dependence of the monomer friction coefficients of PS and TMPC cannot be due to compositional inhomogeneity.

All the analysis presented in this paper so far is based on the hypothesis (which follows from the free volume model) that each component in a homogeneous blend has the same T_∞, i.e. that of the blend. But Chung et al.'s NMR experiments on the blends of two polymers[12] together with Cauley et al.'s results[49] on the blend of polymer and diluent, which could be carried out much closer to T_g than our diffusion measurements, show that this assumption is questionable. Chung et al. defined the effective T_g as that T at which the mean correlation time equals 0.316 s. In their case the T_g of the pure PVE was 278 K and that of pure PI was 218 K. They found in the 50/50 blend the T_g of PVE to be 239 K ($T_{\infty,PVE} = 213$ K) and T_g of PI to be 229 K ($T_{\infty,PI} = 197$ K). The species which had a much larger T_∞ in the pure state had a slightly larger T_∞ in the blend. If in our case TMPC, which has a $T_g = 471$ K in the pure state, and PS, which has a $T_g = 384$ K in the pure state, show the same pattern of behavior as PVE and PI, the T_∞ of TMPC in the 50/50 blend would be somewhat larger than that of PS. If for the 50/50 blend we arbitrarily increase T_∞ of TMPC to 52 K below T_g and decrease T_∞ of PS to 72 K below T_g and replot the monomer friction coefficients, the Vogel–Fulcher plot shown in Figure 12 results. Now the temperature dependence of $\zeta_{o,TMPC}$ is rather similar to that of $\zeta_{o,PS}$ and the magnitude of $\zeta_{o,TMPC}$ becomes close to that of $\zeta_{o,PS}$. The consequential point is that if the assumption that T_∞ must be the same for both species is lifted, B as well as the magnitude of the displacement between the Vogel–Fulcher plots for the two component species also change. Ideally, one should be able to determine both B and T_∞ from the experimental data. Unfortunately, the relatively poor precision of the D^* measurement coupled with the fact that D^* can only be measured at temperatures well above T_g means that curve fitting to determine T_∞ is a meaningless exercise.

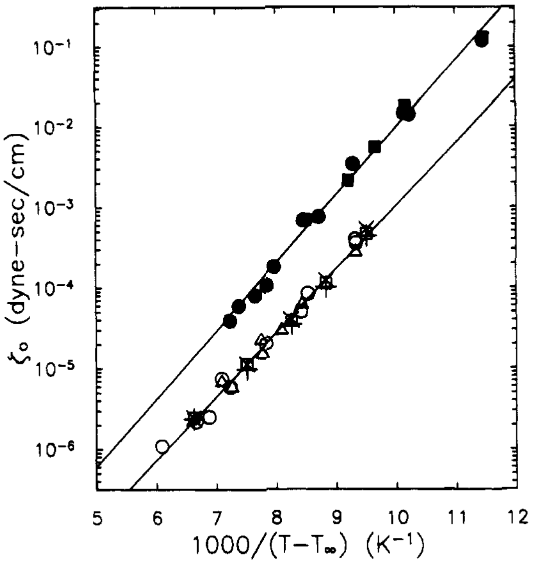

Figure 12. Vogel–Fulcher plot of the monomer friction coefficients in a matrix with $w = 0.5$ when T_∞ of TMPC was arbitrarily increased to 52 K below T_g and T_∞ of PS was decreased to 72 K below T_g.

The idea that each species in the blend has its own glass transition (T_g or T_∞) is appealing on other grounds. It can account qualitatively for the fact that the glass transition of a miscible blend is invariably broader than that of either of the pure components. In the picture developed by Chung et al. the breadth is a consequence of the fact that the T_∞ in the blend of the higher T_g component is somewhat larger than the T_∞ in the blend of the lower T_g component; i.e. the components retain some memory of their T_∞ in the pure state. The lower T_g component in the pure state will relax at a lower temperature in the broad transition region of the blend, and the higher T_g component in the pure state will relax at a higher temperature within this region.

