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Rotation of Methyl Side Groups in Polymers: A Fourier Transform Approach to Quasielastic Neutron Scattering. 2. Polymer Blends

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ABSTRACT: We present a quasielastic neutron scattering (QENS) study of two partially miscible blends: a blend of solution chlorinated polyethylene and poly(methyl methacrylate) (SCPE/PMMA) and a blend of polystyrene and poly(vinyl methyl ether) (PS/PVME). The local dynamics of the ester methyl group in PMMA-d_5 and the ether CH_3 group in PVME are investigated as a function of temperature and blend composition. Both the frequency spectra and the intermediate scattering function $I(Q,t)$ are analyzed in detail, and the results are compared with those of the pure polymers. The rotational motion of the ester CH_3 group in PMMA-d_5 is sensibly altered by blending with SCPE but no effect is detectable in the PS/PVME system. The time domain data analysis shows that blending broadens the distribution of correlation times in SCPE/PMMA. Results of both homogeneous and phase-separated blends are presented, although no changes in the local dynamics are observed upon phase separation. The difference between the behavior of the two blends is discussed in terms of the lattice model and the intrinsic dynamics of the components.

1. Introduction

Polymer blends offer an attractive area of research. From a practical point of view, it is possible to design new materials with desired properties by simply blending well-characterized existing polymers.[1,2] A large number of studies in this area have been devoted to the understanding of the parameters which govern miscibility, although this is not always a requirement for the application of these materials.

A study of the thermodynamics of mixing[1–3] is essential for the understanding of the miscibility behavior which is often governed by the existence of interactions among the polymer pairs. It is a characteristic of polymeric systems that the entropy change upon mixing is very small. As a consequence, the enthalpic term, ΔH_{mix}, becomes important and determines whether a negative value of the Gibbs free energy of mixing can be attained. Generally, a small ΔH_{mix} is obtained for polymers with similar structure, whereas a negative ΔH_{mix} is a result of specific interactions among the blend constituents.

Recently, there has been an increasing interest in the dynamics of miscible blends. The question which is addressed is whether the dynamics of each of the components is altered in the blend. In this respect, the main evidence of a dynamic effect is given by the broad glass transition, T_g, measured by differential scanning calorimetry (DSC).[4] Similarly, the α-relaxation associated with T_g determined by mechanical and dielectric techniques[5] is broader in the blend compared to the pure systems. The larger the difference between the T_g's, the more pronounced is the broadening.

The difference between the dynamics of a blend and its components, close to the glass transition, has been attributed to concentration fluctuations.[6,7] Models, which in accounting for local heterogeneities explain the origin of the distribution of correlation times, have been developed.[6,7] For example, some authors have discussed the dynamics of polymer blends in terms of the coupling model. Here it is assumed that the local environment of the relaxing segments affects the degree of intersegmental cooperativity, giving rise to a distribution of coupling parameters.[8,9] Recently, two-dimensional deuteron exchange NMR studies[10] have shown that the observed dynamic heterogeneity in blends can only be explained by considering both the effect of local composition and the intrinsic difference in chain mobilities.

Secondary relaxations of the individual components in a blend have also been investigated. There are a number of reasons why blending might be expected to alter the sub-T_g relaxations; for example, changes in free volume, specific interactions, or conformational changes induced by mixing might contribute to affect the local dynamics of the components. Recent experiments have demonstrated that a suppression of the low-temperature local relaxation might occur. This is the case for polycarbonate in blends with poly(methyl methacrylate). A suppression of the β-relaxation in BPA–PC was found by dynamic mechanical spectroscopy and deuterium NMR.[11]

Antiplasticization was also observed in a blend of Chloral-PC and PMMA in the form of suppression of the π-flip process in Chloral-PC with some evidence of an apparent coupling between the sub-T_g relaxations and the ester CH_3 rotation of PMMA[12] and in blends of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) (PXE), indicated as a reduction of fast-flipping phenylene groups.[13]

The work reported in this paper deals with the effect of blending on local motions such as methyl group reorientations. We have already reported a detailed

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study of CH_3 relaxations in glassy polymers using quasielastic neutron scattering (QENS).[14] The difference between activation energies measured on a number of polymeric materials evidences the primary influence of molecular structure on CH_3 reorientations. There are other effects. For example, stereoregularity was found to influence the potential barrier hindering the rotation of α-CH_3 in PMMA.[15,16] The activation energy varied from 23 kJ/mol in isotactic PMMA to 32 kJ/mol in the syndiotactic stereoisomer. This increase was attributed to nonbonded interactions between the α-methyl group and the ester group which are nearest neighbor in syndiotactic PMMA. Similar effects might be expected as a consequence of intermolecular interactions in blends.

Two blends were chosen in our study: (a) a blend of solution-chlorinated polyethylene and poly(methyl methacrylate) (SCPE/PMMA) and (b) a blend of polystyrene and poly(vinyl methyl ether) (PS/PVME). Both systems are partially miscible (the term "partially miscible blend" here refers to miscibility in a limited temperature/concentration range) and exhibit a lower critical solution temperature behavior (LCST). Phase separation occurs upon heating.

The SCPE/PMMA blend has been largely investigated by static techniques as a function of both polymer composition and SCPE chlorine content.[17-20] It is known that partially miscible blends can be obtained at high chlorine content (>50%). The negative enthalpy of mixing responsible for the LCST behavior is believed to result from specific interactions between the α-hydrogen of the SCPE chain and the carbonyl oxygen of PMMA. This idea is supported by the mean internuclear distance of ≈3.5 Å between SCPE protons and deuterated PMMA carbons which was measured by cross-polarization magic angle spinning ^{13}C-NMR experiments[21] (CP/MAS).

Attempts have been made to characterize the nature of the interaction responsible for the miscibility of the PS/PVME blend using Fourier transform infrared spectroscopy.[22] It was suggested that the ether lone-pair electrons of PVME and the benzene ring of PS might be involved. This hypothesis seems to be confirmed by measurements of Larbi et al.[23] on selectively deuterated PS.

