Ester methyl group rotation in poly(methyl methacrylate) and in the blend solution chlorinated polyethylene/poly(methyl methacrylate). A quasielastic neutron scattering study*

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Quasielastic neutron scattering (QNS) is employed to study the ester methyl group rotation in poly(methyl methacrylate) (PMMA) and, for the first time, in a solution chlorinated polyethylene/poly(methyl methacrylate) (SCPE/PMMA) blend. The QNS measurements for PMMA, SCPE and SCPE/PMMA were made in the temperature range 7–180, 17–290 and 40–290 K, respectively, and over the Q range 0.25–1.9 $\mathrm{Å}^{-1}$. Our results with respect to the bulk PMMA confirm the earlier assignment of the quasielastic broadening as being due to the ester methyl group rotation which persists at low temperatures, however, with decreasing intensity. Our results with respect to the phase separated—at 55 K above the cloud point curve—SCPE/PMMA blend revealed that blending of PMMA with SCPE produces a stronger effect on the O–CH_3 population than a simple dilution. This is discussed in terms of the different mobilities of the two homopolymers which lead to an increase to the barrier to rotation and the proximity of the homopolymer chains in the blend.

(Keywords: ester methyl group rotation in PMMA; ester methyl group rotation in SCPE/PMMA; quasielastic neutron scattering)

INTRODUCTION

The assignment and identification of the relaxation processes in poly(methyl methacrylate) (PMMA) has been the subject of numerous studies[1]. Mechanical relaxation[1,2] (MR) and dielectric relaxation[1,3,4] (DR) experiments are usually employed to study the primary (α-) relaxation due to segmental motion and the β-relaxation due to rotation of the side group combined with matrix effects. However, the low temperature/high frequency relaxations related to the rotation of the α-methyl (γ-relaxation) and especially the ester methyl (δ-relaxation) groups give rise to very shallow peaks in the MR experiment[5,6] and are not detectable in the DR experiment. Alternatively, quasielastic neutron scattering (QNS) operating at higher frequencies with the use of deuterium labelling is an appropriate technique to study these relaxations.

QNS was employed earlier in the study of PMMA in the temperature range from 150 to 390 K[7]. A quasielastic component with Q-independent linewidth and with a peculiar temperature dependence was resolved and attributed to the ester methyl group rotation. The peculiar temperature dependence was explained by the inclusion of higher terms in the Fourier series expansion of the potential function for the methyl group rotation.

The purpose of the present study is two-fold. First, to extend the measurements of PMMA at lower temperatures (down to 7 K) with emphasis on the ester methyl group rotation and second, to investigate the effect of a complex environment on this low temperature/high frequency relaxation. For the latter study, a blend of the same PMMA with another polymer was used. The requirement is that the structure of this polymer is as simple as possible—with no side groups and preferably with as few relaxations in the glassy state as possible—so that it would not interfere with the ester methyl group rotation. In this way the O–CH_3 group rotation can be used as a fingerprint of molecular mobility in the blend. In view of these requirements, solution chlorinated polyethylene (SCPE) was chosen. It is the first time, to our knowledge, that QNS has been employed to study molecular motion in a blend. SCPE and PMMA have similar glass transition temperatures (T_gs) but they possess different mobilities at low temperatures making the SCPE/PMMA blend a good candidate for the present investigation.

Our QNS results with respect to the PMMA confirm the assignment of the ester methyl group rotation as the relaxation responsible for the quasielastic broadening in the neutron scattering experiment. Furthermore, the temperature dependence of the quasielastic intensity and of the elastic incoherent structure factor (EISF) is discussed in terms of a temperature-dependent number of protons performing angular jumps. For the phase separated SCPE/PMMA blend our results, with respect

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to the elastic intensity and the mean-square-displacement of the protons, reveal that the alteration of the O–CH_3 environment by blending with SCPE has a strong effect on the number of mobile groups at low temperatures.

EXPERIMENTAL

Materials

Two PMMA samples were used: a selectively deuterated PMMA (I) in which all but the ester methyl hydrogens have been replaced with deuterium and a selectively deuterated PMMA in which all but the α-methyl hydrogens have been replaced with deuterium. The synthesis of the samples is described elsewhere[7]. Two SCPE samples with different chlorine content were used and the molecular characteristics of the samples used in the present study are given in *Table 1*. The chlorination procedure of polyethylene (PE) for the preparation of SCPE is described elsewhere[8]. In contrast to suspension-chlorinated PE the SCPE samples are amorphous due to the random distribution of chlorine atoms along the chain. The SCPE/PMMA blend used in the NS study had a 50/50 composition. The chlorine content of the SCPE used in the blend was 63% and the PMMA was deuterated in all but the ester group (sample I, *Table 1*).

The SCPE/PMMA blend has been previously studied mainly by static techniques: differential thermal analysis[9], small-angle neutron scattering[10,11] (SANS), small-angle X-rays[10] (SAXS) and neutron reflection[12] at various compositions and chlorine contents. For this blend the enthalpy of mixing is negative. Moreover, this blend exhibits a lower critical solution temperature (*LCST*) the absolute value of which depends on the chlorine content[13]. For the present SCPE63/PMMA (50/50) blend the *LCST* was estimated at ~400 K. Therefore, it is expected that by annealing the sample above 400 K the blend will phase separate into PMMA- and SCPE-rich components.

