A broad-line n.m.r. investigation of methyl motion in poly(methylmethacrylate)

J. Humphreys, R. A. Duckett and I. M. Ward
Department of Physics, University of Leeds, Leeds LS2 9JT, UK
(*Received 24 November 1983*)

Broad line n.m.r. measurements have been carried out over a wide range of temperatures on poly(methylmethacrylate) (PMMA) and several selectively deuterated forms of this polymer. The line shapes and second moments for the different samples were examined in the light of theoretical calculations based on possible structural models. A spectrum subtraction procedure was particularly useful in confirming the conclusions drawn from consideration of second moment data. A consistent set of conclusions was obtained for the motion of the methyl groups.

(Keywords: poly(methylmethyacrylate); broad line n.m.r.; methyl motion; deuteration)

INTRODUCTION

The hindered rotation of methyl groups in PMMA over a range of temperature has been investigated by a number of workers using dielectric techniques[1], dynamic-mechanical measurements[2], inelastic neutron scattering[3] and broad-line nuclear magnetic resonance[4-6]. Conflicting results have been obtained and consequently the temperatures at which the onset of motion for each methyl group occurs have not been definitely established. In particular, it is not clear whether any methyl motion persists at liquid helium temperatures.

Broad-line n.m.r. is a powerful technique for observing methyl motion because the characteristic triplet signal observed for a rigid methyl group collapses to a narrow singlet signal if motion occurs. This effect can be most readily quantified by determining the second moment of the n.m.r. absorption and the difficulty of distinguishing between different methyl groups in the structure can be readily removed by selective deuteration. In this paper quantitative n.m.r. data are presented for various forms of PMMA in which the protons in one or other or both methyl groups have been replaced by deuterium. The conclusions obtained from second moment measurements have been confirmed by subtraction of the absorption signals for different pairs of deuterated materials. This allowed each methyl signal to be observed directly for comparison with the theoretical line shapes calculated for rigid and rotating triangular groups of nuclei by Andrew and Bersohn[7].

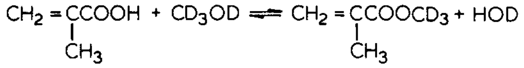
EXPERIMENTAL

Preparation of deuterated materials

Three deuterated forms of methyl methacrylate have been prepared for this work, using the following deuterated monomers.

(i) $CH_2CH_3CCOOCD_3$

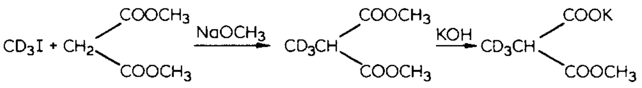
This was prepared by the direct esterification of methacrylic acid using deutero-methanol[8].



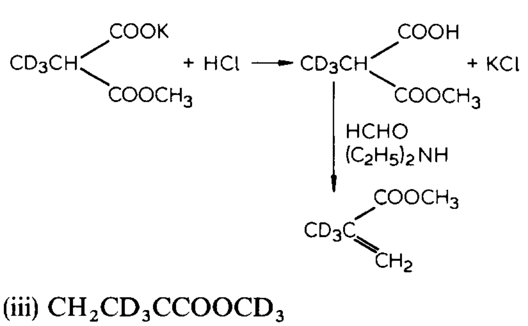
$$CH_2{=}\underset{CH_3}{\underset{|}{C}}COOH + CD_3OD \rightleftharpoons CH_2{=}\underset{CH_3}{\underset{|}{C}}COOCD_3 + HOD$$

(ii) $CH_2CD_3CCOOCH_3$

Deuterated methyl iodide was reacted with dimethyl malonate to give d-methyl dimethyl malonate which was then hydrolysed to form the half-ester salt potassium d-methyl methyl malonate[9]:



This salt was converted to the acid d-methyl methyl hydrogen malonate using hydrochloric acid. The half-ester formed was reacted with formaldehyde solution and diethylamine to produce the required deuterated monomer:



(iii) $CH_2CD_3CCOOCD_3$

Deuterated-methyl malonate was prepared as described in (ii). This was hydrolysed to form a potassium salt which was converted to d-methacrylic acid by the addition of hydrochloric acid[10]:

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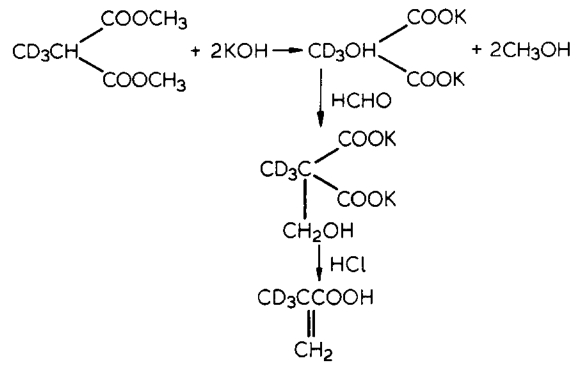
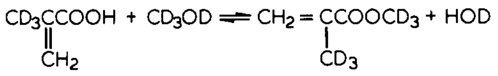


Deuterated methacrylic acid was esterified using deuteromethanol (as in (i)) to give the required deuterated monomer:



$$CD_3C(=CH_2)COOH + CD_3OD \rightleftharpoons CH_2=C(CD_3)COOCD_3 + HOD$$

Each of these monomers was polymerized by ICI Ltd. (Plastics and Petrochemicals Division) using their standard procedures for Perspex to produce standard sheets of PMMA of 1 mm thickness. The high resolution nmr spectra for the deuterated polymers were examined in solution ($\sim 5\%$ concentration by weight in deuterochloroform) at 90 MHz. Following the method established by Bovey and Tiers[11] for identifying the methylene, α-methyl and ester–methyl protons, it was confirmed that the appropriate absorption peaks were absent in each of the deuterated species.