We have shown that, even in homopolymers, intermolecular effects play a major role in the local dynamics of polymers below T_g.[14] This is clearly evidenced by the nonexponentiality of the relaxation process. On the one hand, we might expect that the potential barrier hindering the rotational motion could be altered by specific interactions with neighboring atoms in a blend, and, on the other hand, the local environment of the CH_3 groups will be sensibly altered by blending. The comparison between blends where these interactions are known to act with different strength should clarify the influence of the different contributions.

2. Scattering Law for Rotational Motion[24,25]

Neutrons scattered by an atom or an atomic group undergoing molecular motion in the time scale of the scattering experiment are subjected both to a change in the direction of traveling and to an energy change. In dynamic studies, the scattered intensity is analyzed as a function of the momentum transfer Q $(=4/\pi \sin(\theta/2)$, θ being the scattering angle). The quantity measured is the double-differential scattering cross section $\partial^2\sigma/(\partial E\ \partial\Omega)$ which gives the probability that a neutron is scattered with energy change dE into the solid angle $d\Omega$. Generally, the cross section σ includes both coherent and incoherent contributions, but since for large hydrogen content materials the scattering is mainly incoherent, σ can be identified with the incoherent cross section.

The incoherent scattering is given by:

$$\left(\frac{\partial^2\sigma}{\partial\Omega\ \partial E}\right) = \frac{k_s}{k_i} N \frac{(\langle b^2\rangle - \langle b\rangle^2)}{2\pi} S_{\mathrm{inc}}(Q,\omega) \qquad (1)$$

where k_i and k_s are the incident and scattered wavevectors, N is the number of nuclei, and b is the scattering length. $S_{\mathrm{inc}}(Q,\omega)$ represents the incoherent scattering law:

$$S_{\mathrm{inc}}(Q,\omega) = \int \exp(-i\omega t)\, I(Q,t)\, dt \qquad (2)$$

and $I(Q,t)$ the intermediate scattering function:

$$I(Q,t) = \langle \exp(-i\bar{Q}\cdot[\bar{R}_i(0) - \bar{R}_i(t)])\rangle\, dt \qquad (3)$$

which gives the probability that if a scattering center is at $R_i(0)$ at time $t = 0$, then the same scattering center is at $R_i(t)$ at time t. Hence, the incoherent scattering gives then a measure of the correlations between the positions of the nuclei at time zero and t.

The description of the rotational motion of side groups in molecular crystals relies on the jump reorientational model which assumes that the atoms undergo librational motions during an average time τ, after which they perform instantaneous jumps within a set of preferred orientations. The scattering consists of the sum of an elastic, $A_0(Q)\ \delta(\omega)$, and a quasileastic component:

$$S_{\mathrm{inc}}^{\mathrm{rot}}(Q,\omega) = A_0(Q)\ \delta(\omega) + \frac{1}{\pi}[1 - A_0(Q)]L(\omega) \qquad (4)$$

$A_0(Q)$ is the elastic incoherent structure factor (EISF) which is related to the time-averaged spatial distribution of the protons. For a methyl group:

$$A_0(Q) = \frac{1}{3}[1 + 2j_0(\sqrt{3}Qr)] \qquad (5)$$

$j_0(x)$ being the zero-order spherical Bessel function and $L(\omega)$ a Lorentzian function:

$$L(\omega) = \frac{2\tau/3}{1 + \omega^2(2\tau/3)^2} = \frac{\Gamma}{\Gamma^2 + \omega^2} \qquad (6)$$

The full width at half-height (fwhh) defined by the above equation is equal to 2Γ or $3/\tau$, τ being the average time between two consecutive jumps. Expressions analogous to eq 5 have been developed for various symmetries or complex rotations.

According to eq 6, τ is Q independent. The temperature dependence is expressed by the Arrhenius law:

$$\tau = \tau_0 \exp(E_a/RT) \qquad (7)$$

where E_a is the activation energy and it is related to the height of the potential barrier hindering the rotational motion.

We have recently shown,[14] together with other authors,[26,27] that, when the rotational motion of side groups in polymeric systems is analyzed using a single Lorentzian line and therefore assuming a single relaxation process, a series of inconsistent results are obtained: the rotational frequency shows a non-Arrhenius behavior, and it appears to be resolution dependent.[14] Moreover, the EISF is temperature dependent.

It is a general characteristic of glass-forming liquids that the relaxation processes cannot be described by a single-exponential relaxation time but as the sum of elementary processes, each one characterized by a relaxation time τ. Experimentally, empirical functions are used such as the Kohlrausch–Williams–Watts (KWW) function[28,29] or stretched-exponential function:

$$\exp(-t/\tau_c)^{\beta} \tag{8}$$

The KWW function of eq 8 is characterized by two parameters: the characteristic time τ_c and the exponent β, an empirically determined parameter varying between 0 and 1 which gives a measure of the nonexponentiality and of the breadth of the distribution of relaxation times.

The existence of a distribution of rotational frequencies or relaxation times needs to be considered to interpret the relaxation data of polymeric systems. In particular, for quasielastic neutron scattering data there are two possible ways of accounting for such a distribution. First, as shown by Chahid et al.,[26] the QENS frequency data can be fitted using a Gaussian distribution of rotational frequencies. The rotational scattering law can then be expressed by the following equation:

$$S_{\text{inc}}^{\text{rot}}(Q,\omega) = A_0(Q)\,\delta(\omega) + [1 - A_0(Q)]\sum \frac{1}{\pi} g_i L_i(\omega) \tag{9}$$

where $L_i(\omega)$ are Lorentzian functions whose weight is given by g_i.

