Polymer Vol. 39 No. 26, pp. 6835–6849, 1998
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0032-3861/98/$ - see front matter

PII: S0032-3861(98)00137-2

Secondary relaxation processes in polyethylene terephthalate-additive blends: 1. N.m.r. investigation

A.S. Maxwell[a], I.M. Ward[a,*], F. Lauprêtre[b] and L. Monnerie[b]
[a]*IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK*
[b]*Laboratoire de Physicochimie Structurale et Macromoléculaire Associé au CNRS, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France*
(Revised 19 December 1997)

High-resolution carbon-13 and deuterium n.m.r. experiments have been used to examine the effects that low-molecular weight additives have on the secondary relaxation processes in polyethylene terephthalate (PET). These experiments have revealed that both the phenyl rings and the carbonyl groups in PET undergo small angle oscillations at temperatures below the glass transition temperature. It would, however, appear from the deuterium n.m.r. experiments that the phenyl rings also undergo rapid 180 flips, which appear to be closely related to the relaxation peak that is observed in dynamic mechanical experiments. Extremely little motion has, however, been observed in the ethylene glycol units and it has therefore been concluded that this group does not contribute to the secondary relaxation processes. Finally it has been observed that by blending low-molecular weight additives into the polymer it is possible to significantly reduce the number of the phenyl ring flips in the polymer and thereby suppress the relaxation peak. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polyethylene terephthalate; additive blends; n.m.r.)

INTRODUCTION

It is well established[1–4] that by adding low-molecular weight additives to certain polymers it is possible to reduce the local molecular motions that are responsible for the secondary relaxation processes in the polymer. This type of behaviour is known as ‘antiplasticisation’ and has been extensively studied in polycarbonates[1,2], where it has been shown to significantly enhance the mechanical properties of the polymer. The research described in this publication and the following paper[5], stems from the realisation that relatively little is known about the effects that antiplasticisers have upon the relaxation processes in polyethylene terephthalate (PET), despite the fact that it is known that these relaxation processes significantly affect the properties of the polymer.

In the accompanying paper[5] the affects that low-molecular weight additives have upon the mechanical and dielectric relaxation processes in PET are discussed. The general conclusion is that the main secondary relaxation peak in PET, consists of two different relaxation processes, one on the low temperature side and one on the high temperature side of the peak. When low-molecular weight additives are added to the polymer it has been found that only the high temperature side of the peak is affected. The purpose of this work is therefore to confirm these conclusions through the use of various n.m.r. techniques and to identify the molecular groups that are responsible for each of the relaxation processes.

Among the various techniques that can be used to examine molecular mobility in solid polymers, n.m.r. spectroscopy is one of the most powerful[6]. Many different n.m.r. parameters may be used to investigate the molecular motions that are present in the polymer; however, of particular interest in this work are the chemical shift anisotropy, cross-polarisation times and quadrupole interactions. The main advantage of n.m.r. over the dielectric and mechanical techniques is that it allows the mobility in different parts of the molecule to be examined. These techniques therefore enable us to identify which molecular motions are responsible for each of the relaxation peaks and to determine the affect that the additives have on the molecular mobility in each region of the polymer.

Many different authors[7–13] have investigated the dynamics of PET using n.m.r. techniques. One of the earliest investigations into this subject was published in a series of papers by Ward and co-workers[7,8]. Initial results obtained by Ward indicated the presence of a relaxation process in T_1 measurements with an activation energy of approximately 2 kcal/mol. The relaxation process responsible for this behaviour was observed at relatively low temperatures and its low activation energy was believed to be due to a distribution of correlation times. Subsequent results obtained from a series of polyester samples with successively longer aliphatic units led to the observation that even in the long chain aliphatic units only very small molecular motions could be seen during the β relaxation process. Only above the glass transition temperature at 110°C did the signal show any structure, with both a mobile (narrowline) and an immobile (broadline) fraction appearing in the n.m.r. signal. The narrowline fraction was composed of contributions from both aliphatic and phenyl ring protons and the broadline fraction from rigid phenyl rings and motionally hindered aliphatic protons.

Using selectively deuterated PET samples English[9] has identified significant motion of the ethylene glycol units at the glass transition temperature, which have been assumed to be due to a unique *trans-gauche* motion in the ethylene glycol units. At lower temperatures, however, a second

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* To whom correspondence should be addressed

relaxation process has been identified that appears to be consistent with the β relaxation peak in the mechanical work. This relaxation process has a considerably lower activation energy than the glass transition process and is assumed to be due to the motion of the phenyl rings. It is, however, interesting to note that the ethylene glycol units do not appear to contribute to the relaxation processes present in the β peak. Later work[10,11] has confirmed the importance of phenyl ring flips in PET below the glass transition temperature. It should, however, be noted that both the crystallinity and the degree of orientation[12,13] appear to significantly reduce the relaxation processes present in the polymer.

To improve our basic understanding of the secondary relaxation processes in polymer/additive blends, a series of n.m.r. experiments have been conducted to determine the molecular motions that are responsible for the different relaxation peaks. Through the use of different n.m.r. techniques it has been possible both to identify the different regions within the polymer that are responsible for the relaxation processes and to model the different molecular motions that are present in each part of the polymer. Furthermore, by comparing the molecular motions present in the original polymer to those present in the polymer/additive blends it has been possible to examine the mechanisms by which the low-molecular weight additives suppress the β peak in these blends.

SAMPLE PREPARATION

The additive that has been used to examine the effect that antiplasticisers have on relaxation processes in PET is tetrachlorophthalic dimethyl ester (TPDE), the chemical formula of which is shown in *Figure 1*. To produce the required polymer/additive blend, 10% of the TPDE additive has been blended into the polymer using a tabletop APV twin-screw extruder. This polymer blend was then melted in a hot press and quenched to ensure that the polymer was completely amorphous. It was then cryogenically ground into a fine powder, that was suitable to use in the n.m.r. experiments.

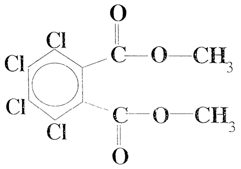


Figure 1 Chemical formula of tetrachlorophthalic dimethyl ester (TPDE)

EXPERIMENTAL

High-resolution carbon-13 n.m.r. has been used to determine the chemical shift anisotropy and $T_{1/2}$ cross-polarisation times in PET blends, over a range of temperatures from 295 to 420 K. These experiments have been conducted at 75.47 MHz on a Bruker 300 spectrometer, using proton dipolar decoupling, magic angle spinning (MAS) and cross-polarisation. To determine the chemical shift anisotropy in samples of pure PET the Herzfeld and Berger technique[14] has been used. This technique allows chemical shift anisotropy results to be determined from the spinning side bands. It is therefore essential in this technique to have well-defined spinning side bands and this is achieved by using a relatively low magic angle spinning rate (4 kHz) with a cross-polarisation contact time of 1 ms. The chemical shift parameters are then calculated from the spinning side-bands using the graphical method developed by Herzfeld and Berger[14]. This allows chemical shift anisotropy parameters to be determined for the protonated and unprotonated aromatic carbons (129 and 133 ppm, respectively) and the carbonyl groups (164 ppm).

To determine the chemical shift anisotropy in polymer/additive blends a static chemical shift anisotropy technique has been used. In this technique magic angle spinning is not used, so that rather than obtaining spinning side bands an entire chemical shift pattern is observed. As a consequence, the chemical shift anisotropy patterns for each type of carbon nuclei are superimposed on top of each other, with the result that it is impossible to identify the individual patterns. To overcome this problem short cross-polarisation contact times are used, so that only signals from the protonated carbons are obtained. As a consequence signals are only obtained from protonated aromatic and aliphatic carbons, which can easily be identified. The advantage of this technique over the Herzfeld and Berger technique is that it allows the chemical shift anisotropy of the protonated aromatic carbons in the PET to be distinguished from the chlorinated aromatic carbons in the additive.

In the cross-polarisation experiments molecular mobility is studied by examining the effect that different cross-polarisation contact times (5–7000 μs) have on the development of magnetisation in protonated aromatic and aliphatic carbons. To obtain a reasonable accuracy it is necessary to have well-defined aromatic and aliphatic peaks, which is achieved by using a magic angle spinning rate of 6.6 kHz, so that the spinning side bands do not interfere with the main carbon peaks. The $T_{1/2}$ cross-polarisation time is defined as the contact time required to produce half the maximum value of magnetisation ($S_{\max}$), that is possible by cross-polarisation. $S_{\max}$ has been derived by extrapolating the decrease that is observed in the ^{13}C magnetisation at long contact times, to zero time.