N.m.r. measurements

Three sets of equipment were employed to carry out the n.m.r. measurements over different temperature ranges. In each case, strips cut from the sheet specimen were tightly packed into a PTFE specimen holder inside the radiofrequency coil and positioned between the poles of the magnet. A Varian DP-60 double-coil spectrometer was used for the majority of room temperature measurements. For measurements in the range 6 K to 80 K, a 30 MHz Q-meter in conjunction with a liquid helium cryostat arrangement was found to give satisfactory results. An electrical heater in a dewar of liquid helium below the magnet drove helium gas through a cryostat positioned between the magnet poles. The specimen was held in the path of the cold helium gas, in the magnetic field. The specimen temperature could be increased to 80 K by a heater positioned below the specimen holder. A similar 60 MHz Q-meter and liquid nitrogen arrangement allowed measurements in the range 200 K to 393 K to be made. Details of the operation, calibration and saturation checks for each of these n.m.r. sets are described elsewhere[12].

The n.m.r. signal obtained for each run was stored in a digital signal averager which summed the integrated absorption spectra obtained by repeated sweeps through the resonance. The accumulated data was transferred to an Amdahl VM/470 computer and the second moment of the signal determined.

THEORY

N.m.r. second moment calculations

The n.m.r. absorption line shape can be quantified in terms of its second moment $\langle \Delta H^2 \rangle$, following the Van Vleck analysis[13]. For the resonance of a single magnetic species this can be written

$$\langle \Delta H^2 \rangle = G/N \sum_{j>k} r_{jk}^{-6}(3\cos^2\beta_{jk} - 1)^2 \qquad (1)$$

where $G = \frac{3}{2}I(I+1)g^2\mu_n^2$, I is the nuclear spin number, μ_n the nuclear magneton, g is the nuclear g factor, N the number of magnetic nuclei over which the sum is taken, r_{jk} the length of the vector joining nuclei j and k, and β_{jk} the angle between the vector $\underline{r}_{jk}$ and the direction of the externally applied magnetic field $\underline{H}$[14].

For an isotropic material (1) reduces to

$$\langle \Delta H^2 \rangle_{\text{iso}} = \frac{4}{5}\frac{G}{N} \sum_{j>k} r_{jk}^{-6} \qquad (2)$$

In the present work, any contributions to $\langle \Delta H^2 \rangle_{\text{iso}}$ from the non-resonant deuterium nuclei have been assumed to be so small that they can be neglected and (2) evaluated for the protons only. The structure for PMMA is not well-defined and it is necessary to assume an appropriate chain conformation in order that the proton positions and isotropic second moment may be calculated. A number of possible conformations have been suggested by various workers for both the isotactic and syndiotactic PMMA chain. For this investigation, typical conformations have been selected and the intramolecular isotropic second moment calculated for each structure. The conformations considered are:

(i) an isotactic 5_1 helix[15-17]
(ii) an isotactic 5_2 helix[18]
(iii) a syndiotactic planar zigzag chain
(iv) a syndiotactic chain, with unequal backbone bond angles, consisting of curved segments 8 to 10 monomers long[19].

Motion of a methyl group has the effect of reducing the contribution to $\langle \Delta H^2 \rangle_{\text{iso}}$ of that methyl group to one quarter of its rigid value[20]. Isotropic second moments have therefore been calculated for each structure in undeuterated and deuterated forms allowing different combinations of methyl motion to occur and these are shown in *Table 1*. It is apparent that the amount by which $\langle \Delta H^2 \rangle_{\text{iso}}$ is reduced when methyl motion takes place is greater than the differences in $\langle \Delta H^2 \rangle_{\text{iso}}$ between different structural models. It can therefore be safely concluded that observations which may be made regarding motion are independent of the chain conformation assumed. Any intermolecular contributions arising from the comparatively large inter-proton distances between protons of neighbouring chains have been neglected because such contributions will be small due to the six power dependence of $\langle \Delta H^2 \rangle_{\text{iso}}$ on inter-proton distances. However, where comparisons between calculated and experimental results are made, this deficiency must not be overlooked. The error in the calculated second moment values is dominated by the accuracy to which the bond angles and bond lengths are known and is approximately 6%.

Methyl and methylene group line shapes

The line shapes for an assembly of triangular groups of nuclei which are rigid and which are allowed to rotate have been calculated[7] and are shown in *Figure 1*. Pake (1948)[21] calculated the line shape for an assembly of proton pairs which is shown in *Figure 2*.