In our recent work we have adopted an alternative procedure to analyze the QENS data of poly(methyl methacrylate) which relies on the Fourier transform. The QENS data were converted to the time domain to derive the intermediate scattering function $I(Q,t)$ which, for a single relaxation process (in the case of a fixed center of mass), is given by:

$$I(Q,t) = A_0(Q) + [1 - A_0(Q)]\exp(-t/\tau) \tag{10}$$

and represents the Fourier transform of the incoherent scattering law defined in eq 4. In order to analyze side-group rotations in polymers, we have accounted for a distribution of relaxation times by expressing the intermediate scattering function $I(Q,t)$ in terms of the empirical KWW function:

$$I(Q,t) = A_0(Q) + [1 - A_0(Q)]\exp(-t/\tau_c)^{\beta} \tag{11}$$

Apart from the obvious disadvantages of having to perform a Fourier transform, the time domain data analysis via eq 11 is rather simple. The nonexponential behavior is immediately recognized by attempting a fit with eq 10 and the EISF can now be extracted directly as the long-time limit of $I(Q,t)$. In addition, the instrumental resolution is easily accounted for by dividing the FFT of the data by that of the resolution. Any convolution problem which is required to fit the frequency data is now eliminated.

3. Experimental Section

3.1. Materials. Solution-chlorinated polyethylene with a 63% chlorine content (SCPE63) was prepared as described in ref 30. The polymer weight-average molecular weight was 210 000, and it showed a glass transition temperature, T_g, at 116 °C (measured by DSC). A selectively deuterated PMMA, PMMA-d_5, was used, where all but the ester CH_3 groups were replaced with deuterium ($M_w = 250\,000$, $T_g = 107$ °C). Details about the polymer synthesis and characterization can be found in ref 16. Poly(vinyl methyl ether) (PVME) was purchased from Scientific Polymer Products ($M_w = 95\,000$, $M_w/M_n = 2.5$, $T_g = 250$ K). Two completely deuterated polystyrene samples were used: PS(I) ($M_w = 56\,600$, $M_w/M_n = 1.26$) and PS(II) ($M_w = 1\,900\,000$, $M_w/M_n = 2.7$).

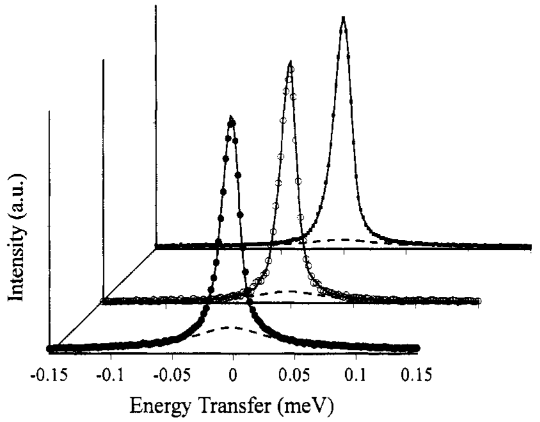

Figure 1. Quasielastic neutron scattering spectra measured at 140 K and 1.78 Å^{-1} for (●) PMMA-d_5, (○) 30-SCPE63/PMMA-d_5, and (■) 50-SCPE63/PMMA-d_5. The continuous lines represent a fit to the experimental data, and the dashed line indicates the quasielastic component.

Thin films of SCPE/PMMA were prepared by solution casting from methyl ethyl ketone (MEK). Two SCPE/PMMA samples were used: (a) a sample of 50/50 composition (by weight) (50-SCPE63/PMMA-d_5) and (b) a sample with 70% PMMA-d_5 content (30-SCPE63/PMMA-d_5). The LCST of 50-SCPE63/PMMA-d_5 was estimated at 400 K. 50-SCPE63/PMMA-d_5 samples were annealed at 400 and 458 K to achieve phase separation, whereas 30-SCPE63/PMMA-d_5 samples were annealed at 383 K, close to the phase boundary, and at 413 K, above the LCST.

PVME/PS-d films were prepared by casting solutions of known weights of PVME and deuterated PS in toluene and evaporating to dryness. Two samples were used: (a) containing 82% by weight of PS(I) and (b) containing 63% of PS(II).

Film thicknesses were chosen to give approximately 10% scattering of the incident neutron beam. This condition ensures that multiple scattering is kept to a minimum.

3.2. QENS Measurements. Measurements were performed on the back-scattering spectrometer *IRIS*[31] at the Rutherford Appleton Laboratory. The energy range covered during the experiments varied from −0.4 to +0.4 meV, the Q-range varied from 0.25 to 1.9 Å^{-1}, and the energy resolution was equal to 15 μeV (PG002 analyzer) and 11 μeV (MI006 analyzer). Measurements on 50-SCPE63/PMMA-d_5 were carried out in the temperature range from 40 to 290 K.[32]

The scattered intensities were corrected for detector efficiency and background effects, and the initial time of flight data were converted to the incoherent scattering law, $S_{\text{inc}}(Q,\omega)$, as a function of the energy transfer using standard RAL routines. The frequency spectra were Fourier transformed using the program FURY[33] to obtain the intermediate scattering function $I(Q,t)$.

4. Results

4.1. Analysis of the Frequency Data. The QENS spectra of two SCPE/PMMA-d_5 samples at 140 K and $Q = 1.78$ Å^{-1} are plotted in Figure 1, together with the QENS spectrum of pure PMMA at the same T and Q. The rotational motion of the ester methyl group in PMMA-d_5 has been studied in a large temperature range and at various energy resolutions.[14,16,32] On the high-resolution spectrometer *IRIS* molecular motion is detectable at temperatures above 60 K.[32] The temperature dependence of the quasielastic broadening has been discussed in a preceding paper.[14] A new approach to the QENS data analysis in glassy polymers was presented.

Here, we are interested in the effect of blending on the rotational motion of the ester side group in PMMA-d_5. The SCPE/PMMA blend is particularly suitable since the dynamics of the second component, SCPE, is not complicated by any secondary relaxations associated with side-group motions. For this reason, the scattering from SCPE is purely elastic below the glass transition temperature (T_g = 389 K), and it is therefore possible to study the dynamics of the PMMA-d_5 component in the blend at low temperature.

Figure 1 shows a distinctive difference between the quasielastic (QE) broadening in PMMA-d_5, 30-SCPE63/PMMA-d_5, and 50-SCPE63/PMMA-d_5. The amount of QE broadening is much smaller in the blends compared to the pure polymer. Furthermore, it follows the expected trend with composition: a decrease with increasing the SCPE content is observed.