Deuterium n.m.r. spectra have been obtained using a Bruker 300 spectrometer which has been fitted with a high power broad band probe and a 10 mm diameter solenoid coil[10]. Due to the width of the deuterium spectra in excess of 180 kHz, a composite pulse sequence has been used[15]. This extends the frequency range over which an undistorted signal can be obtained by 25%, with the result that an undistorted spectra can be obtained over 250 kHz, with a 90° pulse length of 5 μs. To examine the molecular mobility at different positions along the polymer chain, two selectively deuterated PET samples have been examined, one with deuterated aromatic rings and the other with deuterated aliphatic carbons.

RESULTS

High-resolution n.m.r. spectra

The high-resolution solid-state ^{13}C n.m.r. spectra of PET, as observed at room temperature, are shown in *Figure 2*. The molecular groups to which the main peaks in the spectra

Table 1 Assignment of the main peaks in the PET spectrum at room temperature

Molecular group	Peak position (ppm)
Carbonyls	164
Unprotonated aromatic carbons	133
Protonated aromatic carbons	129
Aliphatic carbons	62

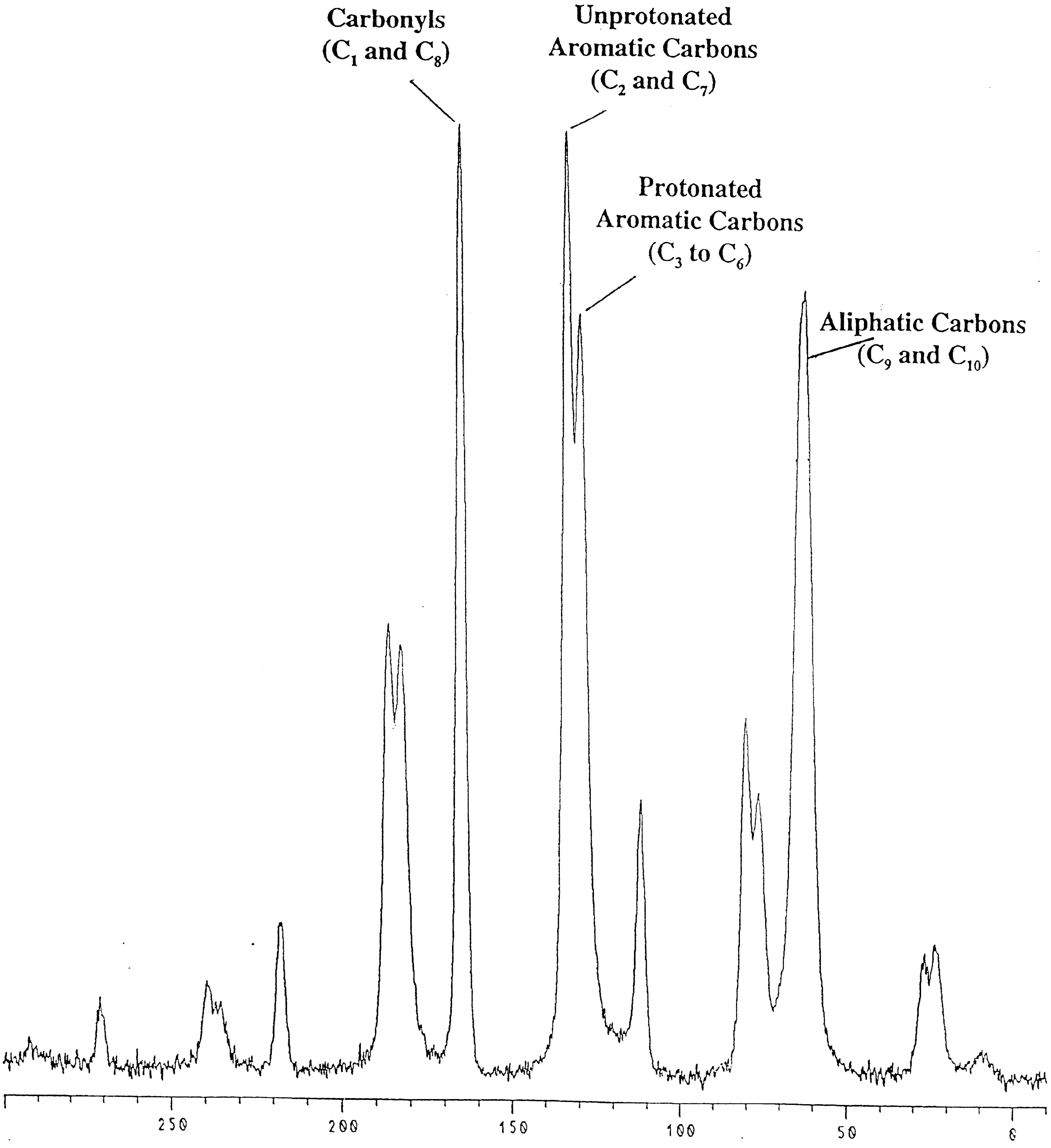


Figure 2 Solid-state carbon-13 n.m.r. spectrum for a sample of powdered PET at room temperature

correspond are given in *Table 1*, and the positions of these groups in the polymer chain are shown in *Figure 3*.

The peaks that have been identified in PET (*Figure 2*), are consistent with those that have been observed by Gabrielse *et al.*[12] in drawn PET yarns. The peak at 164 ppm represents the resonance of the carbons in the carbonyl groups (C_1 and C_8). The partially overlapping peaks that are observed at 133 and 129 ppm are due to the unprotonated (C_2 and C_7) and protonated aromatic carbons (C_3–C_6), respectively, and the peak at 62 ppm represents the aliphatic groups (C_9 and C_{10}). All other peaks in the spectrum are spinning side-bands due to either the carbonyl or aromatic groups. Spinning side-bands are not observed for the aliphatic group, as the chemical shift anisotropy is too small for the side-bands to form.

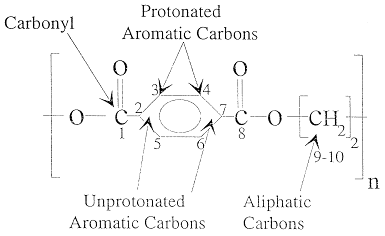


Figure 3 Diagram showing the different carbon nuclei in a PET monomer unit

Identifying the peaks in the PET/TPDE spectrum in *Figure 4* is more complicated than in pure PET, as the peaks from the additive overlap those from the PET. The only additive peak that can be clearly identified (*Figure 4*) is a small peak (54 ppm) on the right hand side of the main aliphatic group. This peak is probably due to the methyl carbons that are present in the additive. The reason that no other peaks from the additive can be identified is that they are covered by much larger peaks from the PET.

Chemical shift anisotropy results

The chemical shift anisotropy of the protonated and unprotonated aromatic carbons and the carbonyls has been determined by deriving the chemical shift parameters σ_{11}, σ_{22} and σ_{33} from the spinning side bands. The chemical shift parameters are orthogonal to each other, with σ_{11} normal to the plane of the phenyl ring and σ_{33} along the 2–7 axis, as shown in *Figure 5*. Chemical shift parameters cannot, however, be obtained for the aliphatic carbons as this group does not have spinning side bands. Values for the chemical shift parameters in samples of PET are given in *Tables 2–4*. To examine the

Table 2 Chemical shift parameters for protonated aromatic carbons in PET

Temperature (°C)	σ_{11}	σ_{22}	σ_{33}	$(\sigma_{33}-\sigma_{11})$
Rigid lattice	−94.8	−26.7	121.5	216.2
22	−92.0	−25.9	117.9	209.9
47	−83.6	−31.1	114.6	198.2
67	−79.1	−31.6	110.7	189.7
87	−73.2	−32.1	105.3	178.5
107	−75.8	−31.8	107.6	183.4
127	−70.8	−31.1	101.8	172.6
147	−63.6	−34.5	98.2	161.8