Table 1 Calculated isotropic second moments

		Calculated isotropic second moment (Gauss^2)*			
Motion	Structure model	Perspex	Ester-CD_3 PMMA	α-CD_3 PMMA	Both-CD_3 PMMA
Both methyl groups mobile	5_1 Helix	11.0	12.3	11.1	17.8
	5_2 Helix	11.7	12.6	10.6	14.6
	Planar zigzag	10.3	11.8	8.9	16.2
	8 Monomer curved zigzag	9.6	11.2	10.1	16.0
	10 Monomer curved zigzag	9.6	11.3	10.1	16.1
Ester—methyl group mobile	5_1 Helix	17.6	22.5	11.1	17.8
	5_2 Helix	20.2	26.0	10.6	14.6
	Planar zigzag	17.2	22.2	8.9	16.2
	8 Monomer curved zigzag	16.1	21.5	10.1	16.0
	10 Monomer curved zigzag	16.2	21.6	10.1	16.1
α-Methyl group mobile	5_1 Helix	17.8	12.3	21.6	17.8
Completely rigid	5_1 Helix	24.6	22.5	21.6	17.8
	5_2 Helix	27.1	26.0	21.4	14.6
	Planar zigzag	23.9	22.2	15.2	16.2
	8 Monomer curved zigzag	22.3	21.5	20.0	16.0
	10 Monomer curved zigzag	22.4	21.6	20.0	16.1

* 1 Gauss = 10^{-4} Tesla

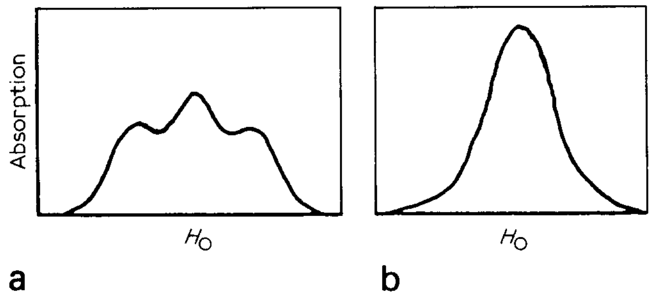


Figure 1 Calculated line shape for an assembly of triangular groups of nuclei which are (a) rigid, (b) mobile [7]

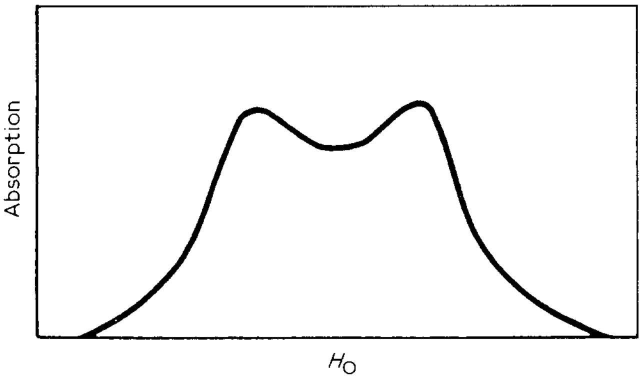


Figure 2 Calculated line shape for an assembly of proton pairs[16]

RESULTS

The values of second moment for each material at temperatures measured are shown in *Table 2*.

Room temperature measurements

At room temperature, a comparatively narrow single absorption peak is obtained for Perspex (*Figure 3*) indicating that motion is present at this temperature but providing no information about the origin or extent of this motion. A single narrow peak is also obtained for ester-CD_3 PMMA at this temperature (*Figure 4*). With this material, the observed n.m.r. signal arises solely from the α-methyl and methylene protons. It may therefore be concluded that the α-methyl protons are mobile at room temperature. No deductions can be made about the motion of the ester–methyl group.

The experimental isotropic second moment for Perspex is in good agreement with that calculated assuming both methyl groups are in motion for all molecular models. Measurements on ester–CD_3 PMMA produce second moment values which are consistent with the predictions for the α-methyl group rotating alone or both methyl groups rotating.

Intermediate temperatures

When the temperature is reduced to 215 K (*Figure 4*), the ester-CD_3 material still produces a single narrow peak indicating that α-methyl motion persists at this temperature. The peak is slightly broader than that obtained at room temperature so the degree of motion may be more restricted. The mobile α-methyl signal swamps the methylene signal which is not observed. At 79 K (*Figure 4*) the breadth of the peak is substantially increased and shoulders arising from a rigid methyl signal are observed on the sides of the peak. From the line shape, it appears that motion of the α-methyl group is therefore

Table 2 Experimental isotropic second moments

Material	Temperature (K)	Measured $\langle \Delta H^2 \rangle_{iso}$ (Gauss^2)
Perspex	293	11.7 ± 0.1
Perspex	6	21.4 ± 0.9
Ester-CD_3 PMMA	293	12.3 ± 1.1
Ester-CD_3 PMMA	240	19.8 ± 1.2
Ester-CD_3 PMMA	215	22.2 ± 1.2
Ester-CD_3 PMMA	79	22.5 ± 0.7
Ester-CD_3 PMMA	40	23.2 ± 0.8
Ester-CD_3 PMMA	6	23.2 ± 0.3
α-CD_3 PMMA	6	13.3 ± 0.1
Both-CD_3 PMMA	6	18.4 ± 0.1