Measurements

The NS experiments were carried out on the IRIS back-scattering spectrometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. The analyser crystals were pyrolitic graphite and the 002 reflection was used. The energy range covered was from −0.4 to 0.4 meV with energy resolution of 15 μeV over a Q range from 0.25 to 1.9 Å^{-1}. The polymer samples were contained in a flat aluminium container and the sample thickness was set to 0.2 mm—in order to suppress multiple scattering—resulting in a transmission of ~89%. The thin films of the bulk polymers and the blend were prepared by evaporating solutions containing known weights of PMMA and/or SCPE to dryness. The aluminium container was then mounted in a variable-temperature liquid helium cryostat at 45° to the incident beam. Measurements were made in the following temperature ranges (ΔT): PMMA: ΔT=7–180 K, SCPE56 and SCPE63: ΔT=17–290 K and SCPE63/PMMA (50/50): ΔT=40–290 K. During the experiment, the temperature dependence of the elastic intensity scattered within a small frequency interval about $\omega \approx 0$ (elastic window scan) was first monitored. In this way, the temperature dependence of the elastic intensity, $S(Q, \omega \approx 0)$, was determined for samples I, II, III and IV over the whole temperature range. The elastic window scan for SCPE63 and SCPE56 gave identical results and is depicted in *Figure 1*. The corresponding scans for PMMA and SCPE63/PMMA are shown in *Figures 2* and *3*, respectively.

Second, long-time measurements were performed at the temperatures of interest. The temperatures chosen were: 7, 15, 20, 30, 40, 60, 80, 100, 120, 140, 160 and

Table 1 Molecular characteristics of the samples

Polymer	M_w ($\times 10^{-5}$) (g mol^{-1})	T_g (°C)	Cl content (%)
PMMA[a] (I)	2.5	107	
SCPE63 (II)	2.1	116	63
SCPE56 (III)	1.9	44	56
SCPE63/PMMA (50/50) (IV)		110	

[a] From n.m.r. analysis: 50% syndiotactic, 40% heterotactic and 10% isotactic triads

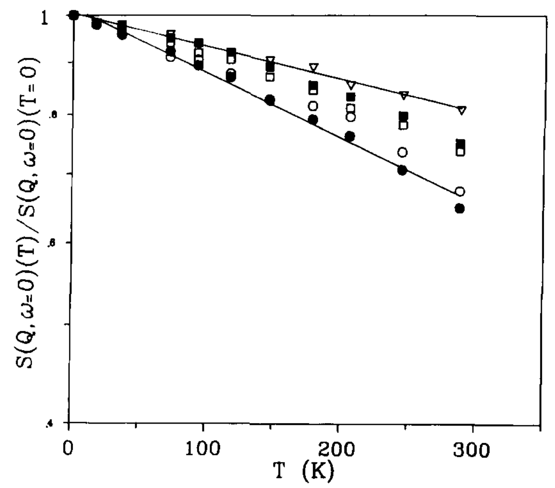

Figure 1 Temperature dependence of the incoherent dynamic structure factor $S(Q, \omega \approx 0)$ for SCPE56 (sample III, *Table 1*) normalized to its value at T=0 K (elastic window scan), plotted for selected Q values: (●) 1.80; (○) 1.62; (□) 1.32; (■) 0.96; (▽) 0.53 Å^{-1}. Data points are averaged within an interval of ±0.1 Å^{-1} about the given Q values. The elastic intensity obeys the Debye–Waller factor up to 290 K

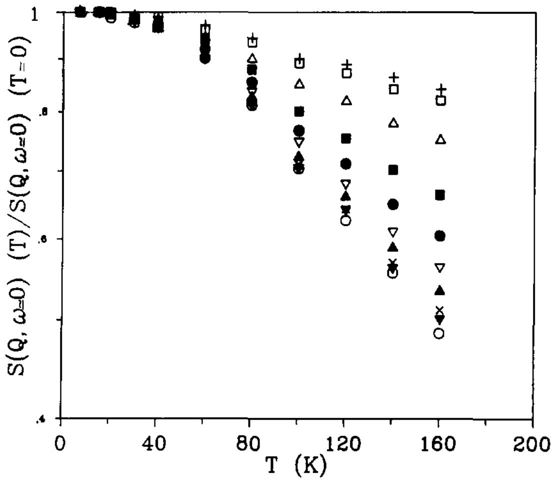

Figure 2 Temperature dependence of the normalized incoherent dynamic structure factor $S(Q, \omega \approx 0)$ for PMMA (sample I, *Table 1*), plotted for selected Q values: (○) 1.86; (▼) 1.78; (×) 1.71; (▲) 1.63; (▽) 1.54; (●) 1.44; (■) 1.32; (△) 1.2; (□) 0.91; (+) 0.76 Å^{-1}. The decrease of the elastic intensity beyond the Debye–Waller factor at T>60 K is due to motion in PMMA

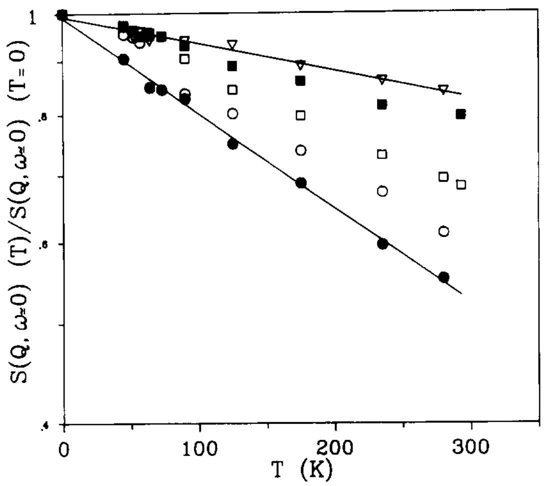

Figure 3 Temperature dependence of the normalized incoherent dynamic structure factor $S(Q, \omega \approx 0)$ for the SCPE63/PMMA (50/50) blend (sample IV, *Table 1*) after annealing at 458 K, plotted for selected Q values: (●) 1.80; (○) 1.62; (□) 1.32; (■) 0.96; (▽) 0.53 Å^{-1}. Data points are averaged within an interval of $\pm 0.1\,\text{Å}^{-1}$ about the given values. The elastic intensity can be described by a Debye–Waller factor up to 290 K