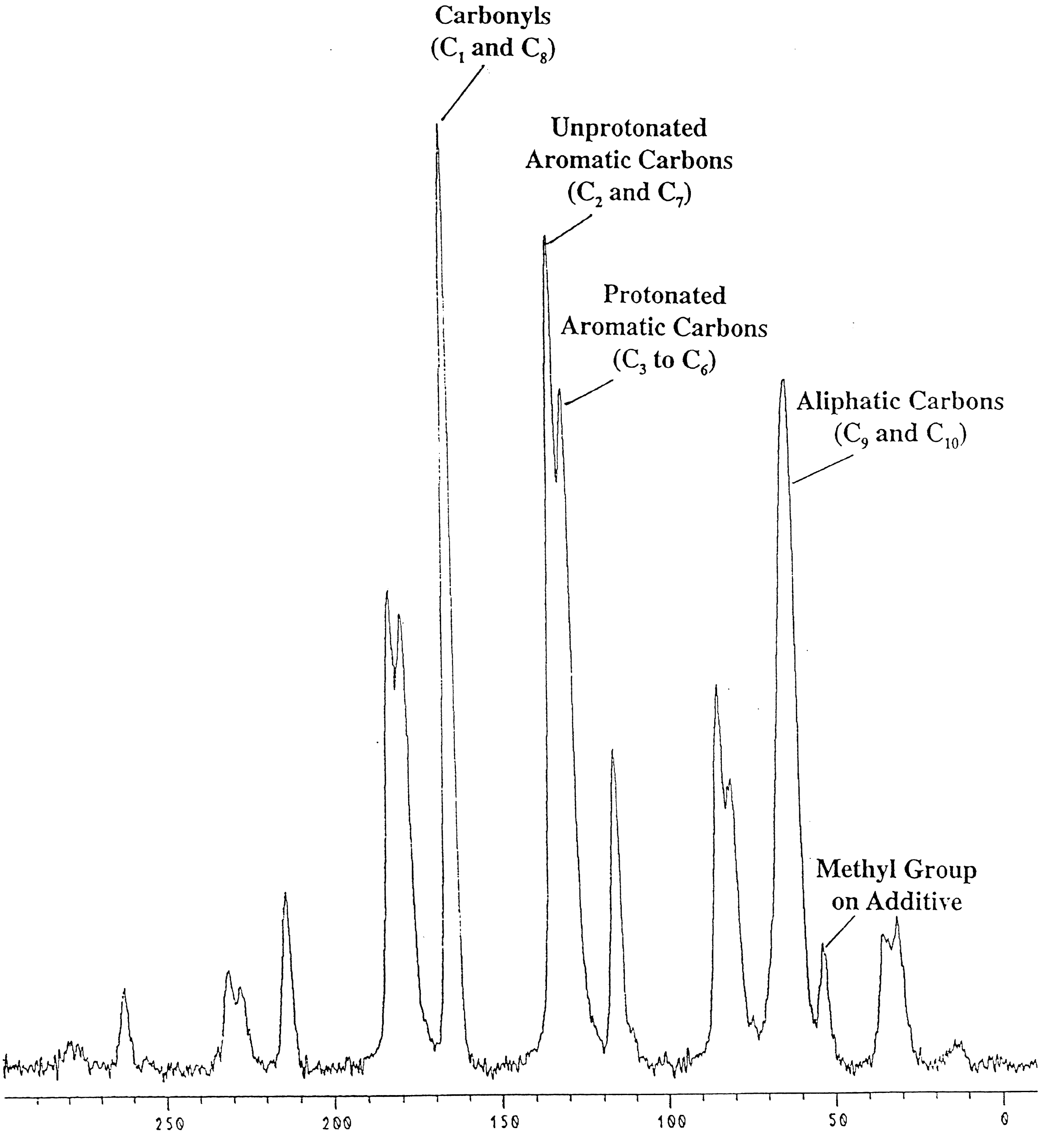


Figure 4 N.m.r. spectrum of a powdered PET/TPDE blend at 25°C

molecular mobility within the polymer, the difference between σ_{11} and σ_{33} has been calculated *Tables 2–4*. This allows the molecular mobility within the polymer to be investigated, as the value of (σ_{33}–σ_{11}) is reduced when the molecule becomes mobile.

The molecular mobilities of the carbonyl and aromatic groups in PET have been examined by plotting the value of (σ_{33}–σ_{11}) as a function of temperature between 20 and 150°C (*Figures 6–8*). In *Figure 8* it can be seen that, as the temperature increases, there is a decrease in the chemical shift anisotropy (σ_{33}–σ_{11}) of the protonated aromatic carbons. This would appear to indicate that there is an increase in the mobility of the aromatic rings at higher temperatures. It can, however, be seen that at 107°C there is a significant increase in the chemical shift anisotropy of the protonated aromatic carbons. This is at a position just above the glass transition temperature of the polymer and would appear to be due to the crystallisation of the polymer. In *Figures 7 and 8* the chemical shift anisotropy of the carbonyl and unprotonated aromatic carbons are displayed as a function of temperature. It can be seen from these results that the decrease in the chemical shift anisotropy in these groups is far less significant than in the protonated aromatic carbons. The results are, however, similar to those of the protonated aromatic carbons, with a gradual decrease in the value of the chemical shift anisotropy (σ_{33}–σ_{11}) up to the glass transition temperature (87°C) and then a slight increase at 107°C due to crystallisation.

Static chemical shift anisotropy

Static chemical shift anisotropy spectra have been used to examine the effect that the additives have on the molecular mobility of the phenyl and aliphatic groups in PET. This has been done by comparing the spectra that are obtained from samples of PET and PET/TPDE, at room temperature and 60°C (*Figure 9*). These spectra consist of two main signals, with an aliphatic signal between 0 and 100 ppm and an aromatic signal between 0 and 250 ppm. It can be seen, however, that the aliphatic signal (0–100 ppm) is not significantly altered at higher temperatures. This would indicate that the aliphatic carbons are not mobile in either the PET or the polymer/additive blends over this frequency range. It can be seen, however, that the shape of the chemical shift pattern that is obtained from the aromatic carbons between 100 and 250 ppm, changes significantly at higher temperatures (*Figure 9*). This is consistent with the chemical shift anisotropy results that have been obtained

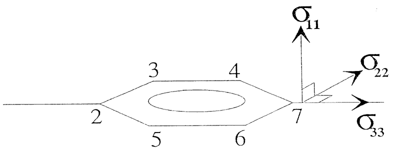


Figure 5 Schematic diagram of the chemical shift parameters in the phenyl ring

Table 3 Chemical shift parameters for unprotonated aromatic carbons in PET

Temperature (°C)	α_{11}	σ_{22}	σ_{33}	(σ_{33}–σ_{11})
Rigid lattice	−98.4	−14.1	112.5	210.9
22	−95.7	−13.7	109.4	205.1
47	−95.5	−13.6	109.1	204.6
67	−93.6	−12.7	106.2	199.8
87	−90.2	−10.8	101.0	191.2
107	−93.6	−8.5	102.1	195.6
127	−93.5	−7.1	100.6	194.1
147	−91.1	−7.6	98.7	189.7

Table 4 Chemical shift parameters for carbonyls in PET

Temperature (°C)	σ_{11}	σ_{22}	σ_{33}	(σ_{33}–σ_{11})
Rigid lattice	−77.4	21.7	55.6	133.0
22	−83.9	35.3	48.6	132.5
47	−85.4	41.1	44.3	129.9
67	−85.9	42.9	42.9	128.8
87	−84.7	42.3	42.3	127.0
107	−86.9	43.5	43.5	130.4
127	−86.0	43.0	43.0	128.9
147	−85.0	42.5	42.5	127.5