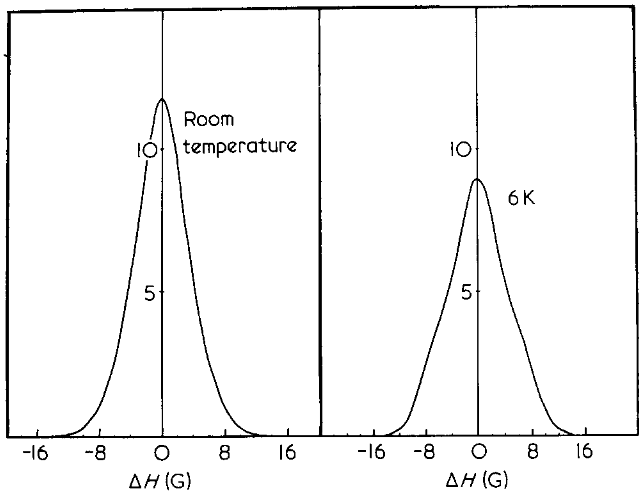


Figure 3 N.m.r. absorption spectra for 'Perspex'

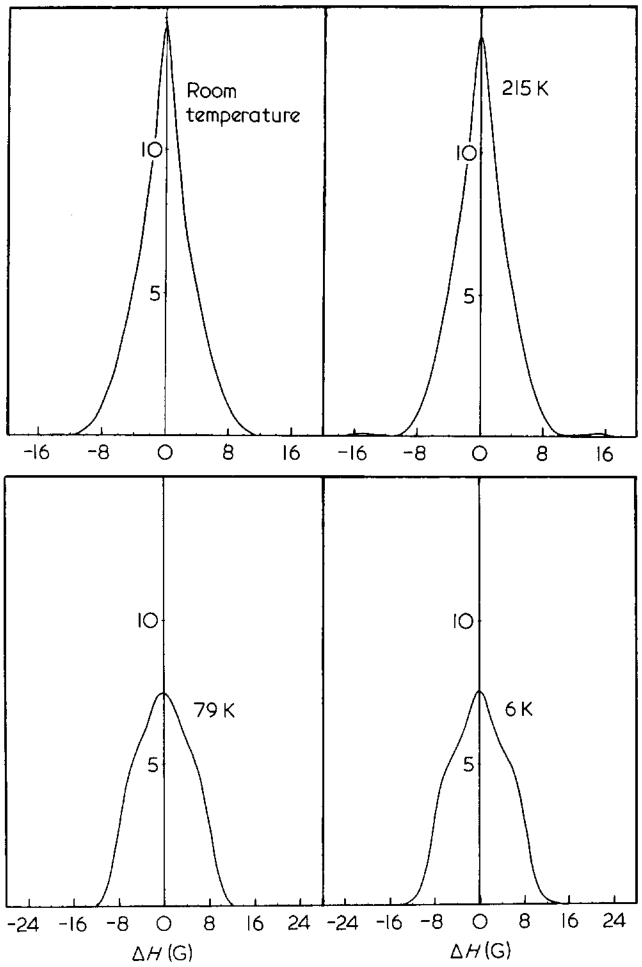


Figure 4 N.m.r. absorption spectra for ester-CD_3 PMMA

absent or much reduced at 79 K. As the temperature is reduced from 79 K to 6 K (*Figure 4*), the peak shoulders become increasingly pronounced although the breadth of the peak does not further increase significantly.

The second moment data obtained for ester-CD_3 samples in the temperature range 215 K to 240 K are less reliable because the signal-to-noise ratio for these runs was poor. Over the range, the second moment decreases from 22.2 Gauss^2 to 19.8 Gauss^2, values which are too small to indicate that the α-methyl groups is completely rigid, but much too large for agreement with the predictions for a rotating α-methyl group. It is suggested that this temperature range is that in which the α-methyl group is just commencing hindered rotation, in agreement with absorption line shape observations.

These preliminary ideas about α-methyl group motion were checked by measuring the isotropic second moment for ester-CD_3 PMMA over the range 6 K to 79 K. As the temperature is increased, the isotropic second moment reduces from 23.2 G^2 to 22.5 G^2, values which are consistent with calculations for the rigid α-methyl group case. It is apparent that the α-methyl group is rigid throughout the range 6 K to 79 K, consistent with the above proposition that the onset of hindered rotation of the α-methyl group occurs over the range 215 K to 240 K.