180 K for PMMA, 40, 60, 80, 100, 120, 140 and 160 K for SCPE63 and 40, 60, 80, 100, 120, 140, 160 and 180 K for the blend SCPE63/PMMA (50/50). The QNS experiment from the selectively deuterated PMMA is dominated by the incoherent scattering of hydrogen atoms, because deuterated PMMA contains C, O, H and D atoms and the incoherent scattering of hydrogen is much higher than the coherent cross-sections of C, O and D atoms. The incoherent scattering from SCPE is again dominated by hydrogen atoms although chlorine atoms can contribute to a small intensity ($\sigma_{\mathrm{Cl}}/\sigma_{\mathrm{H}} \sim 0.066$). Therefore, to a good approximation, QNS measures the incoherent structure factor:

$$S_{\mathrm{inc}}(Q, \omega) \sim \int \exp(-\mathrm{i}\omega t) < \exp\{-\mathrm{i}Q[R(0) - R(t)]\} > \mathrm{d}t \tag{1}$$

thus containing information on both the geometry and the time-scale of the single-particle dynamics. After the initial neutron counts were corrected for detector and monitor efficiency and for background effects the observed time-of-flight spectrum was converted to a differential scattering cross-section $\partial^2\sigma/\partial\Omega\partial E$. The incoherent scattering law $S_{\mathrm{inc}}(Q, \omega)$ was calculated from:

$$S_{\mathrm{inc}}(Q, \omega) = \frac{k_{\mathrm{i}}}{k_{\mathrm{s}}} \frac{1}{(\langle b^2 \rangle - \langle b \rangle^2)} \frac{\partial^2 \sigma}{\partial\Omega\partial E} \tag{2}$$

where k_{i} and k_{s} are the length of the incident and scattered wavevectors, respectively, and b is the scattering length for hydrogen atoms.

RESULTS AND DISCUSSION

Poly(methyl methacrylate)

QNS measurements for two stereoisomers of PMMA have been reported earlier in the temperature range $150 < T < 390\,\mathrm{K}$[7]. Here we extend the temperature range towards lower temperatures, down to 7 K. Firstly, $S(Q, \omega \approx 0)$ was monitored in the temperature range 7 to 180 K for sample I. Values of $S(Q, \omega \approx 0)$ normalized relative to the extrapolated intensity at 0 K are shown in *Figure 2* for different Q values. In the absence of quasielastic broadening, the decrease of the elastic intensity can be described in terms of the Debye model for harmonic solids with a Debye–Waller factor (DWF):

$$\frac{S(Q, \omega \approx 0)(T)}{S(Q, \omega \approx 0)(T=0)} \sim \mathrm{e}^{-\langle r^2 \rangle Q^2} \qquad \langle r^2 \rangle \sim T \tag{3}$$

Thus, $\ln[S(Q, \omega \approx 0)(T)/S(Q, \omega \approx 0)(T \approx 0)] \sim -T$ according to the DWF, and any non-linearity of the elastic window scan shown in *Figure 2* is a result of a motion. A pertinent feature of *Figure 2* is that this non-linearity starts already at low temperatures ($\sim 60\,\mathrm{K}$) and is strongly Q-dependent at higher temperatures. Therefore, a normal DWF *cannot* describe the extra decrease of the elastic intensity in PMMA. Recent mode coupling theory[14–16] (MCT) predicts an anomalous behaviour of the DWF as a result of a 'fast' relaxation, called the 'β-process'. As will be seen, the anomaly of the DWF shown in *Figure 2* for PMMA is not related to the MCT predictions but instead it has a specific molecular origin and occurs at temperatures much below the T_{g}.

To demonstrate the non-linearity of the elastic intensity with temperature the Q^2 dependence of the normalized elastic intensity was exploited. This is shown in *Figure 4* for different temperatures: $\ln S(Q, \omega \approx 0)(T)$ is non-linear in Q^2 for temperatures above 60 K. Already at 60 K, systematic deviations occur which are due to motion. Another interesting feature of *Figure 4* is that the normalized elastic intensity does not approach one at small Q^2 values as would be expected from equation (3). This constitutes a strong indication that equation (3) can no longer describe the elastic intensity at low Q. A temperature-dependent term should be added in the usual DWF to account for the non-zero intercept of $\ln S(Q, \omega \approx 0)$ in the $Q \rightarrow 0$ limit. The origin of this term may be related to the temperature dependence of the incoherent cross-section investigated earlier in a number of polymers at rather high temperatures[17] and/or to multiple scattering and possible absorption effects[18,19].

The T and Q dependence of $S(Q, \omega \approx 0)(T)$ shown in *Figures 2* and *4*, respectively, provide a strong indication for quasielastic motion at $T \geqslant 60\,K$. To explore further the quasielastic broadening of PMMA $S(Q, \omega)$ was measured at different temperatures from 7 to 180 K. The

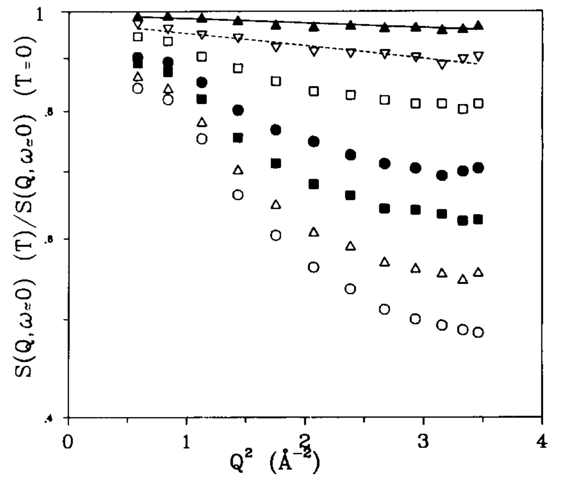

Figure 4 Q^2 dependence of the normalized incoherent dynamic factor for PMMA plotted for selected temperatures: (▲) 40; (▽) 60; (□) 80; (●) 100; (■) 120; (△) 140; (○) 160 K