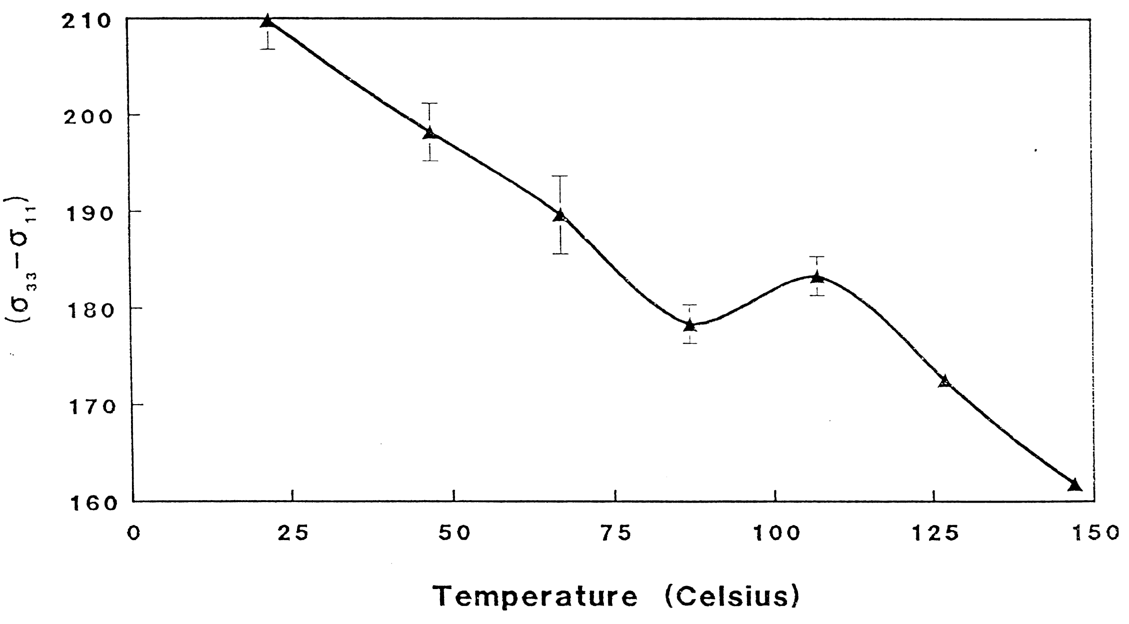


Figure 6 Graph showing a clear decrease in the chemical shift anisotropy of the protonated aromatic carbons (C_3–C_6) in PET

using the Herzfeld and Berger technique and would indicate that the phenyl rings in PET are mobile. It is, however, important to note that the shape of the chemical shift pattern in the PET/TPDE blend (*Figure 9c,d*) is not affected as much as in the pure PET. This would indicate that the phenyl rings in the PET/TPDE blend are not as mobile as in the pure polymer. It would therefore appear from these results that the TPDE additive has reduced the mobility of the phenyl rings.

Cross-polarisation results

$T_{1/2}$ cross-polarisation contact times have been used to examine the molecular mobility of protonated aromatic and aliphatic carbons in PET over a range of temperatures between 20 and 130°C (*Figure 10*). As can be seen, although $T_{1/2}$ increases significantly with temperature in the aromatic carbons, it appears to remain virtually unaltered in the aliphatic carbons, up to the glass transition temperature at approximately 80°C. This is consistent with the chemical shift anisotropy results and would appear to indicate that, although there is an increase in the mobility of the aromatic carbons as the temperature increases, there is little mobility in the aliphatic carbons. It can, however, be seen that at 107°C there is a significant drop in $T_{1/2}$ in both the aliphatic and aromatic carbons, which is believed to be due to the crystallisation of the PET. Furthermore, it can be seen that when the TPDE additive is blended into the polymer there is a significantly drop in the value of $T_{1/2}$ for the aromatic carbons. This would appear to be consistent with the static chemical shift anisotropy results and indicates that the additives reduce the mobility of the phenyl rings.

Deuterium n.m.r. spectra

Deuterium n.m.r. spectroscopy has been used to examine the molecular mobility of the aromatic and aliphatic groups

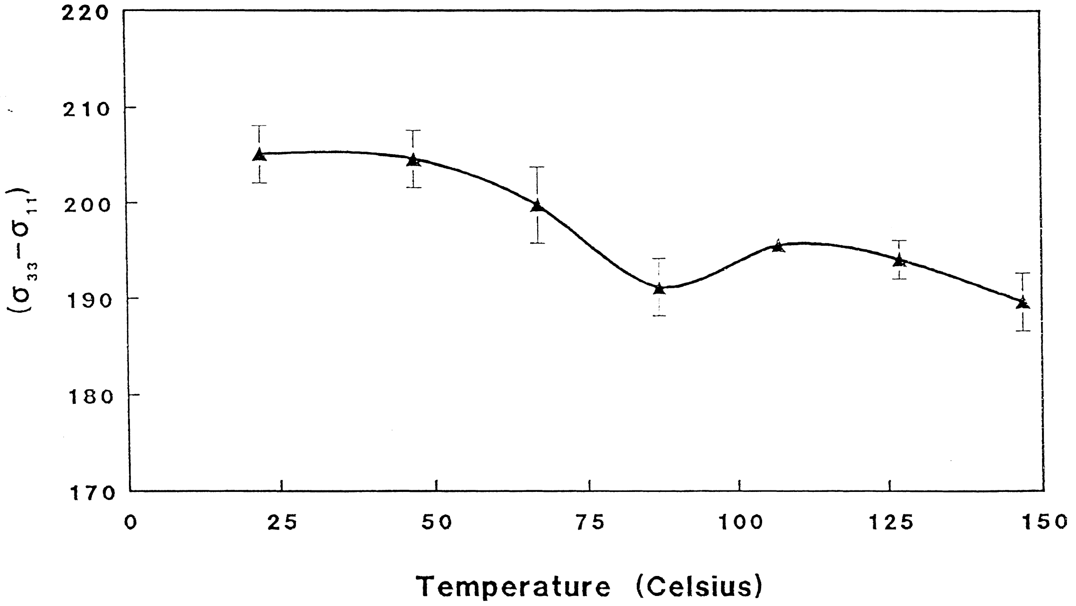


Figure 7 Chemical shift anisotropy results for the unprotonated aromatic carbons (C_2 and C_7) in PET

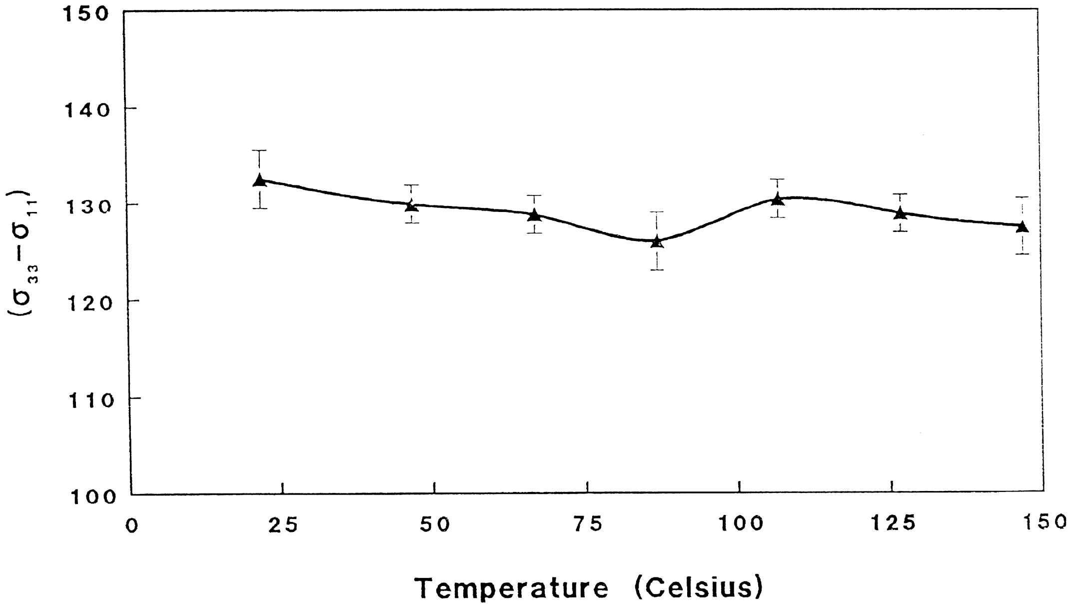
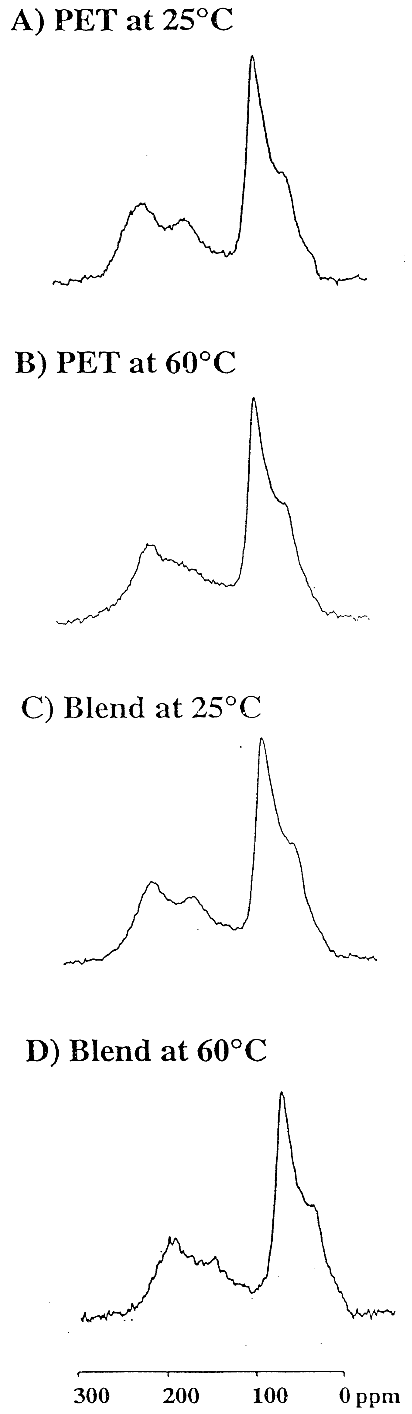