Liquid helium temperatures

Perspex at 6 K (*Figure 3*) exhibits a single peak which is broader than that at room temperature showing that motion persists at helium temperatures but to a lesser extent than at room temperature. Measurements of the isotropic second moment for Perspex at 6 K indicate that one methyl group per monomer only is in motion, the other being rigid. It was thought unlikely, from the work of Sinnot[2,5] and Powles[4], that α-methyl motion should persist at a lower temperature than that of the ester-methyl group, but this had to be confirmed. The second moment for the case of the α-methyl group only rotating has been calculated for the undeuterated 5_1 helix model and found to be 17.8 Gauss^2, a very similar figure to that obtained for the ester–methyl only rotating. It is therefore not possible to identify which methyl group is rigid from Perspex data alone. This highlights the necessity for measurements on selectively deuterated forms of PMMA. The intermediate temperature results above show that α-methyl motion is likely to commence at a higher temperature indicating that the motion persistent at 6 K may be attributed to the ester-methyl group.

The α-CD_3 form of PMMA produces a line shape at 6 K (Fig. 5) which consists of a single peak and is narrower than that for Perspex. The broad component in the Perspex spectrum at helium temperatures therefore appears to arise from the α-methyl group, implying that this is immobile whereas the ester-methyl group is in motion. If the ester-methyl group were rigid at 6 K, then the α-CD_3 PMMA absorption signal would be expected to show signs of the broad, three-peaked line shape associated with rigid triangular groups of nuclei shown in *Figure 1*(*a*).

Ester-CD_3 PMMA at 6 K (*Figure 4*) produces a substantially broader peak than Perspex or α-CD_3 PMMA, showing that ester-CD_3 PMMA has fewer mobile protons compared with these materials at the same temperature. The pronounced shoulders on the ester-CD_3 peak may be explained by considering this peak to be a superposition of the theoretical rigid methyl and methylene line shapes shown in *Figures 1*(*a*) and *2*. The absorption line shape obtained indicates that the α-methyl group is rigid at 6K.

The rigid α-methyl signal is detectable only as a slight shoulder on the Perspex peak at 6 K because this signal consists of a combination of methylene, rigid α-methyl and mobile ester–methyl signals. The mobile ester–methyl signal almost masks the rigid α-methyl signal giving the experimentally observed single peak. The rigid α-methyl signal may only be observed provided the ester–methyl group is deuterated.

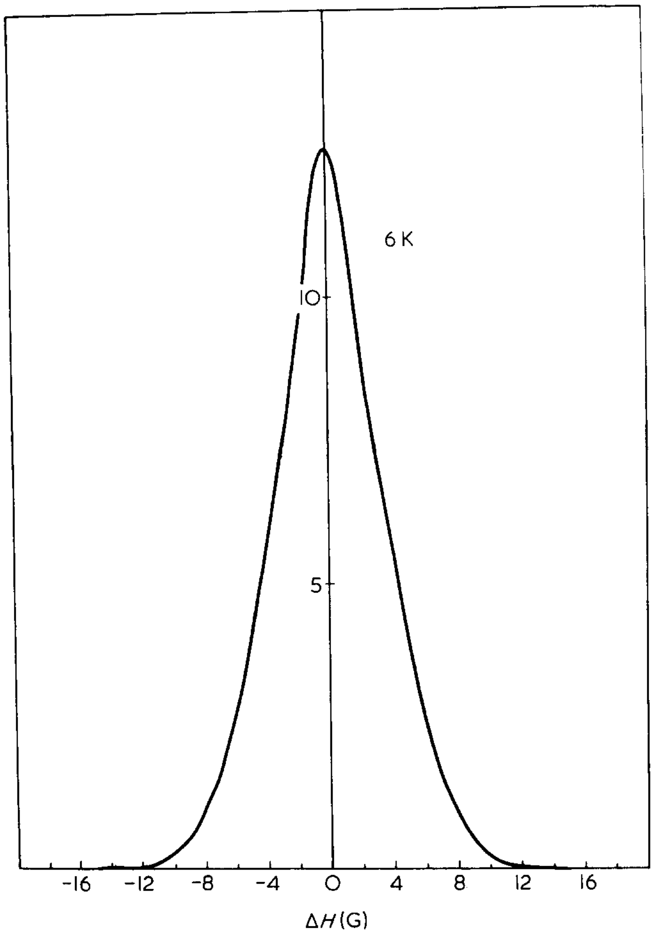


Figure 5 N.m.r. absorption spectrum for α-CD_3 PMMA

No motion was apparent on consideration of the isotropic second moments measured at 6 K in the ester-CD_3 material. Therefore either (a) the structure is completely rigid or (b) only the undetected deuterated ester-methyl group is in motion. The isotropic second moment data for α-CD_3 PMMA at 6 K indicated that motion was present in this material and this must be occurring in the ester–methyl group confirming (b) above. The measured isotropic second moment values for α-CD_3 PMMA at this temperature, although lower than those predicted for the rigid molecule, are appreciably greater than the values calculated assuming that the ester–methyl group is rotating. This would suggest that there is a substantial intermolecular contribution, arising mainly from interactions between ester–methyl protons on adjacent chains. It is also possible that, at 6 K, only limited hindered rotation of the ester–methyl group is occurring. These protons would then give a contribution to the isotropic second moment which is intermediate between that for a rigid and a rotating methyl group.