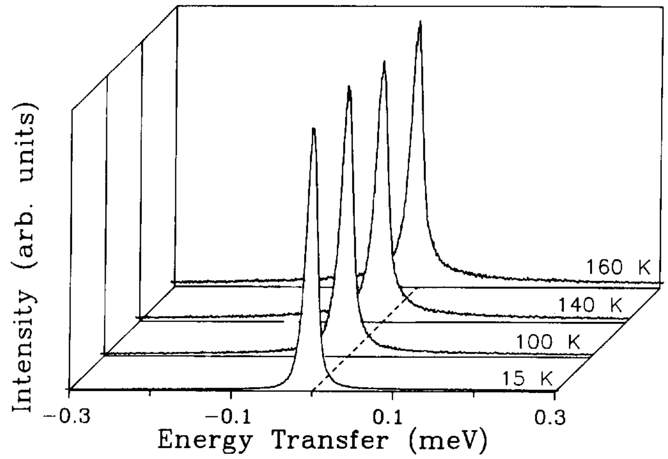

Figure 5 Quasielastic neutron scattering spectra of PMMA as a function of temperature at $Q = 1.78\,\text{Å}^{-1}$

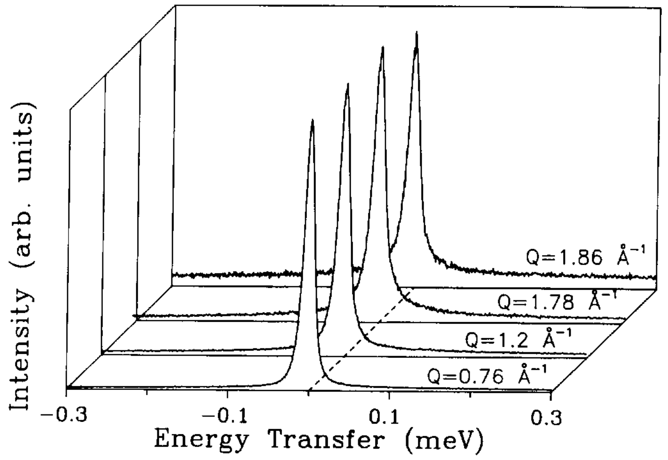

Figure 6 Quasielastic neutron scattering spectra of PMMA at different Q values, as indicated, at $T = 160\,\text{K}$

lowest temperature measurement (7 K) was used as the resolution function. Typical spectra at different temperatures for $Q = 1.78\,\text{Å}^{-1}$ are shown in *Figure 5*. The spectra in *Figure 5* show a quasielastic broadening which becomes more intense with increasing temperature together with an increasing background. The Q dependence shown in *Figure 6* at 160 K exhibits similar behaviour.

The origin of the low temperature quasielastic broadening in PMMA for which all but the ester methyl hydrogens are deuterated can result either from a rotation of the side group as a whole around the C–C bond, or from rotation of the CH_3 group about the O–CH_3 axis. However, experimental[1] and theoretical studies[20] have shown that the barrier to the side group rotation (also called β-relaxation) is much higher ($\sim 75\,\text{kJ mol}^{-1}$) than that of the ester methyl group rotation. The origin of the significant background in the PMMA spectra (*Figures 5* and *6*) which increases both with increasing T and Q is probably due to fast relaxation processes relaxing outside the energy window of the spectrometer. Low energy excitations in various amorphous polymers revealed the existence of a broad excitation peak in the energy range 1–4 meV, irrespective of the chemical structure[21]. With increasing temperature they become stronger but they do not shift in frequency. Moreover, such excitations were not observed in highly crystalline polymers and it was subsequently suggested that low energy excitation is a universal property for amorphous materials. These excitations relaxing outside the energy range of our spectrometer can explain qualitatively the temperature-dependent background.

Selective deuteration can also help to identify the molecular origin of the quasielastic peak. For this purpose, a second PMMA was used in which all but the α-methyl hydrogens have been replaced with deuterium. The result of the comparison between the two selectively deuterated PMMA is shown in *Figure 7*. The quasielastic peak observed in the O–CH_3 PMMA is absent in the O–CD_3, sample. *Figure 7* provides extra support to the claim here and in earlier results that it is the O–CH_3 motion which gives rise to the quasielastic broadening in PMMA and this motion persists at low temperatures due to the low height of the barrier. The hydrogenous α-methyl group in the PMMA sample does not give rise to a quasielastic broadening in the neutron scattering experiment because the barrier height to rotation for this group is much higher[20] ($\sim 28\,\text{kJ mol}^{-1}$) than that of the ester methyl group.

After identifying the molecular mechanism behind the quasielastic broadening in PMMA the measured spectra were fitted with a curve consisting of a delta function, a Lorentzian and a flat background. This is the simplest function which gives a good fit to all experimental data. This curve is then convoluted with the resolution function. *Figure 8* shows a typical spectrum at $T = 180\,\text{K}$ and $Q = 1.84\,\text{Å}^{-1}$ showing the delta function and the broad Lorentzian convoluted with the instrument resolution function. Subsequently, the T and Q dependence and the relative intensity of the quasielastic peak was monitored.