Figure 8 Chemical shift anisotropy results obtained from the carbonyl groups (C_1 and C_8) in PET

in PET. This has been achieved by examining two selectively deuterated PET samples, over a range of temperatures between 20 and 100°C. In one of these samples the phenyl rings have been deuterated (*Figure 11*) and in the other the ethylene glycol units (*Figure 12*). At room temperature it can be seen that both of these samples form Pake doublets, which would indicate that at low temperatures there is little movement in either the phenyl rings or the glycol units. It can, however, be seen that in the deuterated phenyl ring samples an additional narrower set of doublets develops as the temperature is increased (*Figure 11*). It would appear from these spectra that the splitting of this additional doublet is approximately a quarter of that in the main doublet. This is consistent with phenyl rings completing 180° flips about the polymer chain. It can, however, be seen that this additional doublet is not observed in the deuterated glycol spectra (*Figure 12*), which would indicate that there is extremely little mobility in the glycol units below the glass transition temperature.


A) PET at 25°C

B) PET at 60°C

C) Blend at 25°C

D) Blend at 60°C

Figure 9 Static chemical shift spectra of PET and a PET/TPDE blend at room temperature and 60°C

DISCUSSION

Phenyl ring and carbonyl motions

It can be seen from the chemical shift anisotropy results in *Figure 6*, that as the temperature is increased there is an extremely large decrease in the chemical shift anisotropy ($\sigma_{33}-\sigma_{11}$) of the protonated aromatic carbons. This decrease results from the chemical shift anisotropy parameters (σ_{33} and σ_{11}) being averaged as the phenyl rings become mobile as a result of a relaxation process in the polymer. This would appear to be consistent with the large increase that is observed in the cross-polarisation contact times in the protonated aromatic carbons (*Figure 10*), which also arises due to an increase in the mobility of the phenyl rings. It would therefore appear from both the chemical shift anisotropy results and the cross-polarisation times that the mobility of the phenyl rings increases as the temperature is raised from approximately 20–90°C.

To determine whether these n.m.r. relaxation processes are related to the β relaxation process that is seen in mechanical and dielectric experiments, a series of dielectric results has been extrapolated to the frequencies that are used in the n.m.r. experiments (*Figure 13*). The dielectric data which is used in this figure have been obtained from our accompanying paper on the mechanical and dielectric properties of these samples[5]. Through this extrapolation it has been observed that the n.m.r. results occur at approximately the same temperature as the mechanical and dielectric β relaxation peaks are observed. It would, therefore, appear that the relaxations that have been observed in the n.m.r. experiments are closely related to the β relaxation peak that has been observed in the dielectric experiments.

To determine the molecular motions that are responsible for this relaxation process in the phenyl rings, it has been necessary to model the molecular mobility of the protonated and unprotonated aromatic carbons using the chemical shift anisotropy results[16,17] (Appendix A). To model the molecular mobility of the phenyl rings two different types of molecular motion have been considered: (a) ring flips; and (b) oscillations.

In the ring flip model it has been assumed that the phenyl rings complete 180° flips about the chain axis, and that the decrease in the chemical shift anisotropy is due to an increase in the proportion of phenyl rings that are flipping. In the second model it is assumed, that the rings conduct small angle oscillations rather than flips and that the decrease in the chemical shift anisotropy is due to an increase in the amplitude of the oscillations.

It has, however, been found that the chemical shift anisotropy results in both the protonated and unprotonated aromatic carbons are relatively insensitive to phenyl ring flips (Appendix A). It would therefore appear that the large decrease that is observed in the chemical shift anisotropy results must be due mainly to small angle oscillations rather than phenyl ring flips. The chemical shift anisotropy results have therefore been modelled using small angle oscillations. This has been done by calculating the amplitude of the oscillations in the protonated and unprotonated aromatic carbons, over a range of temperatures between 25 and 150°C (*Figure 14*). As can be seen, the amplitude of the oscillations that have been obtained are similar for both the protonated and unprotonated aromatic carbons, which would appear to confirm that the decrease in the chemical shift anisotropy results is due to small angle oscillations. In addition, by modelling the motion of the carbonyl groups using the chemical shift anisotropy results it has also been observed that the carbonyl groups undergo similar small angle oscillations as the phenyl rings.

In addition to the small angle oscillations that are observed in the phenyl and carbonyl groups, it has also been observed using cross-polarisation and deuterium n.m.r. that the phenyl rings undergo 180° flips during the β relaxation process (*Figures 10 and 11*). Unfortunately, as the carbonyl groups cannot be detected using these two n.m.r. techniques, it has not been possible to determine whether the carbonyl groups undergo a similar motion.

Ethylene glycol units

To investigate whether the ethylene glycol units are mobile, cross-polarisation experiments have been used to examine the glycol units. As can be seen from these results (*Figure 10*), the cross-polarisation contact times appear to remain be unaltered up to the glass transition temperature, indicating that the glycol units are not associated with the secondary relaxation processes. This conclusion is confirmed by the deuterium n.m.r. experiments on samples of PET in which the ethylene glycol units have been deuterated (*Figure 12*). As can be seen from the spectra that have been obtained, the spectra do not appear to be significantly altered as the temperature increases. This would appear to confirm that the ethylene glycol units are not mobile, as it would be assumed that a narrower set of doublets or a centre peak would form if the molecules were mobile. These results are, however, rather unexpected as it has been assumed from dynamic mechanical relaxation studies[18] that the ethylene glycol groups are mobile below the glass transition temperature. These results are, however, consistent with deuterium n.m.r. experiments that have previously been obtained by Ward and co-workers[7,8].

Polymer/additive blends

To determine whether the additives reduce the molecular mobility of the aromatic groups in the polymer, $T_{1/2}$ cross-polarisation experiments have been conducted to examine the mobility of the protonated aromatic carbons in PET and the PET/TPDE blends. The advantage of the cross-polarisation experiments is that it makes it possible to distinguish between the motions in PET and those in the additive. This results from the fact that the cross-polarisation contact times in the chlorinated aromatic carbons of the additive are considerably longer than those of the protonated aromatic carbons of the polymer. As a result it can be seen (*Figure 10*) that the $T_{1/2}$ contact times that have been obtained from the aromatic carbons in the PET/TPDE samples are considerably lower than those in the pure PET samples. This shows that the molecular mobility of the aromatic rings in the polymer is greater in the original PET samples than in the PET/TPDE samples. It would therefore appear that the additive reduces the mobility of the phenyl rings in PET.