No information about methyl group mobility can be obtained from the absorption line shape or isotropic second moment for the form of PMMA with both methyl groups deuterated (*Figure 6*). This signal is expected to resemble that in *Figure 2* for an assembly of pairs of nuclei, since only methylene protons remain in this material. In practice, the experimental line shape shows a single peak with shoulders close to the maximum. It is suggested that this unexpected result arises from the anticipated methylene line shape in conjunction with a single narrow peak attributable to a small amount of mobile impurity present in the material. This mobile fraction may be unpolymerized deuterated monomer which would give rise to a narrow peak[22]. This signal is not apparent in the line shapes for other forms of PMMA either because these contain no significant fraction of unpolymerized material or the more intense signal arising from the greater number of protons overshadows that from the mobile fraction.

The indications regarding methyl group motion from the above visual examination of the n.m.r. absorption line shapes and study of isotropic second moment values are summarized in *Tables 3* and *4*.

Subtraction of n.m.r. signals

The successful preparation of selectively deuterated forms of PMMA for this work has allowed us to confirm these conclusions by a very useful spectrum subtraction procedure. A computer programme has been written

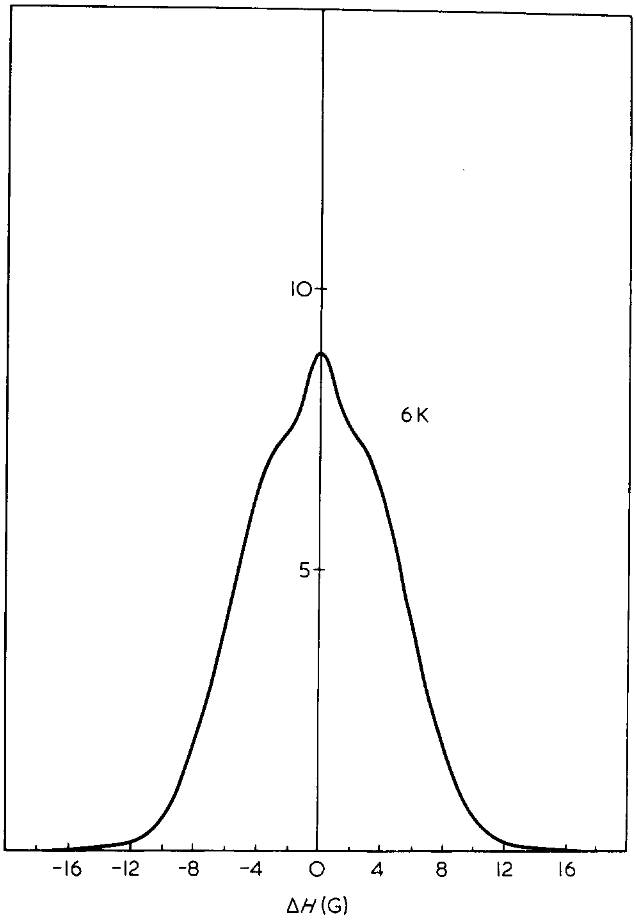


Figure 6 N.m.r. absorption spectrum for PMMA with both methyl groups deuterated

Table 3 Summary of results from visual examination of line shapes for isotropic materials

Material	Temperature (K)	Information obtained about methyl motion
Perspex	293	Some degree of mobility
Perspex	6	Some degree of mobility
Ester-CD_3 PMMA	293	α-CD_3 group mobile
Ester-CD_3 PMMA	215	α-CD_3 group mobile
Ester-CD_3 PMMA	79	α-CD_3 motion possibly just commencing
Ester-CD_3 PMMA	6	α-CD_3 rigid
α-CD_3 PMMA	6	Ester-CH_3 mobile
Both-CD_3 PMMA	6	–

which allows the n.m.r. absorption spectrum for, say, isotropic ester-CD_3 · PMMA to be subtracted from that of, for example, isotropic Perspex measured at the same temperature. Prior to subtraction, an appropriate normalization is made to allow for the differing number of protons per monomer in the two materials. In the above example, every data point in the ester-CD_3 spectrum must be multiplied by a factor of 5/8. The signal remaining after subtraction is that due solely to the ester–methyl groups in the Perspex specimen. Visual comparison of this signal with the calculated line shapes in *Figure 1* gives a clear indication as to whether these methyl groups are mobile.

A number of different combinations of subtractions were performed. These are shown in *Table 5* together with the methyl group about which information should be yielded in each case. The relevant figure number for each subtracted spectrum is also indicated.

Both *Figures 7* and *10* show the 6 K ester–methyl line shape obtained by performing a different subtraction in each case (as shown in *Table 5*). *Figure 7* exhibits well-defined shoulders low down on the sides of the peak whereas *Figure 10* shows only a single peak. Neither show the line shape characteristic of rigid methyl groups (*Figure 2*). *Figure 7* indicates that ester–methyl motion may be starting to 'freeze out' at 6 K, but *Figure 10* implies that the ester–methyl group is mobile at this temperature. At 6 K, if the ester–methyl group is just mobile, then the line shape may well be very sensitive to temperature in this region and a fluctuation of only a degree between runs may affect the observed signal significantly. To obtain the line shape in *Figure 10* data from PMMA with both methyl groups deuterated is employed which is the most unreliable set of experimental data since only two protons per monomer remain giving a poor signal-to-noise ratio. *Figure 7* uses comparatively reliable data. Therefore, it seems likely, from the line shape of *Figure 7*, that the ester–methyl group is just commencing hindered rotation at 6 K.