Now, we tried to estimate T_g and the corresponding B by defining an effective T_g at which the monomer friction coefficients of each of the two components are the same as those of the respective pure components at their T_g's. The conventional definition of the monomer molecular weight M_o in eq 2 has been based on the structural repeating unit and therefore the values for the two species were very different ($M_{o,d\text{-}PS} = 112$ and $M_{o,d\text{-}TMPC} = 316$). This monomer size difference (by a factor of about 3) should be partly responsible for the larger value of the monomer friction coefficient for TMPC. For the purpose of eliminating this factor, we redefined $M_{o,i}$ to be the hypothetical molar monomer

Table 3. Glass Transition Temperature T_g (°C) for Each Species at Various compositions Using $\log \zeta_o = 1.35$

	w		
	0	0.5	1
PS	167	140	111
TMPC	198[a]	164	134

[a] Measured by DSC as described in section 3.

volume, v_0 (=175 cm^3/mol), which is taken as the geometric mean of the molar volume of PS and TMPC monomers, divided by the specific volume of the component i. Then we calculated, from the extrapolation by the Vogel–Fulcher equation (with T_g(DSC) − T_∞ = 62 °C), the monomer friction coefficients of d-PS in a PS matrix and that of d-TMPC in a TMPC matrix at their respective T_g's, which were determined unambiguously by DSC measurements. Interestingly, they do not differ significantly; $\zeta_{0,\mathrm{PS}}$ at T_g(DSC) of PS was 20.6 (dyn s)/cm and $\zeta_{0,\mathrm{TMPC}}$ at T_g(DSC) of TMPC was 24.4 (dyn s)/cm. Therefore, we took the average of these two values (ζ_0 = 22.5 (dyn s)/cm[51]), and the T_g's of each species for various compositions were taken as the temperatures where the monomer friction coefficient equaled this value. The previously determined T_g was used for the extrapolation of ζ_0 to the new T_g using the Vogel–Fulcher equation, and this process was iterated until T_g did not vary any more. The differences in the T_g's of the two components for various compositions turned out to be 23–31 °C where PS had the smaller T_g. The resulting T_g's are tabulated in Table 3 and are plotted as a function of composition and compared with the T_g's and their breadth measured by DSC in Figure 13. For w = 0.5, the T_g of PS thus obtained lay inside the range of T_g(DSC) and the T_g of TMPC was about 7 °C larger than the highest temperature in the transition region. Considering the error which might have been caused when estimating T_g by the extrapolation process, these results seem to support the argument that each component in the blend has its own T_g. The glass transition temperature obtained from the temperature dependence of ζ_0 of the one chain in the pure matrix of the other chain (i.e. $T_{g,\mathrm{PS}}$ at w = 0 and $T_{g,\mathrm{TMPC}}$ at w = 1) were also in accord with the range of the broadening of the DSC glass transition found on adding higher concentrations of one homopolymer to the other. The Vogel–Fulcher plots (given by eq 5) for ζ_0 corresponding to segments with the same molar volume are plotted in Figure 14a–c using these newly determined T_∞'s (=T_g − 62 °C) for each species. In this case, the magnitude of ζ_0's are similar at the same $1/(T - T_\infty)$, and the B's for two chains become nearly identical and independent of composition (the open symbols in Figure 9). This result would also mean that the WLF parameters c_1 and c_2 using these T_g's as a reference temperature would be nearly the same for all compositions.

If each species in the blend has its own glass transition behavior, it now follows that each species can be expected to have its own monomer friction coefficient, which could be quite different in magnitude from that of the other species. Indeed, a logical rule-of-thumb would be that the monomer friction coefficient of the species with the larger T_g in the pure state and thus the larger T_g (or T_∞) in the blend would be larger than that of the species with the smaller T_g in the pure state (and thus smaller T_g in the blend). It is a remarkable fact that this rule-of-thumb turns out to be correct for all miscible polymer blend systems studied to date. Not only does the fact that $\zeta_{0,\mathrm{TMPC}} > \zeta_{0,\mathrm{PS}}$ correlate with $T_{g,\mathrm{TMPC}} > T_{g,\mathrm{PS}}$ but $\zeta_{0,\mathrm{PXE}} > \zeta_{0,\mathrm{PS}}$[1] follows from $T_{g,\mathrm{PXE}} > T_{g,\mathrm{PS}}$, $\zeta_{0,\mathrm{PMMA}} > \zeta_{0,\mathrm{SAN}}$[52] follows from $T_{g,\mathrm{PMMA}} > T_{g,\mathrm{SAN}}$, and $\zeta_{0,\mathrm{PMMA}} > \zeta_{0,\mathrm{PEO}}$[53] follows from $T_{g,\mathrm{PMMA}} > T_{g,\mathrm{PEO}}$ where PMMA = poly(methyl methacrylate), SAN = poly(styrene-*co*-acrylonitrile), and PEO = poly(ethylene oxide). This rough rule-of-thumb unfortunately represents the current limits of our understanding of what controls the magnitude of the monomer friction coefficients in miscible blend systems.