To confirm that the additives reduce the molecular mobility of the phenyl rings the chemical shift anisotropy has also been examined. Unfortunately, as it is not possible to distinguish between the signals obtained from the PET and the additive, the chemical shift anisotropy of the PET/TPDE blends cannot be studied using the Herzfeld and Berger technique[14]. This problem was, however, overcome by using static chemical shift anisotropy spectra (*Figure 9*), which allow the chemical shift anisotropy of the protonated aromatic carbons in the PET to be distinguished from the chlorinated aromatic carbons in the additive. As a result it was possible to confirm that the molecular mobility of the PET phenyl rings is reduced by the additive. It is, however, important to note that the additives appear to affect the cross-polarisation results considerably more than the chemical shift anisotropy. As it is known that cross-polarisation is considerably more sensitive to phenyl ring

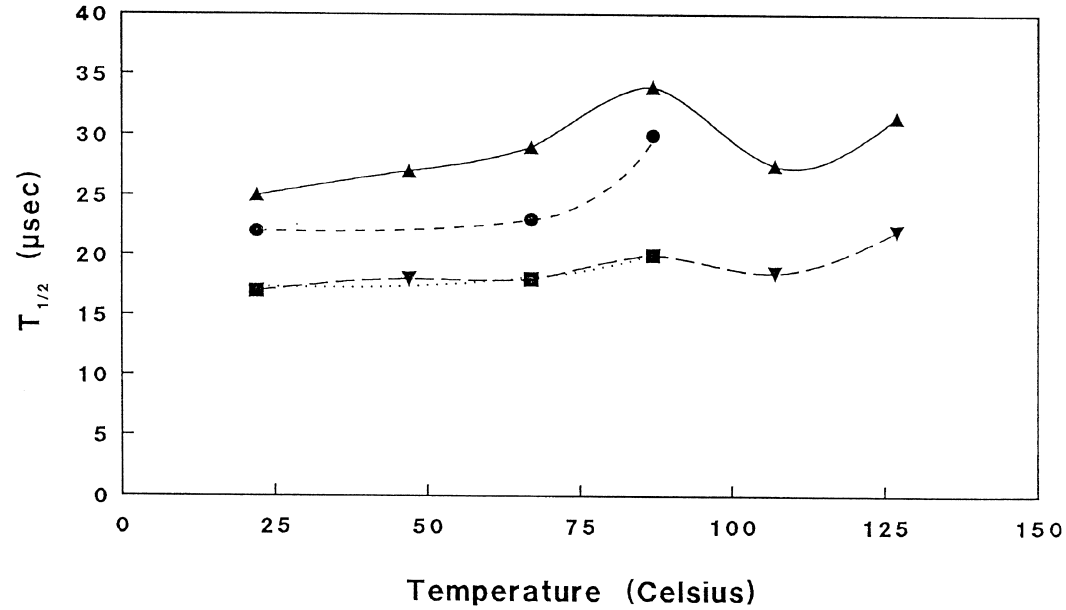


Figure 10 Graph showing the cross-polarisation contact times for the aliphatic carbons in the glycol units and the aromatic carbons in the phenyl rings, in both the original PET and the PET/TPDE blend: (▲) aromatic carbons in PET; (●) aromatic carbons in the blend; (▼) aliphatic carbons in PET; (■) aliphatic carbons in the blend

flips than small angle oscillation, it would appear reasonable to assume that the additives suppress the phenyl ring flips considerably more than small angle oscillations.

To determine the effect that the additives have on the mobility of the phenyl rings, the number of ring flips in the polymer have been estimated using the cross-polarisation results[19] (Appendix B). The fact that some of the values are negative is due to experimental error in the cross-polarisation results, the value of the cross-polarisation contact time being slightly lower than that theoretically predicted for a rigid sample. As can be seen from the results (*Figure 15*), as the temperature is increased there is a significant increase in the number of ring flips in the polymer. As has already been observed this increase in the mobility of the phenyl rings would appear to be due to the β relaxation process. It can, however, be seen that there is a significant drop in the number of ring flips at temperatures above 100°C, which is probably due to crystallisation of the polymer. It is, however, particularly interesting to note that there are considerably fewer ring flips in the

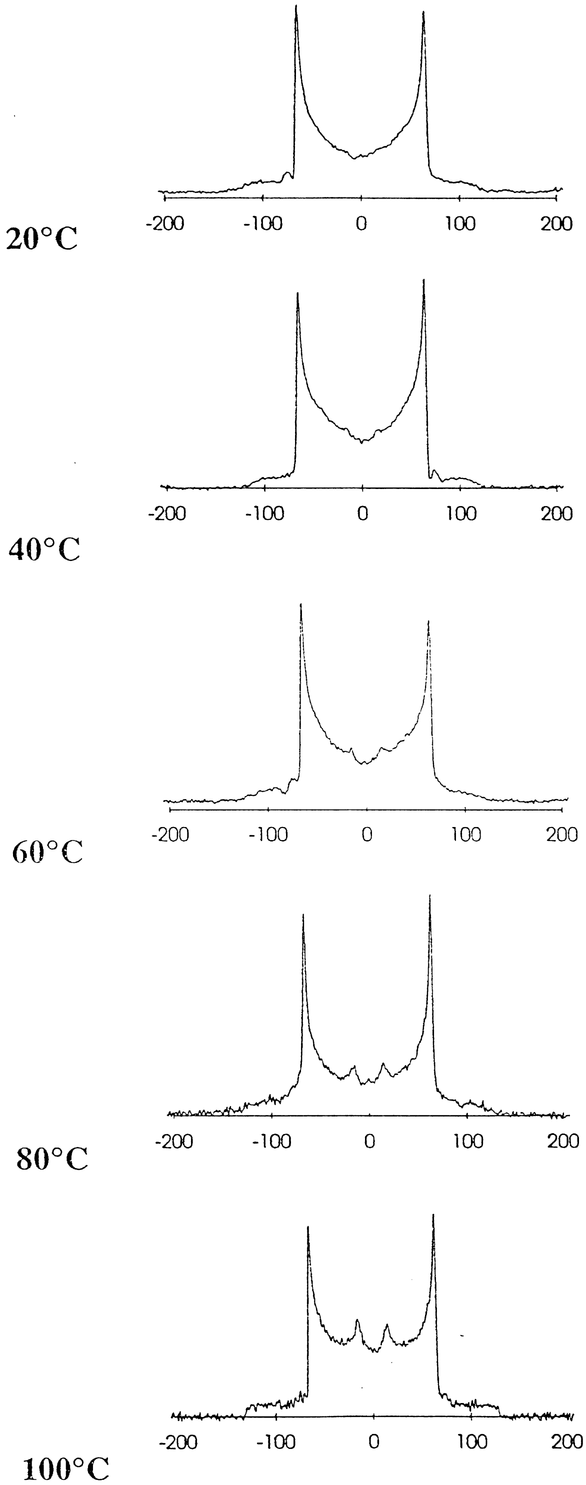


Figure 11 N.m.r. spectra of PET with deuterated phenyl rings, at 20°C the spectra is a typical 'Pake spectra' with the two peaks separated by 180 kHz

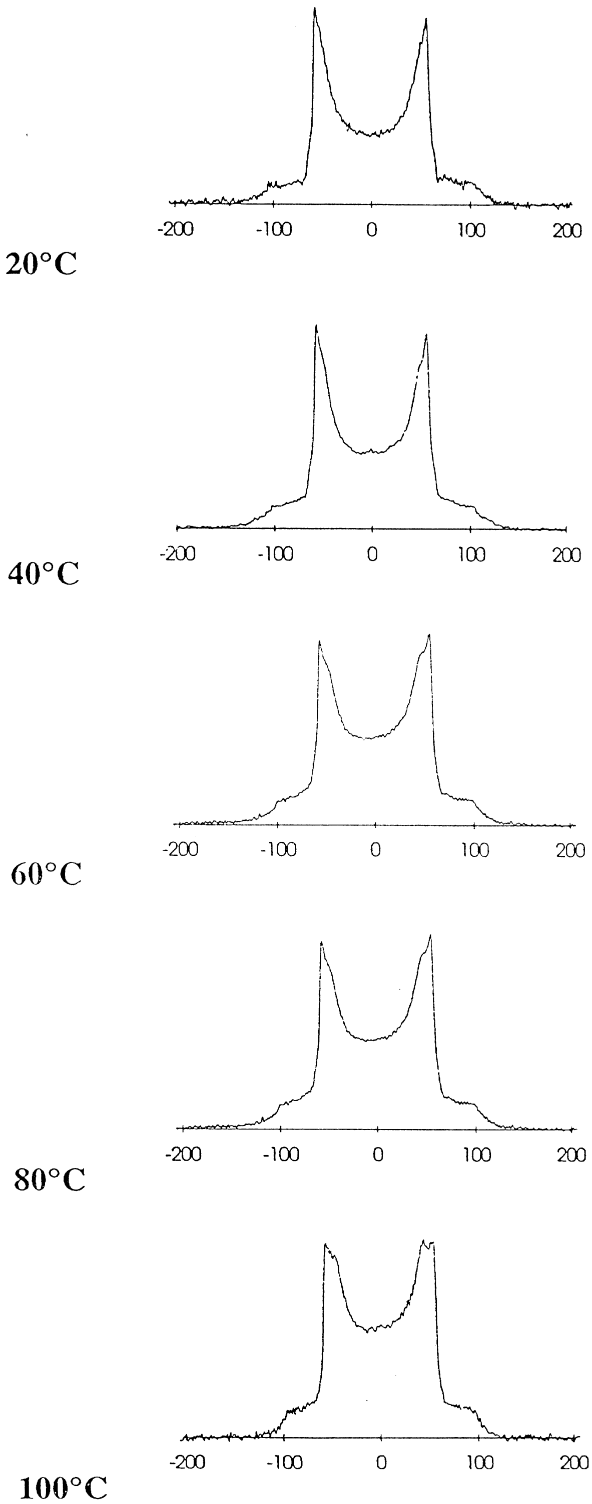


Figure 12 N.m.r. spectra of deuterated glycol units in PET, with 180 kHz splitting