Figures 8 and *9* show the α-methyl signal at 6 K obtained by subtracting combinations of absorption line shapes (shown in *Table 5*). The line shape in *Figure 9* closely resembles that calculated for rigid triangular groups of protons (*Figure 1(a)*) and clearly indicates that the α-methyl group is rigid at this temperature. The signal shown in *Figure 8* should, of course, be identical to that of *Figure 9* and this deviation from the anticipated line shape may be explained as follows: this signal is obtained by subtracting the α-CD_3 PMMA signal from that for commercial Perspex. As in the case of PMMA with both methyl groups deuterated, it is likely that free monomer may persist in this form of PMMA after polymerization. (This was not evident in the α-CD_3 PMMA absorption spectrum which was dominated by the rotating ester-methyl signal). 'Perspex' is produced by a large scale commercial process and contains negligible free monomer. Although the deuterated materials for this work were polymerized by the same process, this small scale polymerization appears to have been less efficient. Therefore, when the α-CD_3 PMMA (with free monomer present) signal is subtracted from that for Perspex (with no free monomer), the observed line shape is obtained

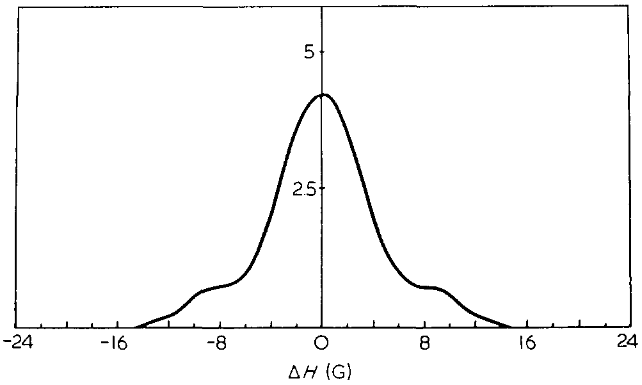


Figure 7 Ester-CH_3 signal at 6 K

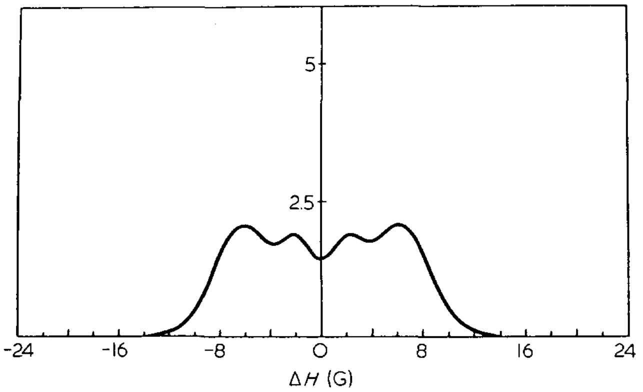


Figure 8 α-CH_3 signal at 6 K

Table 4 Summary of isotropic second moment results: Motion

Temperature	Material	α-Methyl group	Ester–methyl group
Room temperature	Perspex	In motion	In motion
Room temperature	Ester-CD_3 PMMA	In motion	–
215 K → 240 K	Ester-CD_3 PMMA	Just commencing motion	–
6 K → 79 K	Ester-CD_3 PMMA	Rigid	–
6 K	Perspex	1 CH_3 rigid,	1 CH_3 in motion
6 K	Ester-CD_3 PMMA	Rigid	–
6 K	α-CD_3 PMMA	–	Motion just beginning to 'freeze out'
6 K	Both-CD_3 PMMA	–	–

Table 5 Subtraction of absorption signals

Temperature (K)	Signals subtracted	Information yielded	Figure number
6	Perspex – Ester-CD_3 PMMA	Ester–methyl motion	7
6	Perspex – α-CD_3 PMMA	α-Methyl motion	8
6	Ester-CD_3 PMMA – Both-CD_3 PMMA	α-Methyl motion	9
6	α-CD_3 PMMA – Both-CD_3 PMMA	Ester–methyl motion	10
293	Perspex – Ester-CD_3 PMMA	Ester–methyl motion	11