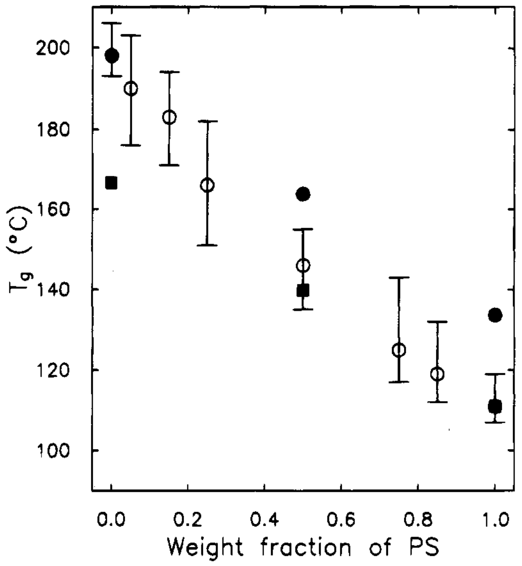

Figure 13. Glass transition temperature T_g of PS (●) and TMPC (■) as a function of composition obtained by assuming that T_g for each component is the temperature at which the monomer friction coefficient equals 22.5 (dyn s)/cm. The glass transition temperature (○: inflection point) and its breadth (starting and ending point of the transition) measured by DSC are also shown.

Thus current evidence, most of it indirect, strongly points to the conclusion, admittedly heretical from a free volume perspective, that each component in a miscible blend has its own T_g which is a reflection of its T_g as a pure substance. As demonstrated above, moreover, the fact that the mean T_g's of the components in the blend differ cannot be attributed to the presence of composition fluctuations since magnifying the composition fluctuations by approaching the spinodal in the PS/TMPC system decreases the ratio of the monomer friction coefficients, rather than increasing it. While the two T_g hypothesis is a sharp departure from the conventional view of miscible polymer blends, it can be presented somewhat differently as follows: The temperature dependence of ζ_0 depends on both intrinsic constraints to segmental motion (these are largely intramolecular) and extrinsic constraints (these are largely intermolecular and thus matrix dependent). The glass transition temperature of a pure component thus depends on both these extrinsic and intrinsic constraints, but adding a second miscible component to form a blend changes primarily the extrinsic constraints. These extrinsic constraints are the most important and are the same for both components in the blend, leading to the largest part of the change in T_g for each component upon blending. However any difference in intrinsic constraints between the two components still remains in the blend, giving rise to a difference in ζ_0 and thus to a different temperature at which the component relaxes at a given slow rate; i.e., the components will have somewhat different T_g's. Whether this interpretation is the correct one or not,