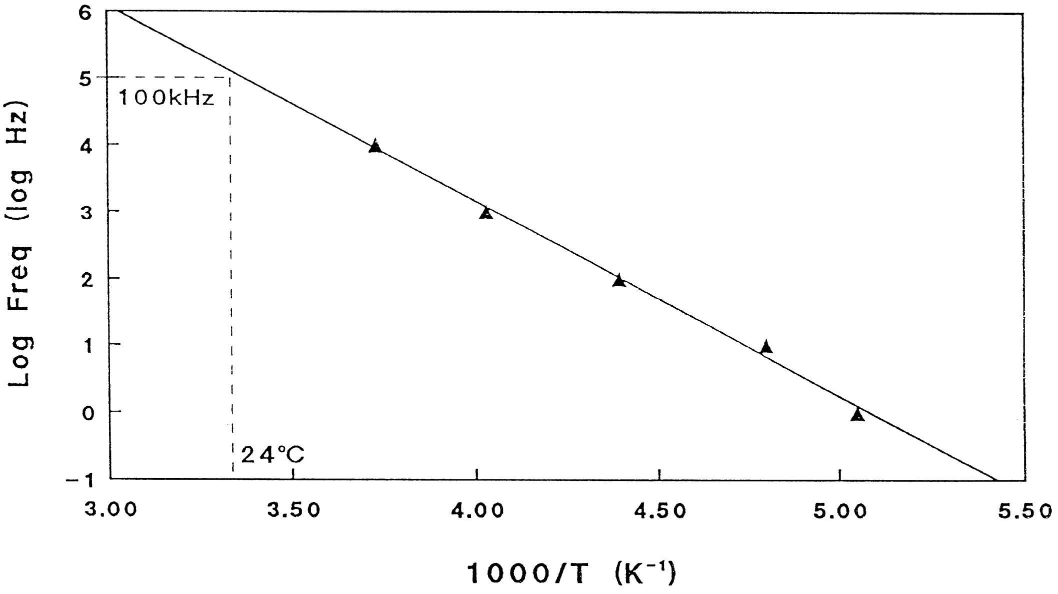


Figure 13 Extrapolating the dielectric results to frequencies that are similar to those used in n.m.r. (100 kHz) it can be seen that the dielectric and n.m.r. relaxation peaks occur at approximately the same temperature

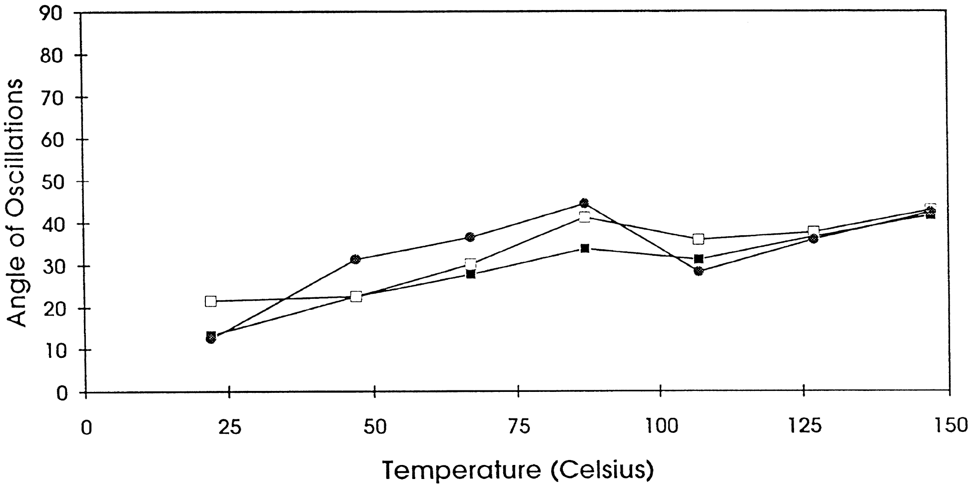


Figure 14 Amplitude of the oscillations in the phenyl rings and carbonyl groups: (■) protonated carbons; (□) unprotonated carbon; (●) carbonyls

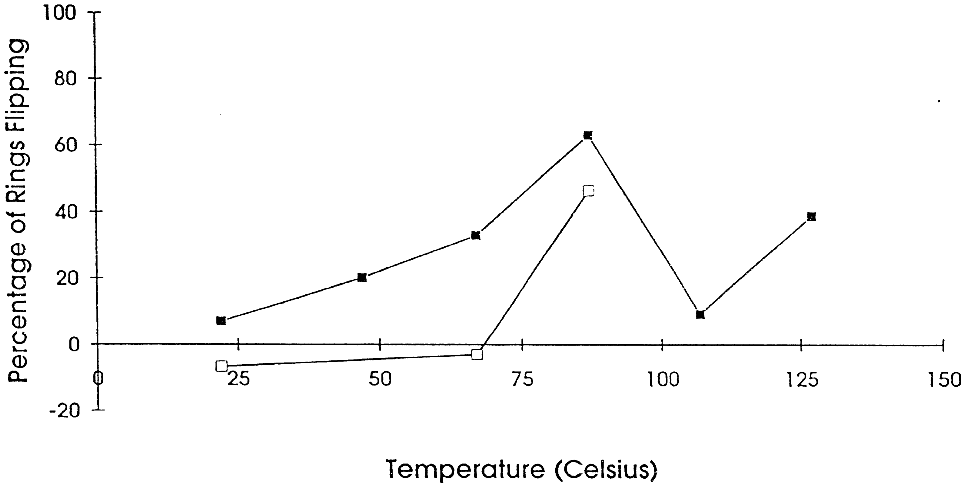


Figure 15 Estimate of the number of phenyl rings that are flipping in PET (■); and the PET blend that contains 10% TPDE (□)

polymer/additive blends than in the pure polymer. This would indicate that the presence of low-molecular weight additives in the polymer reduces the ability of the phenyl rings to flip.

CONCLUSIONS

(1) Chemical shift anisotropy and cross-polarisation experiments both indicate that there is a significant increase in the molecular mobility of the phenyl rings at temperatures and frequencies consistent with that of the β relaxation process.

(2) Modelling the molecular mobility of the phenyl rings, using the chemical shift anisotropy results, indicates that the phenyl rings oscillate at amplitudes of approximately ± 40° during the β relaxation process. In addition it has been observed from deuterium n.m.r. experiments that the phenyl rings also undergo 180° flips during the β relaxation.

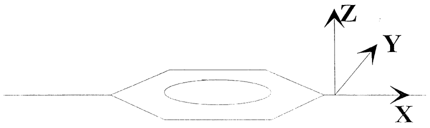


Figure 16 Diagram showing the three main axes of the chemical shift tensor for the unprotonated aromatic carbons on the phenyl ring in PET

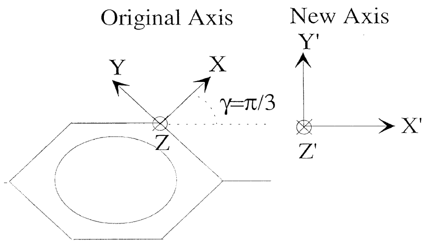


Figure 17 The three main axes of the chemical shift tensor for the protonated aromatic carbons in PET

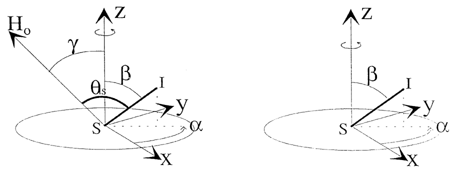


Figure 18 Diagram showing how M_2 is place in a frame of reference, so that H_o is parallel to the axis about which the molecule rotates

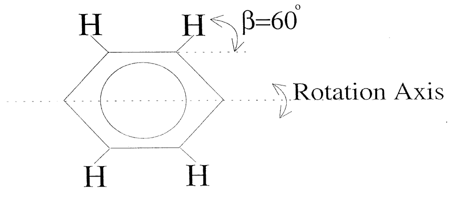


Figure 19 Diagram showing that the angle between the vector of the carbon–hydrogen bond and the axis of rotation in phenyl rings is 60°

(3) Using the chemical shift anisotropy results to model the molecular mobility of the carbonyls, it has been found that the amplitude of the small angle oscillations in the carbonyl groups is similar to that of the phenyl rings.

