Ester Methyl Group Dynamics in the Poly(methyl methacrylate) Stereocomplex: A Neutron Scattering Study.

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SUMMARY: Quasielastic neutron scattering was employed to investigate the ester methyl group dynamics of isotactic poly(methyl methacrylate) (PMMA) and atactic PMMA when incorporated into the PMMA stereocomplex. The data were analysed using the Rotational Rate Distribution Model. The results were compared to those for atactic PMMA and a non-complexed blend of isotactic PMMA and atactic PMMA. The activation energy, attempt frequency and variance values of the isotactic PMMA ester methyl group in the stereocomplex suggests that this group is involved in an interaction within the stereocomplex.

Introduction

Liquori and co-workers first reported the PMMA stereocomplex[1)] in 1965. Since then numerous investigations have been conducted on the phenomenon of PMMA stereocomplexation, a good review having been published by Spěváček and Schneider in 1987[2)].

While much work has been conducted into the structure of the stereocomplex, thought to be a 9/1 double stranded helix in which the syndiotactic PMMA wraps around the isotactic PMMA[3)], the interactions within the stereocomplex are still not fully understood. So far, three models have been proposed. The first suggestion is that there is an interaction involving the ester groups of both the isotactic PMMA and syndiotactic PMMA[4)]. The

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second opinion states that the isotactic PMMA ester group interacts with the syndiotactic PMMA α-methyl group[5,6)], while the third idea suggests that the stereocomplex forms due to a good steric fit[7)]. If the PMMA ester methyl group is interacting with another ester or α-methyl group one might expect the motion of either methyl group to be altered due to this interaction. In this paper we report quasielastic neutron scattering (QUENS) results for atactic PMMA and three blends of PMMA in order to clarify the interactions occurring within the PMMA stereocomplex.

Experimental

Materials

Fully deuterated and selectively deuterated isotactic PMMAs and atactic PMMAs were used, as listed in Table 1. Isotactic PMMA was obtained by polymerising MMA in toluene at -78°C under N_2 using sec-butyl lithium and propan-2-ol as an initiator [8)]. Synthesis of the atactic PMMA sample was carried out under N_2 at 50-55°C using 2,2'-azobis(isobutyronitrile) as an initiator[9)].

Three PMMA blends were made, a stereocomplexed blend of isotactic d5 and atactic d8 PMMA (sc1), a non-complexed blend of isotactic d5 PMMA and atactic d8 PMMA (non-sc1) and a stereocomplexed blend of isotactic d8 PMMA and atactic d5 PMMA (sc2). The stereocomplexed blends of PMMA (samples sc1 and sc2) were made by adding the appropriate solutions of isotactic PMMA in acetone and atactic PMMA in acetone together and stirring for 4 hours at 22°C. The ratio of isotactic PMMA to atactic PMMA was 1:1.5. The solutions were precipitated in a 10 fold excess of methanol, filtered and dried at 40°C for 67 hours. The samples were then crushed into a fine powder and pressed into films of the desired thickness. The film thickness was calculated as to allow 90% transmission of the neutron beam to minimise the probability of multiple scattering. The non-complexed blend of isotactic d5 PMMA and atactic d8 PMMA (sample non-sc1) was produced by heating sample sc1 at 200°C for 15 minutes in a vacuum oven.

All the PMMA blends were checked for complexation using differential scanning calorimetry. Samples sc1 and sc2 showed a melting peak at 170°C, indicating that the blends contained stereocomplexed PMMA. Sample non-sc1 showed only a glass transition temperature at 105°C, indicating a non-complexed blend of stereospecific PMMAs.

Table 1. PMMA samples used.

PMMA sample	formula	$M_w/1000$	M_w/M_n	Tacticity, s:h:i
atactic d5	CD_3 CCD_2 $COOCH_3$	250		50:40:10
atactic d8	CD_3 CCD_2 $COOCD_3$	167	2.3	60:30:10
isotactic d5	CD_3 CCD_2 $COOCH_3$	550		0:0:100
isotactic d8	CD_3 CCD_2 $COOCD_3$	515	3.0	0:8:92

QUENS measurements

Neutron scattering experiments were performed using the quasielastic neutron scattering instrument, IRIS10), at Rutherford Appleton Laboratory, UK. The energy range covered was –0.4 to +0.4 meV, the q range 0.51 to 1.82 $Å^{-1}$, and the energy resolution was 15 μeV (PG002 analyser). A temperature range of 4-200K was investigated. Data reduction was performed according to RAL routines in order to obtain the dynamic structure factor $S(Q,\omega)$ as a function of energy transfer.