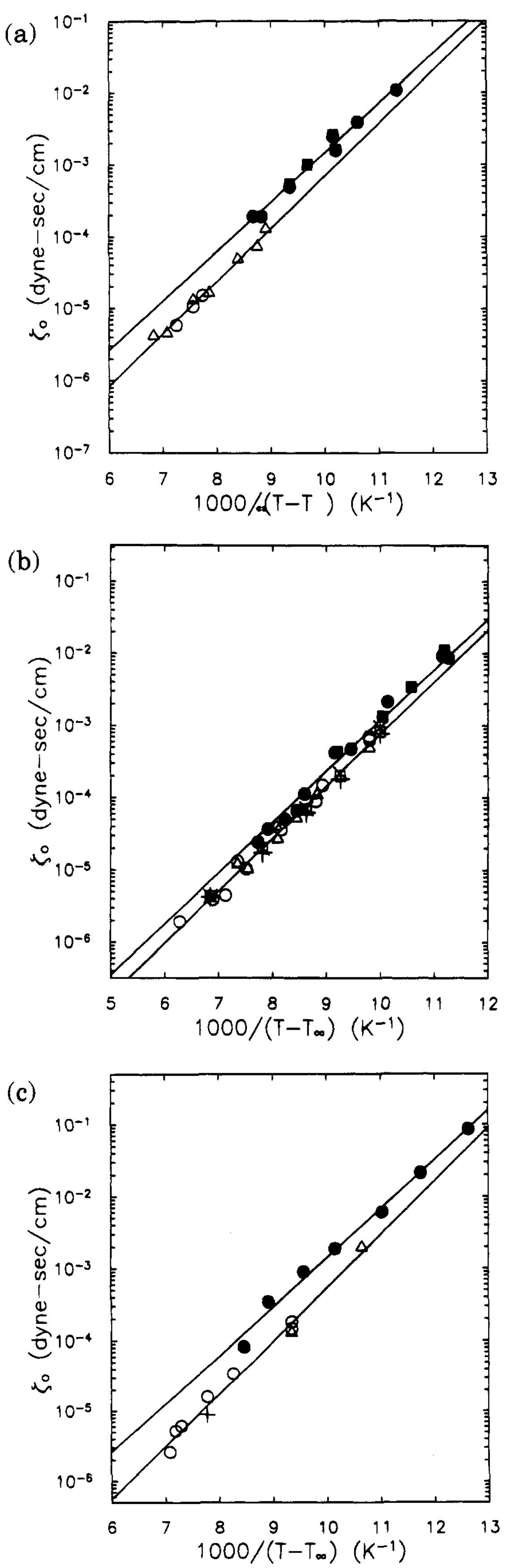

Figure 14. Temperature dependence of ζ_0 (Vogel–Fulcher plot; eq 5) of d-PS and of d-TMPC in matrices with different compositions. Same symbols were used as in Figure 4. Lines are linear least squares fit to the data. The T_∞'s used were obtained from $T_g - T_\infty = 62$ °C where T_g's for each species used are given in Table 3. (a, top) In a matrix with $w = 0$. (b, middle) In a matrix with $w = 0.5$. (c, bottom) In a matrix with $w = 1$.

the challenge for the future will be to develop better microscopic models of the glass transition of these individual components without invoking composition fluctuations as the mechanism.

6. Conclusions

(1) For large enough molecular weight matrices, the diffusion mechanism of d-PS and d-TMPC tracer polymers is reptation.

(2) Fully or only partially labeling with deuterium did not affect the tracer diffusion coefficient or monomer friction coefficient of polystyrene in the blend.

(3) In contrast to previous results in blends of PS/PXE, the D^* of TMPC was more strongly temperature dependent than that of PS for matrices with w of 0, 0.5, and 1. This different temperature dependence would lead to the breakdown of the time–temperature superposition for the relaxation processes of the blend, a breakdown which is not predicted by the simple free volume model.

(4) Both $\zeta_{0,\mathrm{PS}}$ and $\zeta_{0,\mathrm{TMPC}}$ increased with w of the matrix until a w of ~0.5 was reached and then remained roughly constant at constant $T - T_g$(DSC). When the friction coefficients were shifted to the iso-free volume temperature, both of the friction coefficients showed a maximum with w.

(5) The influence on ζ_0 of changing the composition of the matrix was similar for d-PS and d-TMPC: the ratio of these two varied much more weakly than the same ratio for PS/PXE blends.

(6) Over all compositions, $\zeta_{0,\mathrm{PS}}$ was less than $\zeta_{0,\mathrm{TMPC}}$ by more than 100 times at temperatures 45 °C above T_g(DSC), in agreement with the observations that the component with the lower T_g as a pure component showed a smaller ζ_0 in the blend. This observation can be rationalized if each chain retains its own T_g, which reflects its T_g as a pure component, even in a miscible blend.

(7) The monomer friction coefficients of d-PS in pure PS and of d-TMPC in pure TMPC at T_g(DSC) were shown to be nearly the same (the average value was 22.5 (dyn s)/cm). Subsequent analysis which is based on the assumption that there is a T_g for each species in a blend and that this T_g corresponds to the temperature where the monomer friction coefficient equals that for the pure component at its T_g shows that these T_g's were in reasonable agreement with the broad T_g measured for the blend by DSC.