The effect of blending with SCPE on the dynamics of the CH_3 group in PMMA-d_5 has already been discussed qualitatively[32] considering the temperature dependence of the incoherent dynamic structure factor $S_{inc}(Q,\omega)$ and of the mean-square displacement. In both cases, the absence of a pronounced quasielastic component in the blend was noticed. However, it needs to be pointed out that two effects contribute to increasing the elastic scattering in the blend: (1) a genuine blending effect possibly due to interactions between SCPE and PMMA-d_5 chains and (2) a "dilution effect" due to the protons in hydrogenous SCPE. The latter needs to be estimated in order to confirm the existence of any blending effect. No attempt was made in that early work to distinguish between the two contributions.

To follow our previous analysis of the ester CH_3 rotation in PMMA-d_5,[14,16,32] we first fit the QENS spectra using a δ function and a Lorentzian line, convoluted with the instrumental resolution function, plus a flat background. The experimental data together with the fit and the resolved quasielastic component are plotted in Figure 1 as a function of the SCPE content. The full widths at half-height (fwhh) of the Lorentzian line are comparable to those of PMMA-d_5. It is the elastic incoherent structure factor (EISF) which is much higher than that reported for pure PMMA-d_5. Again this is partly a consequence of the elastic scattering contribution of SCPE in the blend.

The method of Dianoux[34] is here adopted to correct the EISF for the dilution effect. In the calculation, the incoherent contribution of hydrogen (σ_{inc} = 80.27 barn) and chlorine (σ_{inc} = 5.3 barn) atoms in SCPE is taken into account, the incoherent cross section of the other nuclei being negligible. Since the contribution of the SCPE is purely elastic, only the δ-function component of the rotational scattering law is affected. Thus, the scattered intensity of the blend is proportional to:

$$x_{SCPE}[2.175\sigma_H + 1.285\sigma_{Cl}]\delta(\omega) + x_{PMMA}(3\sigma_H)S_{inc}^{rot}(Q,\omega) \quad (12)$$

where x_{SCPE} and x_{PMMA} are the molar fractions of SCPE and PMMA, respectively. $S_{inc}^{rot}(Q,\omega)$ is the incoherent rotational scattering law which was already defined in eq 4 for a single relaxation process. The term within square brackets in eq 12 was calculated considering the weight percentage of Cl atoms in SCPE. After normalizing the incoherent scattering law, we obtain:

$$S(Q,\omega) = \frac{p_f}{p_{tot}}\delta(\omega) + \frac{p_m}{p_{tot}}S_{inc}^{rot}(Q,\omega) \quad (13)$$

where p_f and p_m are the fraction of "fixed" and "mobile" scattering sites, respectively ($p_f + p_m = p_{tot}$). Looking at the blend, the coefficient of the δ-function is no longer the EISF, $A_0(Q)$, which is related to the geometry of the molecular motion, but it now represents an apparent value, $A_0'(Q)$, defined by:

$$A_0'(Q) = \frac{p_f}{p_{tot}} + \frac{p_m}{p_{tot}}A_0(Q) \quad (14)$$

for the 50-SCPE63/PMMA-d_5 blend:

$$[A_0'(Q,T)]_{50-Blend} = 0.522 + 0.478[A_0(Q,T)]_{PMMA} \quad (15)$$

and for the 30-SCPE63/PMMA-d_5 blend:

$$[A_0'(Q,T)]_{30-Blend} = 0.320 + 0.680[A_0(Q,T)]_{PMMA} \quad (16)$$

Equations 15 and 16 allow a direct comparison of the experimental EISF of PMMA-d_5 [$A_0(Q,T)$] and the blends. The temperature dependence of the EISF relative to pure PMMA-d_5, [$A_0(Q,T)$] in eqs 15 and 16, has been largely discussed in our previous publication,[14] and it is a consequence of the use of a bimodal distribution instead of a distribution of rotational frequencies. In that work, the temperature dependence of the EISF of pure PMMA was modeled using the following relationship:

$$[A_0'(Q,T)] = \frac{p_f}{p_{tot}}(T) + \frac{p_f}{p_{tot}}(T)\,[A_0(Q)] \quad (17)$$

which is equivalent to assuming two dynamic populations of methyl groups, the first one detectable within our energy range, the mobile CH_3, and the second one, the fixed CH_3 having a rotational frequency smaller than our instrumental resolution. Equation 17 can equally be used to interpret the EISF of the blends provided the elastic contribution from the protons of SCPE is taken into account (eqs 15 and 16).

The experimental EISFs of 50-SCPE63/PMMA-d_5 and 30-SCPE63/PMMA-d_5, $A_0'(Q,T)$, are plotted in parts a and b of Figure 2, respectively. Values calculated from the experimental EISF of PMMA-d_5 using eqs 15 and 16 are also shown. Comparison between calculated and experimental values clearly indicates that dilution effects cannot alone account for the high EISF values measured experimentally in the blend. We conclude that the dynamics of the ester CH_3 group in the blend is hindered, although there still exists some detectable broadening due to motion. Qualitatively, the dynamic effect is more pronounced in the blend with higher SCPE content.

To quantify the suppression of dynamics due to blending, it is necessary to consider the amount of coherent scattering. By assuming that the coherent scattering mainly arises from the deuterated PMMA component, it is possible to subtract this contribution, thus extracting the apparent EISF [$A_0'(Q,T)$].