Rotational Rate Distribution Model (RRDM) for Methyl Group Rotations

When investigating molecular motion using a neutron scattering experiment, the experimentally measured quantity is the double differential cross-section $\delta^2\sigma/\delta E\ \delta\Omega$, which is the probability that a neutron is scattered with energy change δE into a solid angle $\delta\Omega$. For hydrogenous polymers the scattering is dominated by the large incoherent cross-section of the hydrogen atoms, σ_{inc} = 80.27 barns (where 1 barn = 10^{-28} m^2) compared to $\sigma_{inc} = 2.005$ barns for deuterium and $\sigma_{inc} = 0.001$ barns for carbon17). By selectively deuterating a polymer you can distinguish the motion of a chosen group. So for instance, by using d5 PMMA, CD_3 CCD_2 $COOCH_3$, with only the ester methyl group hydrogenous, the majority of the incoherent scattering originates from the ester methyl group with only a small contribution from the α-methyl group and the polymer backbone, therefore effectively masking the motion of the α-methyl group and the polymer backbone. The coherent contribution is normally small, however it may produce a static structure factor in selectively deuterated polymers that affects the analysis of the Q dependence17).

The RRDM, as introduced by Chahid and co-workers11), was used to analyse the QUENS data. The RRDM uses a Gaussian distribution of Lorentzians to describe the different rates of rotation present in glassy polymers. The rotational scattering law associated with the methyl group motion can be written as:

$$S^{rot}(q,\omega) = A(q)\delta(\omega) + [1-A(q)] \sum_{j=1}^{N} [g_i L_i(\omega)] \qquad \text{with} \quad \sum_{i=1}^{N} g_i = 1 \qquad (1)$$

where $S^{rot}(q, \omega)$ is the incoherent dynamic structure factor associated with the methyl group movement, q is the scattering vector, ω is the energy, A(q) is the elastic incoherent structure factor, $\delta(\omega)$ is a delta function, $L_i(\omega)$ are the Lorentzian functions with a half-width at half-maximum (hwhm) h_i and a weight g_i.

A log-Gaussian distribution is used to model the distribution of jumping rates. This leads to g_i being:

$$g_i \propto g(\ln h_i) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[(1/2\sigma^2)\ln^2(h_i/h_o)\right] \qquad (2)$$

where the proportionality constant ensures that $\sum_{i=1}^{N} g_i = 1$,

σ is the variance of the Gaussian distribution and h_o is the half-width at half-maximum (hwhm) of the most probable Lorentzian component.

The activation energy, E, can be calculated from equation:

$$h_o(T) = h_\infty \exp(-E/RT) \qquad (3)$$

where h_∞ is related to the attempt frequency and R is the gas constant.

Results and Discussion

Figure 1 shows an example of the quasielastic spectra, in this case for sc1 at q =1.096 Å^{-1} at 100K and 140K, along with their fits and quasielastic components. Figure 2 shows the differences between the quasielastic spectra for samples sc1 and non-sc1 at the same temperature, 140K, and same q, 1.096 Å^{-1}. A summary of the results obtained for all samples is given in Table 2. The temperature independent variance11), σ_E, was calculated using $\sigma_E = \sigma RT$.

Table 2. A comparison of the RRDM parameters for the ester methyl group dynamics in atactic PMMA and blends of stereospecific PMMA.

Sample	Ester methyl group monitored	E (kJmol^{-1})	h_∞ (meV)	σ_E
scl	isotactic	5.7	2.8	1.7
non-scl	isotactic	6.4	4.8	2.6
sc2	atactic	4.6	1.5	1.5
atactic PMMA	atactic	4.4	1.5	1.6

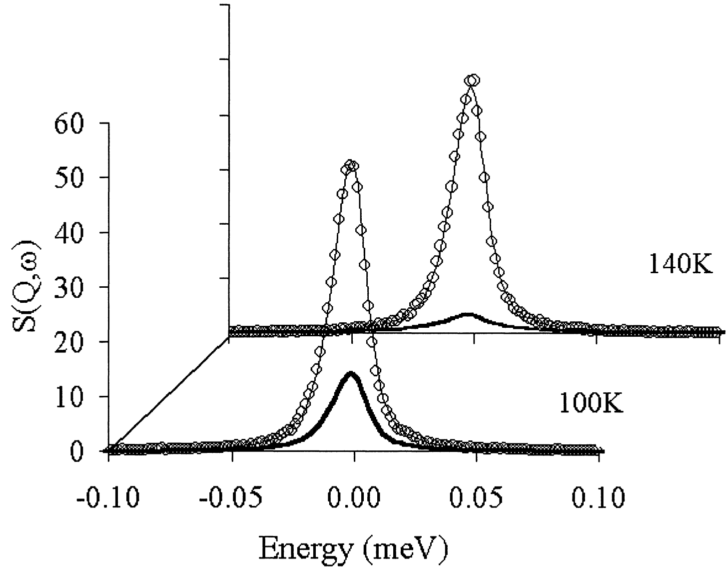

Fig. 1. Typical quasielastic neutron scattering data (o) for sample scl at 100K and 140K at q = 1.096 Å^{-1} fitted with the RRDM (solid line). The thick solid line represents the quasielastic component of the RRDM.