(8) Different heterogeneous compositional environments during the conformational transitions cannot explain the difference in magnitude and temperature dependence of the monomer friction coefficients of PS and TMPC.

Acknowledgment. This work was supported by the Division of Materials Research, NSF Polymers Program Grant No. DMR-9223099, and by fellowship support from Monsanto Chemical Co. through the Polymer Outreach Program of the Materials Science Center at Cornell University. The authors are grateful to David J. Walsh at DuPont for measuring *PVT* properties on PS/TMPC blends. We also appreciate M. H. Rafailovich for providing the partially deuterated PS, J. A. Kornfield for sending us a preprint of ref 12, and G.-C. Chung, R. H. Colby, and W. W. Graessley for useful discussions. We especially thank one of the reviewers for suggesting the extrinsic/intrinsic interpretation for the difference in T_g between the components in the blend.

References and Notes

(1) Composto, R. J.; Kramer, E. J.; White, D. M. *Polymer* **1990**, *31*, 2320.

(2) Composto, R. J.; Kramer, E. J.; White, D. M. *Macromolecules* **1992**, *25*, 4167.

(3) Green, P. F.; Adolf, D. B.; Gilliom, L. R. *Macromolecules* **1991**, *24*, 3377.

(4) Lang, S.; Sillescu, H. *Makromol. Chem.* **1989**, *190*, 797.

(5) Colby, R. H. *Polymer* **1989**, *30*, 1275.

(6) Roovers, J.; Toporowski, P. M. *Macromolecules* **1992**, *25*, 1096.

(7) Roovers, J.; Toporowski, P. M. *Macromolecules* **1992**, *25*, 3454.

(8) Fischer, E. W.; Zetsche, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 78.

(9) Zetsche, A.; Kremer, F.; Jung, W.; Schulze, H. *Polymer* **1009**, *31*, 1883.

(10) Fytas, G. In *Structure and Dynamics of Interacting Colloids and Supramolecular Aggregates in Solution*; Chen, S.-H., et al., Eds.; Kluwer Academic Publisher: Dortrecht, The Netherlands, 1992; p 777.

(11) Roland, C. M.; Ngai, K. L. *J. Rheol.* **1992**, *36*, 1691.

(12) Chung, G.-C.; Kornfield, J. A.; Smith, S. *Macromolecules* **1994**, *27*, 964.

(13) Le Menestrel, C.; Kenwright, A. M.; Sergot, P.; Laupretre, F.; Monnerie, L. *Macromolecules* **1992**, *25*, 20.

(14) Brosseau, C.; Guillermo, A.; Cohen-Addad, J. P. *Polymer* **1992**, *33*, 2076.

(15) Brosseau, C.; Guillermo, A.; Cohen-Addad, J. P. *Macromolecules* **1992**, *25*, 4535.

(16) Zhao, Y.; Jasse, B.; Monnerie, L. *Polymer* **1989**, *30*, 1643.

(17) Zhao, Y.; Prud'homme, R. E.; Bazuin, C. G. *Macromolecules* **1991**, *24*, 1261.

(18) Zawada, J. A.; Ylitalo, C. M.; Fuller, G. G.; Colby, R. H.; Long, T. E. *Macromolecules* **1992**, *25*, 2896.

(19) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.

(20) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, 1789.

(21) Lodge, T. P.; Rotstein, N. A.; Prager, S. *Adv. Chem. Phys.* **1990**, *79*, 1.

(22) Graessley, W. W. *Soc. Chem. Faraday Div. Faraday Symp.* **1983**, *18*, 7.

(23) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.

(24) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2702.

(25) Green, P. F.; Kramer, E. J. *J. Mater. Res.* **1986**, *1*, 202.

(26) Mumby, S. J.; Smith, B. A.; Samulski, E. T.; Yu, L.-P.; Winnik, M. A. *Polymer* **1986**, *27*, 1826.

(27) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.

(28) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; New York, 1980; Chapter 11.

(29) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.