Parts a and b of Figure 3 show plots of [$A_0'(Q,T)$] for the 50-SCPE63/PMMA-d_5 and 30-SCPE63/PMMA-d_5

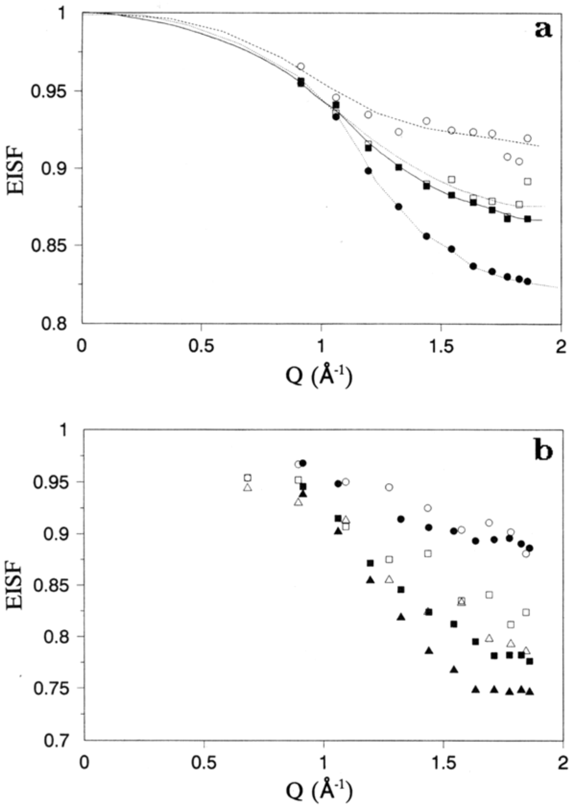

Figure 2. (a) Experimental EISF of 50-SCPE63/PMMA-d_5 at (○) 100 and (□) 140 K and comparison with values of EISF of PMMA-d_5 calculated from eq 15 at (■) 100 and (●) 140 K. (b) EISF of 30-SCPE63/PMMA-d_5 at (○) 80, (□) 120, and (△) 160 K and comparison with EISF of PMMA-d_5 calculated from eq 16 at (●) 80, (■) 120, and (▲) 160 K.

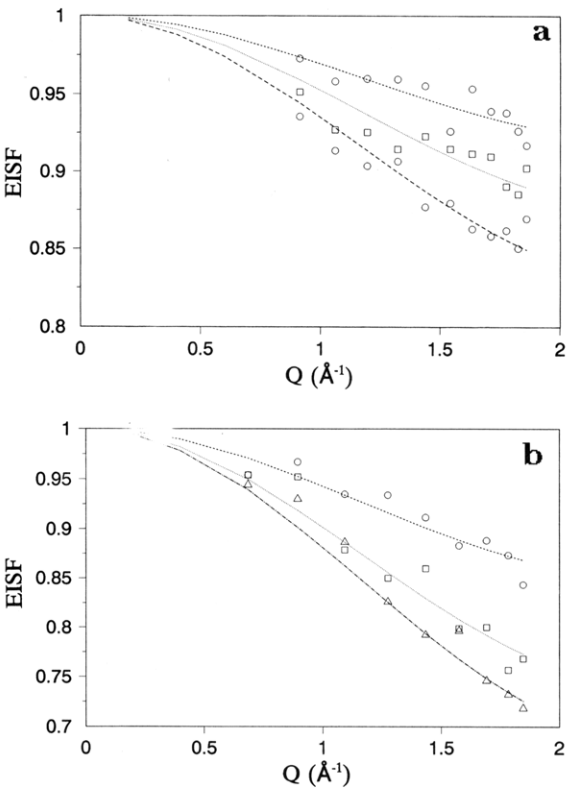

Figure 3. (a) EISF of 50-SCPE63/PMMA-d_5 after subtraction of coherent scattering at (○) 80, (□) 100, and (○) 140 K (lower EISF values). (b) EISF of 30-SCPE63/PMMA-d_5 at (○) 80, (□) 120, and (△) 160 K. The lines indicate a fit to the EISF using eq 17.

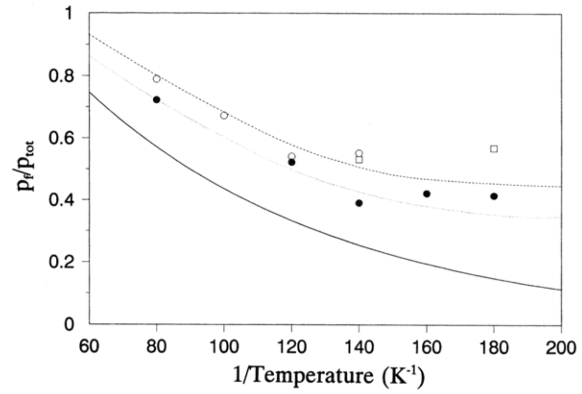

Figure 4. Ratio p_f/p_{tot} of 50-SCPE63/PMMA-d_5 (○,□) and (●) 30-SCPE63/PMMA-d_5. The dotted and dashed lines are guidelines through the experimental points, whereas the continuous line represents the PMMA-d_5 data.

blends. The lines indicate a fit using eq 17.

The fraction of fixed methyl groups, p_f/p_{tot}, is plotted in Figure 4 as a function of temperature, after subtraction of the elastic contribution from the SCPE protons. Calculated values for the miscible blends fall above the experimental points of PMMA-d_5. The largest difference is observed for the blend richer in SCPE.

We also attempted to study the effect of phase separation in blends. The 30-SCPE63/PMMA-d_5 sample was annealed at temperatures close to and above the phase boundary. A comparison between the ratios p_f/p_{tot} indicates that the results are consistent with the conclusion drawn earlier for the 50/50 blend, i.e., that there is a negligible difference between the behavior in the one- or two-phase region.[32]

The second blend investigated in this work, PS/PVME, shows a rather different behavior. The QENS data were analyzed at first as described for SCPE/PMMA samples. As noted for PVME, the temperature dependence of fwhh can be described by the Arrhenius law with an activation energy of 2.7 kJ mol^{-1}. This value is close to that reported by us for pure PVME (2.9 kJ mol^{-1}).[14]

The EISF of PS/PVME can be directly compared with the EISF of PVME. Any additional elastic contributions arising from the deuterium atoms in PS could be accounted for by the following equation:

$$8x_{PS}\sigma_D\delta(\omega) + 6x_{PVME}\sigma_H S_{inc}(Q,\omega)_{PVME} \qquad (18)$$

but it would only give small corrections both for the 18-PS(I)/PVME blend:

$$M(Q,T)_{18} = 0.0037 + 0.9963M(Q,T)_{PVME} \qquad (19)$$

and for the 37-PS(II)/PVME:

$$M(Q,T)_{37} = 0.010 + 0.990M(Q,T)_{PVME} \qquad (20)$$

The EISFs of the 18-PS(I)/PVME and of the 37-PS(II)/PVME blends were compared with the EISF of PVME in the temperature range from 100 to 200 K considering eqs 19 and 20. The results are in contrast with those observed for SCPE/PMMA-d_5 where the dynamics of the ester methyl group was found to be sensibly altered by blending. This could be attributed to the weaker interaction in the PS/PVME blend.