In previously published results for the ester methyl in atactic PMMA[12-16] the activation energy quoted for different experiments varies between 4.5 and 5.9 kJ mol^{-1}. Given this wide range, and the fact that in the current experiments we only have observation of the isotactic PMMA in mixtures, we cannot be certain that there is a significant difference ester methyl group rotation for isotactic and atactic PMMA, although a comparison of lines 2 and 4 in Table 2 does suggest this.

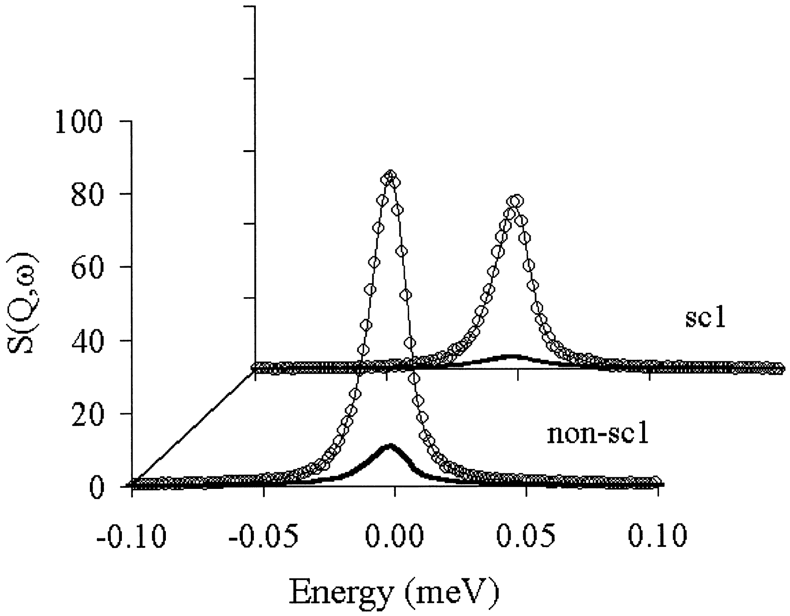

Fig. 2. The differences between the quasielastic components in samples non-sc1 and sc1 at the same temperature, 140K and at the same q, 1.096 Å^{-1}. The data is represented by 'o', the RRDM by the solid line and the quasielastic component of the RRDM is represented by the thick solid line.

Comparing lines 1 and 2 in Table 2 there does to be an indication of a difference in the motion of the isotactic ester methyl in the complexed and non-complexed mixtures with atactic PMMA, although the differences are small. The activation energy seems to decrease on stereocomplexation, although this difference is within experimental error. The attempt frequency also seems to decrease on stereocomplexation, implying the methyl group rotates at a slower speed within the stereocomplex, but this too is within experimental error. However, the distribution of activation energies decreases on stereocomplexation, which could be due to the crystallinity of the stereocomplex reducing the number of different local environments experienced by the ester methyl group. Overall, we suggest that the ester methyl group rotation on the isotactic PMMA component is being modified by being incorporated in the stereocomplex, which in turn implies that the ester methyl group on the isotactic PMMA component at the centre of the double helix may be participating in an interaction.

Comparing lines 3 and 4 of Table 2 there seems to be no significant difference in the activation energies, attempt frequencies and variances for the ester methyl group dynamics of atactic PMMA in the stereocomplex and in pure atactic PMMA. This suggests that the ester methyl group on the atactic PMMA component is not participating in an interaction.

Conclusions

The ester methyl group dynamics of PMMA molecules in various stero mixtures were investigated using quasielastic neutron scattering. The results suggest that the atactic ester methyl group dynamics are not altered by being incorporated into the PMMA stereocomplex, implying the atactic ester methyl group it is not involved in any interactions within the stereocomplex. However, the isotactic ester methyl group dynamics are altered on being incorporated in the stereocomplex, implying that this group is involved in some sort of interaction occurring within the stereocomplex.

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