(30) Yang, H.; O'Reilly, J. M. *Mater. Res. Soc. Symp. Proc.* **1987**, *79*, 129.

(31) Kim, E.; Kramer, E. J.; Osby, J. O.; Walsh, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1995**, *33*, 467.

(32) Composto, R. J.; Kramer, E. J.; White, D. M. *Macromolecules* **1988**, *21*, 2580.

(33) Lomellini recently indicated that Arrhenius behavior is not observed for polystyrene (Lomellini, P. *Polymer* **1992**, *33*, 4983) and polycarbonate (Lomellini, P. *Makromol. Chem.* **1992**, *193*, 69) until at least 185 °C above T_g, which is higher than the temperature range studied in this work by more than 100 °C. He claimed that, because of the large size of the rotational units, more free volume is needed to attain Arrhenius behavior, which may occur at a very high temperature.

(34) Guo, W.; Higgins, J. S. *Polymer* **1990**, *31*, 699.

(35) Kim, C. K.; Paul, D. R. *Polymer* **1992**, *33*, 1630.

(36) Mills, P. J.; Green, P. F.; Palmstrom, C. J.; Mayer, J. W.; Kramer, E. J. *Appl. Phys. Lett.* **1984**, *45*, 957.

(37) Green, P. F.; Mills, P. J.; Palmstrom, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.

(38) Mills, P. J.; Green, P. F.; Palmstrom, C. J.; Mayer, J. W.; Kramer, E. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1.

(39) Kim, E.; Krausch, G.; Kramer, E. J.; Osby, J. O. *Macromolecules* **1994**, *27*, 5927.

(40) Illers, K. H.; Heckmann, W.; Hambrecht, J. *Colloid Polym. Sci.* **1984**, *262*, 557.

(41) Wisniewsky, C.; Marin, G.; Monge, P. *Eur. Polym. J.* **1984**, *20*, 691.

(42) Ougizawa, T.; Dee, G. T.; Walsh, D. J. *Polymer* **1989**, *30*, 1675.

(43) Kim, E. Ph.D. Dissertation, Cornell University, Ithaca, NY, 1994.

(44) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.

(45) On the other hand it can be asserted that the ratio, T_g/T_∞, is universal (Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139) on the basis of a consideration of the conformational entropy of the glass transition. The fixed value of T_g/T_∞ was also used to estimate T_∞ at $w = 0$ and at $w = 0.5$.The results were also analyzed using this T_∞, but the essential points we make in this work are not altered by the choice of T_∞.

(46) The observation of Wisniewsky et al. conflicts with the prediction of free volume theory ($T_g - T_\infty = f_g/\Delta\alpha$; see eq 3) if f_g is constant, since our *PVT* study on this blend shows that $\Delta\alpha$ is a function of composition (Figure 3).

(47) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.

(48) The assumption that f_g is constant for all compositions is questionable since the different packing of the molecules may result in different f_g's.

(49) Cauley, B. J.; Cipriani, C.; Ellis, K.; Roy, A. K.; Jones, A. A.; Inglefield, P. T.; McKinley, B. J.; Kambour, R. P. *Macromolecules* **1991**, *24*, 403.

(50) We also measured the mutual diffusion coefficients as a function of temperature and composition,[31] and these were used to extract χ from its relation with the tracer diffusion coefficient and the degree of polymerization.

(51) Assuming that the relaxation time τ for the segmental motion associated with the glass transition is 1 s, the root mean square displacement during τ was estimated from the Rouse model—the motion of the chain is not constrained by the entanglement (Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, U.K., 1986; p 212).

$$\langle (R(\tau) - R(0))^2 \rangle^{1/2} = \left(\frac{k_B T a^2 \tau}{\zeta_o} \right)^{1/4}$$

where τ is the relaxation time and a is the statistical segment length (taken to be 11.7 Å). For example it was 7.8 Å at 437 K, and when τ was increased to 10 s, this number became 13.9 Å.

(52) Kim, E.; Kramer, E. J.; Wu, W. C.; Garrett, P. D. *Polymer* **1994**, *35*, 5706.

(53) It was observed in the PMMA matrix that the tracer diffusion of d-PEO is too fast to be measured using FRES while that of d-PMMA was measured (unpublished result).

MA941242K