Assuming a three-fold symmetry for the ester methyl group rotation, the incoherent scattering law corresponding to a proton jumping between three equidistant equivalent sites for an unoriented sample is[22]:

$$S_{\text{inc}}(Q,\omega) = \frac{1}{3}\delta(\omega)\left(1 + \frac{2\sin\sqrt{3}Q\alpha}{\sqrt{3}Q\alpha}\right) + \frac{2}{3}\left(1 - \frac{\sin\sqrt{3}Q\alpha}{\sqrt{3}Q\alpha}\right)\frac{1}{\pi}L\left(\frac{3}{\tau}\right) \tag{4}$$

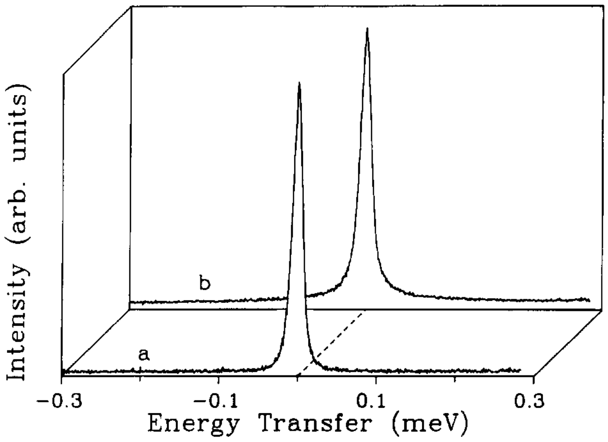

Figure 7 Quasielastic neutron scattering spectra of two PMMA samples at $T = 140\,\text{K}$ and $Q = 1.84\,\text{Å}^{-1}$: (a) PMMA with all but the α-methyl hydrogens replaced with deuterium; (b): PMMA with all but the ester methyl hydrogens replaced with deuterium. The quasielastic broadening observed in (b) is absent in (a) (see text)

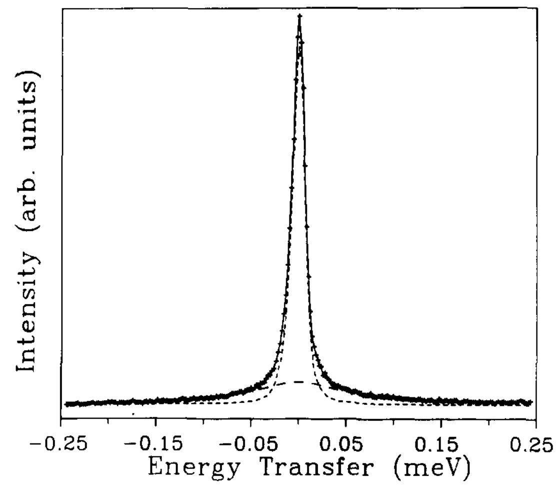

Figure 8 Quasielastic neutron scattering spectrum of PMMA (sample I, *Table 1*) at $T=180\,K$ and $Q=1.84\,\text{Å}^{-1}$ showing a delta function (----), a broad Lorentzian (— — —) (convoluted with the instrument resolution function) on top of a 'flat' background

with

$$L\left(\frac{3}{\tau}\right)=\frac{3/\tau}{(3/\tau)^2+\omega^2} \qquad (5)$$

Equation (4) for $S_{\text{inc}}(Q,\omega)$ is a summation of an elastic part (delta function) and a quasielastic part (broad Lorentzian) with Q-independent linewidth. The linewidth of the quasielastic component provides information about the time-scale of the motion and the coefficient of the delta function, which has the dimension of a structure factor and is the EISF, gives information on the geometry of the motion. In *Figure 9* is plotted the measured EISF from the fitting procedure described earlier with respect to *Figure 8*, defined as the ratio of the integrated intensity of the elastic peak over the total intensity under the elastic and quasielastic peaks. The Q dependence of the calculated EISF from the elastic part of $S_{\text{inc}}(Q,\omega)$ [equation (4)] given by:

$$\text{EISF}=\frac{1}{3}\left(1+\frac{2\sin\sqrt{3}Q\alpha}{\sqrt{3}Q\alpha}\right) \qquad (6)$$

for $\alpha=1.032\,\text{Å}$ is also shown in *Figure 9*. Apparently, there exists a big discrepancy between the measured and the calculated EISF at all temperatures. Although this discrepancy can be partially removed by taking into consideration the coherent contamination of the measured EISF[7], this correction cannot explain the pronounced temperature dependence shown in *Figure 9*. It is worth mentioning at this point that calculation of the EISF from equation (6) is independent of temperature. To explore further the peculiar behaviour of the EISF, which has been observed in a number of systems[7,23,24], extra pains were taken to measure the absolute intensities of the elastic and quasielastic peaks as a function of T and Q. It was found that the elastic intensity decreases with increasing temperature beyond the normal DWF and at the same time all the extra intensity lost reappears into the quasielastic component. For example, at $Q=1.78\,\text{Å}^{-1}$ the elastic intensity drops by ~55% in the temperature range 80–160 K and the quasielastic intensity increases by ~40%, the difference being due to the normal DWF. Therefore, the quasielastic component becomes more intense with increasing temperature through the mechanism $I_{\text{el}}\rightarrow I_{\text{qel}}$. A possible explanation for this interplay is given by considering a temperature-dependent number of methyl groups participating in this motion. In this picture, at low temperatures, only a small fraction of protons performs angular jumps. Most of the protons are 'frozen in' contributing only to the elastic intensity and giving rise to the observed high values of the EISF. With increasing temperature, an increasing number of ester methyl protons begin to perform angular jumps and as a result the elastic intensity decreases—because of decrease in the number of immobile protons—and at the same time the quasielastic intensity increases—because of increase in the number of mobile protons. During the process of the 'unfreezing' of methyl groups the rotational frequency need not change. In view of this finding, it is suggested that a variable number of protons should be introduced in the calculation of the EISF as a function of temperature.