4.2. Time Domain Data Analysis. It has been already shown in recent publications that the dynamics

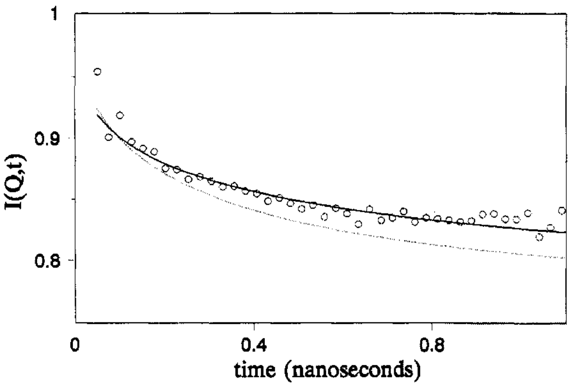

Figure 5. Intermediate scattering function $I(Q,T)$ of a 50/50 blend at 120 K and Q = 1.83 Å^{-1}. The continuous line indicates a fit to the experimental data using eq 11, whereas the dotted line was calculated from the PMMA-d_5 data adding the elastic contribution of SCPE (see text).

of side groups such as methyl groups in amorphous polymers can be described correctly in terms of a distribution of relaxation times or, alternatively, correlation times. In particular, we have recently revised QENS data of the ester CH_3 group reorientation in PMMA-d_5 by considering a distribution of relaxation times[14] which was neglected in previous work.[16,32] We have also shown that, in agreement with other authors,[26,27] the use of a bimodal distribution leads to numerous inconsistent results: the temperature dependence of the EISF, the non-Arrhenius behavior, and the resolution dependence of the fwhh. We anticipate that our main conclusions on the blending effect will not be altered by using a distribution instead of two populations of CH_3 groups. However, it is interesting to compare our findings in the blends with those of the pure polymers using the analysis of the intermediate scattering function, $I(Q,t)$.

The intermediate scattering function $I(Q,t)$ of the 50/50 blend at 120 K and Q = 1.83 Å^{-1} is plotted in Figure 5 together with a fit using eq 11. The $I(Q,t)$ determined from the PMMA-d_5 data at the same temperature and Q is also shown in Figure 5. The "dilution effect" was taken into account by adding the extra elastic contribution due to the SCPE protons to the intermediate scattering function of PMMA-d_5 in a way similar to that described in the preceding section. If the reduced quasielastic broadening observed in the QENS spectra were merely a consequence of dilution, then the $I(Q,t)$ calculated from PMMA-d_5 and the experimental data of the 50/50 blend should match. The difference between the two lines in Figure 5 has to be attributed to the presence of the SCPE component. We conclude that blending alters the dynamics of the ester CH_3 group, and, in order to quantify this effect, we compare the fitting parameters of pure PMMA-d_5 and blended with SCPE.

The correlation times are plotted in Figure 6a as $2/\tau$ versus inverse temperature. As noted previously for PMMA-d_5, the behavior is Arrhenius but the activation energy E_a differs in the blend compared to the pure polymers. Values of E_a amount to 6.2 kJ/mol in the 50/50 blend and 5.3 kJ/mol in the 30/70 blend compared to a value of 4.6 kJ/mol measured for PMMA-d_5. E_a increases with SCPE content, thus indicating that the second component, SCPE, hinders the rotational motion of the CH_3 group.

However, it is the parameter β that reveals the most pronounced effect due to blending as illustrated in Figure 6b. In contrast to the PMMA data,[14] the width of the distribution of correlation times appears to be temperature independent. Furthermore, β values are distinctly lower in the blend than in PMMA-d_5. This indicates that the distribution of correlation times broadens considerably in the blend compared to the pure polymers.

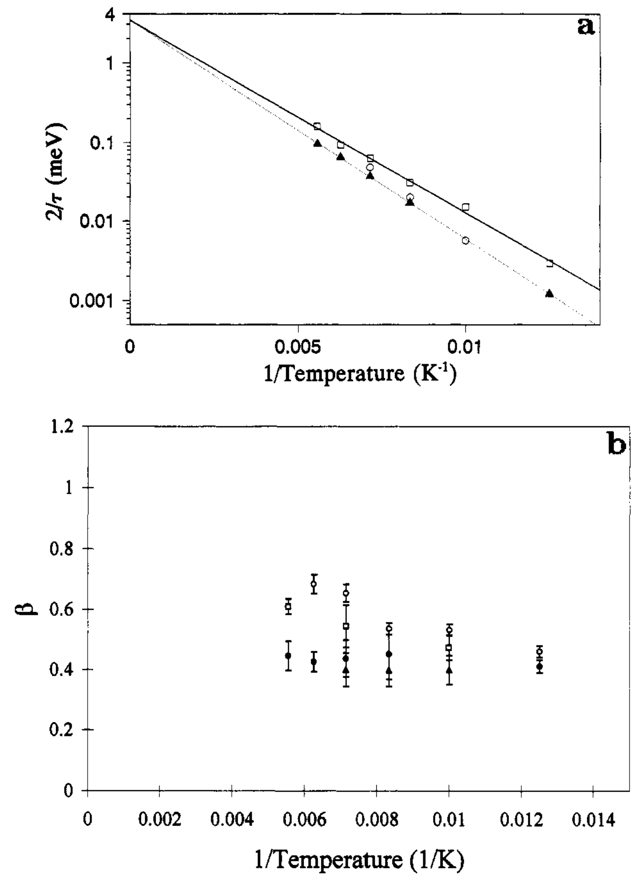

Figure 6. (a) Characteristic times, plotted as $2/\tau$ in meV, versus inverse temperature for PMMA-d_5 (□), 30-SCPE63/PMMA-d_5 (▲), and 50-SCPE63/PMMA-d_5 (○). The lines indicate a fit to the PMMA and SCPE/PMMA data. (b) Parameter β as a function of inverse temperature for PMMA-d_5 (○,□) and 30-SCPE63/PMMA-d_5 (●) and 50-SCPE63/PMMA-d_5 (▲).