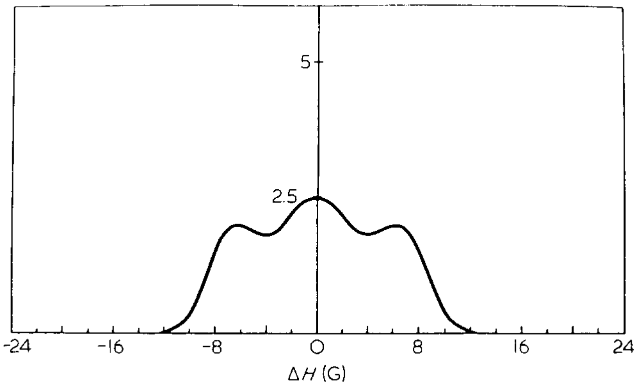


Figure 9 α-CH_3 signal at 6 K

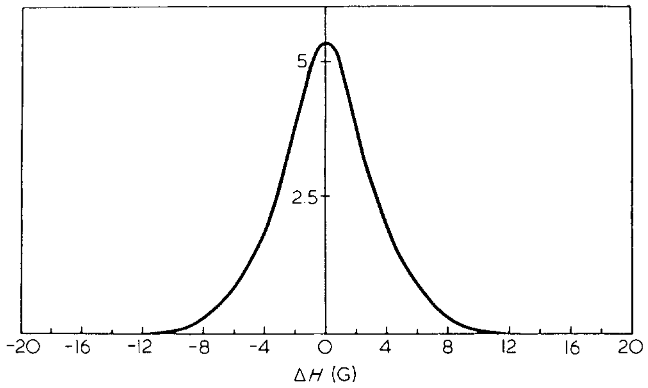


Figure 10 Ester-CH_3 signal at 6 K

(*Figure 8*); that is, a rigid methyl signal (as shown in *Figure 1(a)* and *9*) with an additional central minimum arising from the subtraction of the free monomer signal.

Figure 11 shows the room temperature signal obtained by subtracting the ester-CD_3 PMMA signal from that of Perspex. This should yield the room temperature ester–methyl line shape but instead of the single peak characteristic of rotating methyl groups (shown in *Figure 1(b)*), a double peak is observed. As in the Perspex-α-CD_3 PMMA case, a central minimum arises because data from material containing unpolymerized monomer has been subtracted from that for commercial Perspex. The observed signal is a single mobile methyl peak from which a sharper peak associated with the free monomer has been subtracted. If the ester–methyl group were rigid at this temperature, a curve of the form of *Figure 8* would be produced. Therefore, despite difficulties in interpretation of the subtracted spectrum arising from the presence of free monomer, it may be concluded that the ester–methyl group is in motion at room temperature.

Table 6 summarizes the information obtained about methyl group motion by subtraction of absorption signals.

CONCLUSIONS

A consistent picture of the motion of methyl groups within the PMMA molecule emerges from this work. It has been demonstrated that the α-methyl group undergoes hindered rotation at room temperature. As the temperature is reduced, the degree of motion decreases and is significantly diminished at 240 K. At 79 K, α-methyl motion is effectively quenched although there is some evidence that a very limited degree of mobility may persist even at this temperature. Measurements made at lower temperatures show that this methyl group is rigid at 6 K.

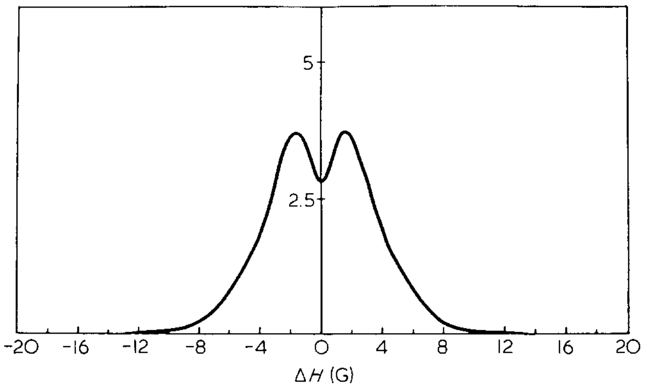


Figure 11 Ester-CH_3 signal at 293 K

Table 6 Results from subtraction of absorption signals

Temperature (K)	Motion of ester–methyl group	Motion of α-methyl group
293	Ester–methyl in motion	No information
6	Ester–methyl motion just commencing	α-methyl rigid

At room temperature, the ester–methyl group is also mobile and this motion persists throughout the temperature range investigated down to liquid helium temperature. Measurements at 6 K show that ester–methyl motion is just starting to 'freeze out' at this temperature.

These conclusions are consistent with those of Sinnott[2,5] who postulated that the ester–methyl group undergoes hindered rotation below 4.2 K and that both types of methyl group are in motion at 250 K, but only the ester–methyl motion persists at 77 K. The onset of α-methyl motion in the temperature range 100 K to 250 K was also observed by Odajima *et al.*[6] for both isotactic and syndiotactic forms of PMMA. Similar results have also been obtained by Gabrys and Higgins using inelastic neutron scattering[3].

The results however conflict with those of Powles[4] who concluded that both types of methyl group were rigid at 77 K, and only one type was in motion at room temperature (this motion commencing over the range 130 K to 200 K), the onset of the other occurring just above 340 K.

ACKNOWLEDGEMENTS

We are indebted to Dr A. H. Milburn for his help in preparing the deuterated forms of methyl methacrylate and to Mrs J. Tilley of I.C.I. Limited (Plastics and Petrochemicals Division) for undertaking their polymerization. We wish to thank Dr N. Boden and Dr L. Clark for obtaining high resolution n.m.r. spectra of these materials, Dr A. J. Manuel for assistance with experimental aspects of the broad-line n.m.r. work and Mr I. S. Davidson who wrote the initial computer programs which facilitated analysis of the n.m.r. data.

One of us (JH) is indebted to the Science and Engineering Research Council for a Research Studentship.

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