Apart from the EISF, we are also interested in the Q and T dependence of the quasielastic broadening. The Q dependence of the quasielastic peak for the PMMA sample at 180 K is shown in *Figure 10*. The linewidth is

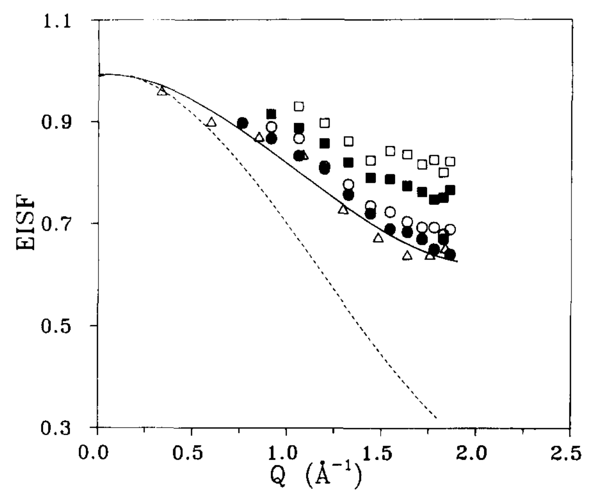

Figure 9 Measured incoherent structure factor (EISF) from the fitting procedure described with respect to *Figure 8*, of PMMA for different temperatures: (□) 100; (■) 120; (○) 140; (●) 160; (△) 180 K. The broken line is the calculated EISF according to equation (6). Notice the temperature dependence of the measured EISF

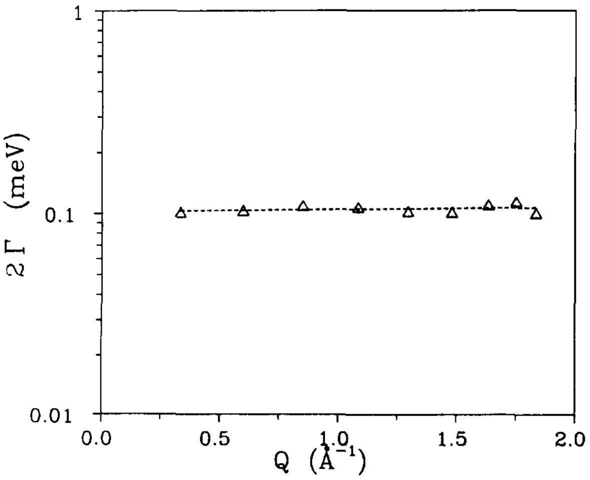

Figure 10 Q dependence of the full-width at half-maximum of the quasielastic broadening of PMMA at 180 K

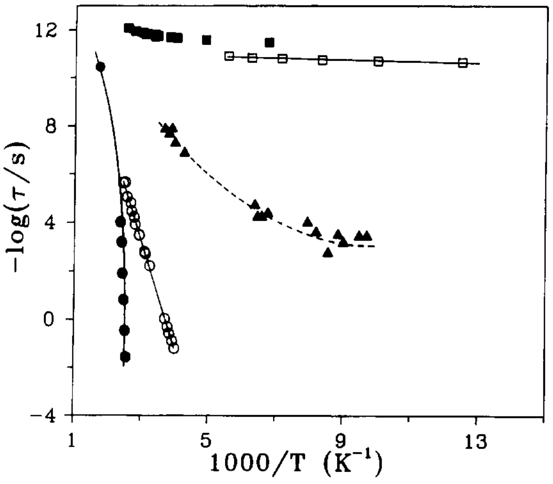

Figure 11 Transition map for predominantly syndiotactic PMMA showing the primary (α-) relaxation (●, dynamic light scattering[25]), the β-relaxation (○, dielectric relaxation[3,4]), the γ-relaxation (▲, mechanical relaxation[26]) and the δ-relaxation from quasielastic neutron scattering (■, ref. 7; □, this work)

independent of Q at all temperatures, as expected for the very localized rotation of the ester methyl group. Furthermore, 2Γ, displays a very weak temperature dependence with an activation energy of $\sim 0.7\,\text{kJ}\,\text{mol}^{-1}$ in the temperature range from 80 to 180 K.

Figure 11 contains the complete relaxation map for predominantly syndiotactic PMMA. It includes literature data for the primary (α-) relaxation due to segmental relaxation (from dynamic light scattering[25]), the β-relaxation associated with the rotation of the side group assisted by the main chain (from DR[3,4]), the γ-relaxation due to the α-methyl rotation (from MR[26] measurements) and the fast δ-relaxation due to the ester methyl group rotation at high[7] and low temperatures (this study). Ester methyl group rotation has been detected in MR[5,6] and n.m.r.[27] experiments in PMMA at very low temperatures, either as quasi-maxima in the shear modulus at $T < 5$ K or as minima in the spin-lattice relaxation time *versus* temperature. However, it is difficult to understand how a symmetric rotation of a methyl group can give rise to mechanical loss as such. One possibility is that the barrier to rotation contains multiples of three potential minima such that the minima are not energetically equivalent. On the other hand, QNS operating at higher frequencies than conventional MR and DR techniques together with deuterium labelling has led to unambiguous identification of the rotation of the ester methyl group as the molecular mechanism behind this low temperature relaxation in PMMA.