The behavior of the PS/PVME blends is very similar to that of the pure polymer. The intermediate scattering functions $I(Q,t)$ of 18-PS(I)/PVME and 37-PS(II)/PVME are practically indistinguishable, at a given temperature and Q from those for PVME. Therefore, both the characteristic times and the parameter β are unchanged in the blend, as illustrated in parts a and b of Figure 7 where $2/\tau$ and β are plotted.

5. Discussion

The QENS spectra of SCPE/PMMA-d_5 and PS/PVME show a quasielastic component which is attributed to the reorientational motion of the ester methyl group in PMMA-d_5 and the ether CH_3 in PVME.

The local dynamics of PVME in blends with PS is very similar to that of the pure polymer, whereas a strong influence due to blending was detected in the SCPE/PMMA blend. Such a discrepancy between the results of the two blends is not surprising, and indeed it has already been noted that dynamic effects produced by blending appear to be highly dependent on the system investigated. For example, both small effects in sub-

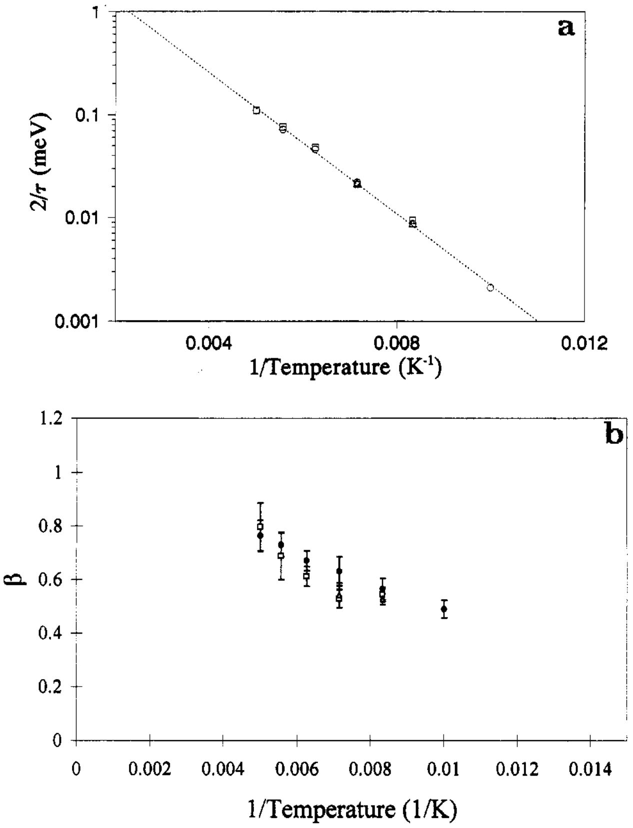

Figure 7. (a) Characteristic times, plotted as $2/\tau$ in meV, versus inverse temperature for PVME (○), 18-PS(I)/PVME (□), and 37-PS(II)/PVME (△). The line represents a fit to the experimental data. (b) Parameter β as a function of inverse temperature for PVME (●), 18-PS(I)/PVME (□), and 37-PS-(II)/PVME (△).

glass relaxations[35] and a pronounced antiplasticization effect have been observed.[11-13]

A suppression of secondary relaxations was observed in polycarbonate/PMMA[11,12] and polystyrene/poly(2,6-dimethyl-1,3-phenylene oxide) (PS/PXE)[13] blends. The local motion of the Chloral-PC units which is attributed to π flips of the phenylene groups appeared to be suppressed by the presence of the second component, PMMA.[12] Similarly, deuterium NMR line-shape analysis has shown that the population of fast π flippers in PS/PXE blends is slightly reduced compared to the pure PS component, at the same temperature. Our results for the SCPE/PMMA system seem to be consistent with these findings, i.e., that by adding a second polymeric component the sub-T_g relaxation is reduced. However, this is only a feature of the present system and not a general characteristic of blends. The same motion, a methyl group rotation, appeared in fact to be unaltered in the PS/PVME system.

To explain our results we compare the behavior of the SCPE/PMMA and PS/PVME blends using the lattice model with six nearest neighbors. Following the procedure of de los Santos et al.,[12] we define a lattice site as containing one PMMA or one PVME repeat unit. The number of SCPE and PS monomer units occupying one lattice site can be estimated from the ratio between the molar volumes of the components in the blend. From a knowledge of the volume fractions it is possible to define p as the fraction of lattice sites occupied by PMMA or PVME units and d as the number of lattice sites containing the second components, SCPE or PS.

The fraction of PMMA or PVME units F_i, where i represents the nearest-neighbor lattice sites occupied by the second component, can be calculated. A purely statistically random arrangement of the neighboring lattice sites is assumed.

Table 1. Populations Calculated According to the Lattice Model for the SCPE/PMMA and PS/PVME Blends

	50/50 SCPE/PMMA	30/70 SCPE/PMMA	18/82 PS/PVME	37/63 PS/PVME
ϕ (PMMA or PVME)	0.408	0.616	0.898	0.767
p	0.537	0.730	0.829	0.645
d	0.463	0.270	0.171	0.355
F_0	0.0832	0.284	0.473	0.173
F_1	0.287	0.420	0.389	0.381
F_2	0.371	0.233	0.120	0.315
F_3	0.213	0.0574	0.0165	0.116
F_4	0.0459	0.0053	0.00085	0.0159
f_u	0.0832	0.284	0.473	0.173
f_a	0.917	0.711	0.527	0.827

The results of our calculations of the fractions F_i for i varying between 0 and 4:

$$\begin{aligned} F_0 &= p^4 \\ F_1 &= 4p^3d \\ F_2 &= 6p^2d^2 \\ F_3 &= 4pd^3 \\ F_4 &= d^4 \end{aligned} \qquad (21)$$

are listed in Table 1 for the SCPE/PMMA and PS/PVME systems.