Solution chlorinated polyethylene

Two SCPE samples with different degree of chlorination were used in the present study (*Table 1*). The elastic window scan gave similar results for both SCPE63 and SCPE56 in the temperature range 0–290 K. The $\ln S(Q,\omega\approx 0)(T)$ for the SCPE56 sample shown in *Figure 1* displays a linear dependence on temperature up to 290 K. In contrast to *Figure 2* for PMMA, where the decrease of the elastic intensity beyond the expected decrease from the DWF has been attributed to quasielastic broadening, *Figure 1* for SCPE56 shows no such evidence. In fact, a normal DWF can explain the linear temperature dependence of $\ln S(Q,\omega\approx 0)$ up to 290 K. This is better demonstrated in *Figure 12* where the normalized elastic intensity is plotted *versus* Q^2 for different temperatures. Again, in contrast to *Figure 4* for PMMA, $\ln S(Q,\omega\approx 0)(T)$ for SCPE is linear in Q^2 for temperatures up to 290 K. However, as with PMMA, $\ln S(Q,\omega\approx 0)(T)$ does not approach one at low Q values. This again demonstrates the need for a temperature-dependent term in equation (3). Extension of the elastic window scan at even higher temperatures will result in a further decrease of the elastic intensity as a result of a motion around T_g. This motion and the effect of plasticization of the polymer dynamics is the subject of separate studies[28,29].

Solution chlorinated polyethylene/poly(methyl methacrylate) (50/50) blend

The two polymers studied above, with different mobilities at low temperatures—one (PMMA) with a quasielastic broadening as a result of the ester methyl group rotation and one (SCPE) with no quasielastic broadening at low T—constitute a good system for the study of possible microphase separation in polymer blends by means of QNS. A 50/50 SCPE63/PMMA (I) blend was prepared by the same homopolymers used above. The sample was then annealed at 458 K thus phase separating into PMMA and SCPE components. The elastic window scan for this blend (*Figure 3*), mimics the elastic window scan of SCPE (*Figure 1*) in that it displays a linear dependence of $\ln S(Q,\omega\approx 0)(T)$ up to 290 K. However, the elastic intensity drop is higher in the blend than in the bulk SCPE. Furthermore, the $S(Q,\omega\approx 0)(T)$ *versus* Q^2 plot in *Figure 13* shows similar characteristics to the bulk SCPE (*Figure 12*).

The mean-square-displacement, $\langle r^2\rangle$, can in principle be calculated from the slopes of *Figures 12* and *13* for SCPE and SCPE/PMMA, respectively. However, this is not the case for PMMA (*Figure 4*) due to the non-linearity discussed earlier in terms of motion. For this reason a specific Q value was chosen to compare the $\langle r^2\rangle$ values obtained from the elastic window scans shown in *Figures 1, 2* and *3* for SCPE, PMMA and SCPE/PMMA, respectively. This comparison for $\langle r^2\rangle$, determined at $Q = 1.86\,\text{Å}^{-1}$, is shown in *Figure 14*. A pertinent feature of *Figure 14* is the linear temperature dependence of the

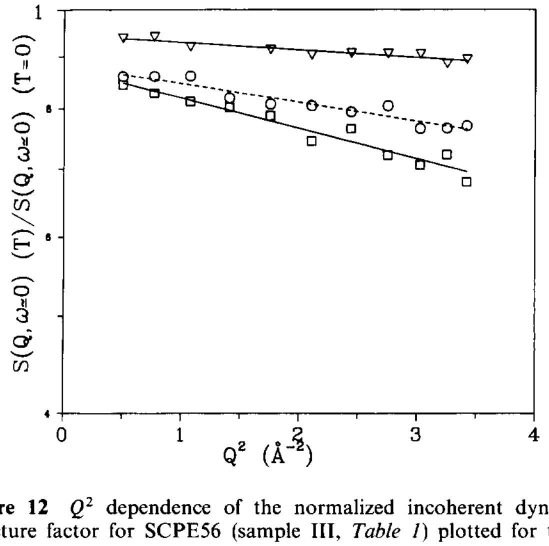

Figure 12 Q^2 dependence of the normalized incoherent dynamic structure factor for SCPE56 (sample III, *Table 1*) plotted for three temperatures; (▽) 95; (○) 210; (□) 245 K

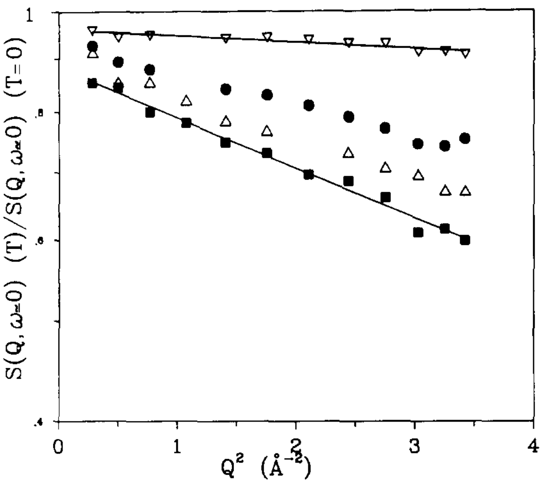

Figure 13 Q^2 dependence of the normalized incoherent dynamic structure factor for the blend SCPE63/PMMA (50/50) (sample IV, *Table 1*) plotted for selected temperatures: (▽) 45; (●) 125; (△) 175; (■) 235 K

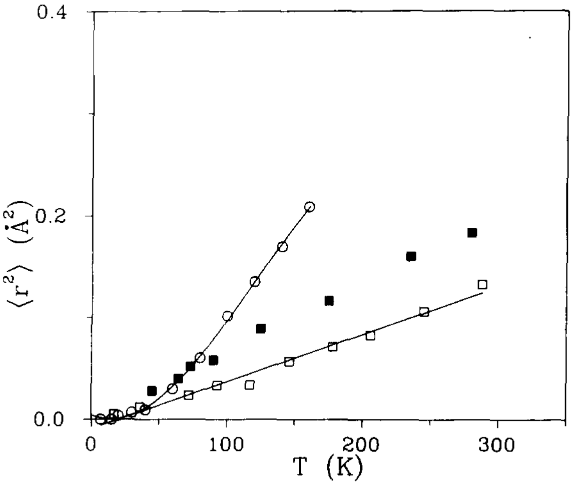

Figure 14 Temperature dependence of the mean-square-displacement $\langle r^2 \rangle$ calculated at $Q = 1.86\,\text{Å}^{-1}$ for PMMA (○), SCPE (□) and the blend SCPE/PMMA (■)

mean-square-displacement of the blend which mimics that of SCPE. A linear increase of $\langle r^2 \rangle$ with temperature is typical for a Debye solid which shows no quasielastic broadening. In contrast, the same quantity for PMMA is linear only up to 50 K. At higher temperatures, $\langle r^2 \rangle$ increases more strongly than the extrapolated value from low T for reasons discussed earlier. Apparently, the drop of the elastic intensity and the concomitant increase of $\langle r^2 \rangle$ in the SCPE/PMMA blend mimics the behaviour of SCPE, however, with higher amplitude.

The conclusion was drawn earlier from the temperature dependence of both the elastic window scan and the mean-square-displacement that in the blend there is no strong quasielastic component as with PMMA. This can be visualized by comparing the two homopolymers with the blend at the same T and Q value (*Figure 15*). An intense quasielastic component does not appear in the blend when this is compared with the bulk PMMA. Therefore, all findings for the blend are consistent in that there is higher mobility of O–CH_3 hydrogens than those in SCPE but this does not give rise to an intense quasielastic peak. In the following we will try to account for the absence for a pronounced quasielastic component in this microphase-separated blend.

Specific interactions (i.e. hydrogen bonding) between hydrogen atoms of SCPE and the carbonyl group of PMMA are thought to be the reason for the negative enthalpy of mixing and the partial miscibility in the SCPE/PMMA blend. The existence of interactions in the single-phase region is supported by recent cross-polarization magic angle spinning n.m.r. experiments in a SCPE/PMMA (25/75) blend[30] which revealed that the mean distance from the SCPE protons to deuterated PMMA carbons is ~3.5 Å suggesting close proximity and probable interactions between the two polymer chains. Before the effect of specific interactions on the mobile ester methyl group population is examined, some simple remarks are made. First, the mobile ester methyl groups have been reduced by 50% in the blend and second, phase separation into SCPE- and PMMA-rich phases will create environmental dissimilarities for the ester methyl groups. In one such environment—the SCPE-rich phase—ester methyl groups are surrounded by the less mobile SCPE. In the other environment—the PMMA-rich phase—a number of ester methyl groups could rotate but this is only a small fraction of the total number of ester methyl groups in PMMA which then gives rise to the small quasielastic component observed. In both cases, the ester methyl group environment in the bulk PMMA is drastically altered by blending with SCPE. Methyl groups in the blend find themselves in an environment—created by the slow SCPE chains—relaxing in a longer time-scale. This 'slow' environment alters the barrier height to rotation and consequently diminishes the number of groups capable of local rotational motion. This effect is similar to the secondary intensity suppression effect reported earlier in some systems[31]. This effect has been observed in the mechanical spectra of some polymer/additive mixtures whereas its absence is reported in other systems[31,32]. To explain the secondary suppression effect in these systems the free volume fluctuation model was employed[31]. According to this model, local density fluctuations can be suppressed in a polymer/additive mixture depending on the polymer involved. In the SCPE/PMMA blend, each polymer can be considered the additive of the other. However, amorphous polymers have a similar level of density

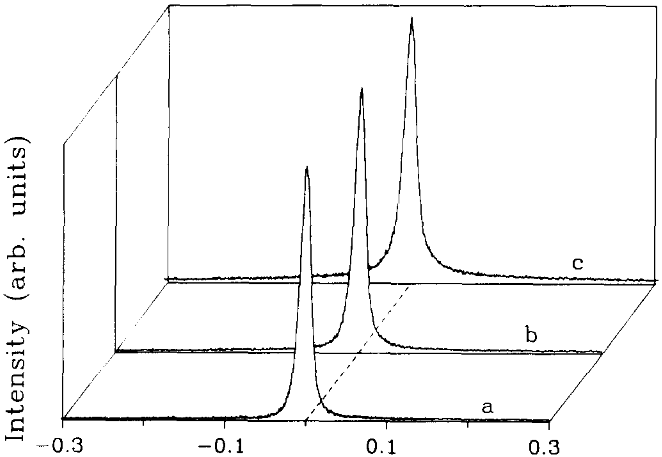

Figure 15 Quasielastic neutron scattering spectra of (a) SCPE63, (b) SCPE63/PMMA (50/50) and (c) PMMA at $T = 140$ K and $Q = 1.78\,\text{Å}^{-1}$

fluctuations in the glassy state and the intensity suppression effect is not expected.

Alternatively, long range interactions between the two homopolymers could produce a similar effect on the mobile ester methyl group population. However, with the present blend composition it is difficult to distinguish between the two effects. In this respect, a blend in which PMMA is the major component is more suited for this distinction. Clearly, the possible interpretation for the absence of quasielastic broadening in this phase-separated blend given above is speculative. However, the major conclusion, namely, that blending with SCPE produces a strong effect on the mobile ester methyl group population, is not speculative, but firmly based on experimental evidence (*Figure 14*).

CONCLUSIONS

The low temperature/high frequency relaxation of PMMA in the bulk and in a blend with SCPE has been examined using incoherent QNS. There are two main characteristics of the quasielastic peak observed in the bulk PMMA at low temperatures: the insensitivity of the linewidth with Q and T and the strong temperature dependence of the integrated intensity. The former is discussed in terms of a very localized motion with a small activation energy ($\sim 0.7\,\mathrm{kJ\,mol^{-1}}$) due to the ester methyl group rotation and the latter in terms of a temperature-dependent number of groups participating in the motion. Alteration of the O–CH_3 environment by blending with the less mobile SCPE has a strong effect on the mobile ester methyl group population.

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