It has already been noted that the suppression of the β-relaxation in BPA-PC or Chloral-PC, following the addition of a second polymeric component, is similar to the effect observed after addition of a low molecular weight diluent.[38] In both cases, i.e., for the blend and the polymer/diluent system, three types of polymer units were distinguished:[12,38] (1) those surrounded only by the same polymer units, (2) units which are in contact with only one diluent molecule or second polymer component, and (3) units surrounded by lattice sites occupied by more than one second component unit. It was assumed that units surrounded by the same monomers relax as in the pure polymer system, whereas antiplasticization occurs when one neighboring site is occupied by the second component due to improved packing. Polymer units which are in contact with two or more diluent units were assumed to show increased mobility with respect to the pure polymer, as a consequence of the fast rotational diffusion of the diluent.[38] The development of an additional low-temperature minimum in the proton $T_{1\varrho}$ data of the BPA-PC/diluent system due to phenylene groups moving more rapidly than in the pure polymer confirmed that clusters of diluent molecules have a pronounced effect on sub-T_g relaxations.[38] The Chloral-PC/PMMA system[12] showed a similar behavior with the development of a new relaxation process at high PMMA concentrations which was attributed to Chloral-PC units relaxing cooperatively with the ester side-group rotation in PMMA.

The situations in the Chloral-PC/PMMA system and in our SCPE/PMMA blend differ considerably. The SCPE component does not exhibit any relaxation below the glass transition due to the absence of side groups, as also confirmed experimentally.[32] Therefore, we expect a population of PMMA-d_5 units which relax as in the pure polymer, $f_u = F_0$ in eq 21, and a second population, $f_a = F_1 + F_2 + F_3 + F_4$ that corresponds to PMMA-d_5 units with at least one SCPE unit as a neighbor. The latter fraction of polymer units is associated with the suppression of sub-T_g relaxations. Values of f_u and f_a are reported in Table 1. By simple statistical arguments a pronounced dynamic effect is expected in the SCPE/PMMA system with a fractional population of antiplasticized units which is as large as 0.917 in the 50/50 blend.

The PS/PVME blend may behave very differently compared to SCPE/PMMA but close to the Chloral-PC/PMMA system. Although polystyrene is less mobile than PVME having a higher glass transition temperature, it exhibits a low-temperature relaxation which has been identified with a small fraction of phenylene groups undergoing π flips.[36,37] Following the results on the Chloral-PC/PMMA blend,[12] cooperative motion might take place when the PVME units are surrounded by lattice sites occupied by two or more PS lattice units. However, our QENS results do not give any direct evidence for the existence of three types of PVME units and in particular for the presence of cooperative relaxations between the two polymer components. For this reason only two fractional populations of PVME units are reported in Table 1: (a) $f_u = F_0$ which indicates the fractional population of PVME units whose dynamics is unaltered and (b) f_a which represents units whose dynamics is altered by the presence of the second component. Although values of f_a are very close for the two blends, one must bear in mind that the intrinsic dynamic of the added polymer might determine the extent of the suppression of sub-T_g relaxations. For the SCPE/PMMA blend f_a represents the antiplasticized component, but for PS/PVME f_a might include PVME units which relax cooperatively with PS units and therefore still give a substantial contribution to the dynamics.

By applying the lattice model and considering the intrinsic dynamics of the added polymeric component, it is possible to explain qualitatively the difference between the dynamic behavior observed for the SCPE/PMMA and the PS/PVME blends. The lattice model considers mixing of the two polymer species as a purely statistical random process. However, due to the existence of polymer−polymer interactions, deviations from random mixing might take place. These effects are expected to be more pronounced in the SCPE/PMMA blend compared to the PS/PVME system due to the stronger specific interaction in the former blend.

6. Conclusions

We have examined in detail the local dynamics of two polymer blends: PS/PVME and SCPE/PMMA. Both systems are partially miscible and exhibit a lower critical solution temperature behavior. The local motions of interest in our study were the ester methyl group rotation in PMMA-d_5 and the ether CH_3 reorientation in PVME. These high-frequency motions were investigated in detail using quasielastic neutron scattering.[14]

In this work we have studied the effect of blending following the local dynamics of one of the components as a function of temperature below T_g. Although the specific molecular motion probed is similar in the two blends, with values of apparent activation energy and width of the distribution of relaxation times which are very close in the two pure polymers, PMMA-d_5 and PVME, we observe that the addition of a second polymeric component appears to produce a very different effect on the CH_3 dynamics in the two systems.

In particular, the SCPE component in SCPE/PMMA-d_5 appears to have a pronounced effect on the ester CH_3 dynamics. This is indicated by the higher activation energy and by the lower β values measured in the blends. The distribution of relaxation times broadens considerably in the SCPE/PMMA system. In contrast, no effect was observed in the PS/PVME blend.

We have attempted to explain these differences considering the lattice model, hence on a purely statistical basis. Although the model is very simplified, it indicates that, if one considers random mixing and intrinsic differences among the mobilities of the second component in the blend, there is good agreement with the experimental results. In particular, the absence of any dynamic effect on the methyl group rotation in the PS/PVME blend is here considered to be a consequence of the dynamics of the PS units compared to that of SCPE in the SCPE/PMMA blend. In addition, the weaker interaction between PS and PVME might be responsible for the differences observed in the two blends.

The agreement with the experimental data is only qualitative, and we made no attempt to explain in a quantitative way our findings. The broadening of the distribution of relaxation times and the higher activation energy measured in the blend for the ester CH_3 rotation in PMMA-d_5 give only an indication of a general slowing down of the motion. However, this is a more complicated picture than assumed by the lattice model. For the SCPE/PMMA system, the lattice model considers only the existence of two populations of PMMA-d_5 units: units that are relaxing as in the pure polymer and units which are antiplasticized.

We pointed out in section 4.1 that, in the SCPE/PMMA system, no difference between the behavior in the one- and two-phase region could be detected. This might appear at first surprising but can be explained considering that the two coexisting phases in a phase-separated blend are not constituted by the pure polymers but consist of a mixture of the SCPE and PMMA of different composition (and near the critical composition these may not be very different). The local environment in the two phases might not therefore differ enough from that of the blend in the miscible region to be detectable by QENS.

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