(4) Cross-polarisation and deuterium n.m.r. experiments indicate that there is relatively little mobility of the ethylene glycol groups in PET, below the glass transition temperature.

(5) Cross-polarisation and static chemical shift anisotropy experiments indicate that the TPDE additive reduces the molecular mobility of the phenyl rings during the β relaxation process.

ACKNOWLEDGEMENTS

We wish to acknowledge the financial support for Dr A.S. Maxwell from ICI PLC and we also wish to thank Dr D.J. Blundell and Dr P. Mills for helpful discussions and providing samples and Dr R. Hann for providing the TPDE additive for the project. We also wish to thank Dr F. Beaume for assistance with the n.m.r. measurements undertaken at ESPCI.

APPENDIX 1

1.1. Chemical shift anisotropy model

To examine the relaxation processes that are present in the polymer, the molecular mobility of the aromatic and carbonyl atoms have been modelled using the chemical shift anisotropy results. This has been achieved by examining the effect that small angle oscillations and phenyl ring flips have upon the chemical shift anisotropy results for the different types of carbon nuclei. First a model for the unprotonated aromatic carbons will be considered and then a model for the protonated aromatic carbons.

1.2. Unprotonated aromatic carbons

For the unprotonated aromatic carbons it can be seen that the nucleus lies directly along the main axis of the polymer chain. It is therefore possible in this case to define the three main axes (*x*,*y*,*z*) of the chemical shift tensor, so that the *x*-axis of the tensor is parallel to the rotating axis in the molecule, as in the diagram below (*Figure 16*). The chemical shift tensor for stationary unprotonated aromatic carbon is therefore given by the following tensor:

$$\sigma_{(x,y,z)} = \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}$$

If, however, the carbon nucleus rotates about the *x*-axis by an angle, its chemical shift tensor is given by:

$$\sigma_{(x,y,z)^{(\alpha)}} = R_{(\alpha)} \cdot \sigma_{(x,y,z)} \cdot R_{(\alpha)}^{-1}$$

where R_α is defined as:

$$R_\alpha = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix}$$

hence at an angle α the chemical shift tensor becomes:

$$\sigma_{(x,y,z)^{(\alpha)}} = \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 \cos^2 \alpha + \sigma_3 \sin^2 \alpha & (\sigma_2 - \sigma_3) \cos \alpha \sin \alpha \\ 0 & (\sigma_2 - \sigma_3) \cos \alpha \sin \alpha & \sigma_2 \sin^2 \alpha + \sigma_3 \cos^2 \alpha \end{pmatrix}$$

Using this transformed tensor it is now possible to determine the effect that different types of molecular motion have upon the chemical shift tensor.

1.2.1. Small angle oscillations

First it will be assumed that the phenyl rings undergo rapid small angle oscillations between angles of $+\alpha$ and $-\alpha$. The tensor will therefore pass through all possible angular positions between $+\alpha$ and $-\alpha$ and it is therefore necessary to average the tensor over this entire range of angles:

$$\left\langle \sigma_{(x,y,z)^{(\alpha)}} \right\rangle_{\mathrm{Oscil}} = \frac{1}{2\alpha} \int_{-\alpha}^{+\alpha} \sigma_{(x,y,z)^{(\alpha)}} \, \mathrm{d}\alpha$$

The chemical shift tensor for small angle oscillations is therefore given as:

$$\left\langle \sigma_{(x,y,z)^{(\alpha)}} \right\rangle_{\mathrm{Oscil}} = \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \frac{\sigma_2 + \sigma_3}{2} + (\sigma_2 - \sigma_3) \frac{\sin 2\alpha}{4\alpha} & 0 \\ 0 & 0 & \frac{\sigma_2 + \sigma_3}{2} (\sigma_2 - \sigma_3) \frac{\sin 2\alpha}{4\alpha} \end{pmatrix}$$

With the principal components of the chemical shift tensor as follows:

$$\sigma_{1(\alpha)}^{\mathrm{Oscil}} = \sigma_1$$

$$\sigma_{2(\alpha)}^{\mathrm{Oscil}} = \frac{\sigma_2 + \sigma_3}{2} + (\sigma_2 - \sigma_3) \frac{\sin 2\alpha}{4\alpha}$$

$$\sigma_{3(\alpha)}^{\mathrm{Oscil}} = \frac{\sigma_2 + \sigma_3}{2} - (\sigma_2 - \sigma_3) \frac{\sin 2\alpha}{4\alpha}$$

It can be seen from the principle components of the chemical shift tensor, that as the amplitude of the oscillations increases the difference between σ_2 and σ_3 is gradually reduced, whereas σ_1 remains unchanged.

1.2.2. Ring flips

When a carbon nucleus undergoes rapid flips of an amplitude, it is equally probable that it will be in its flipped position as its original position. The chemical shift tensor is therefore obtained by averaging the flipped and unflipped chemical shift tensors:

$$\left\langle \sigma_{(x,y,z)^{(\delta)}} \right\rangle_{\mathrm{flips}} = \frac{1}{2} \left(\sigma_{(x,y,z)} + \sigma_{(x,y,z)^{(\delta)}} \right)$$

The average chemical shift tensor that is obtained during ring flips is therefore:

$$\left\langle \sigma_{(x,y,z)^{(\delta)}} \right\rangle_{\mathrm{flips}} = \frac{1}{2} \begin{pmatrix} 2\sigma_1 & 0 & 0 \\ 0 & \sigma_2 (1 + \cos^2 \delta) + \sigma_3 \sin^2 \delta & (\sigma_2 - \sigma_3) \sin \delta \cos \delta \\ 0 & (\sigma_2 - \sigma_3) \sin \delta \cos \delta & \sigma_2 \sin^2 \delta + \sigma_3 (1 + \cos^2 \delta) \end{pmatrix}$$

Assuming that the phenyl rings undergo complete 180° flips, it is found using Eigen values, that the principal components of the chemical shift tensor for the unprotonated aromatic carbons remain unchanged, i.e.

$$\sigma_1^{\pi - \mathrm{flips}} = \sigma_1$$

$$\sigma_2^{\pi - \mathrm{flips}} = \sigma_2$$

$$\sigma_3^{\pi - \mathrm{flips}} = \sigma_3$$

It can therefore be seen that any changes in the chemical shift tensor of the unprotonated aromatic carbons must be due to small angle oscillations rather than phenyl ring flips.

1.3. Protonated aromatic carbons

To consider the effects that molecular motions have on the chemical shift tensor of the protonated aromatic carbons it is necessary to transform the principal axes of the tensor to those in which the molecular motions occur (*Figure 17*). Converting the axes is achieved by using a Euler transformation matrix as shown below:

$$\sigma_{(x',y',z')} = R_{(\gamma)} \cdot \sigma_{(x,y,z)} \cdot R_{(\gamma)}^{-1}$$

where,

$$R_{(\gamma)} = \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The chemical shift tensor for stationary protonated aromatic carbons is therefore:

$$\sigma_{(x',y',z')} = \begin{pmatrix} \frac{\sigma_1}{4} + \frac{3\sigma_2}{4} & \frac{\sqrt{3}}{4} (\sigma_1 - \sigma_2) & 0 \\ \frac{\sqrt{3}}{4} (\sigma_1 - \sigma_2) & \frac{3\sigma_1}{4} + \frac{\sigma_2}{4} & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}$$

If the carbon nuclei rotate about the x-axis by an angle α, the chemical shift tensor becomes:

$$\sigma_{(x',y',z')^{(\alpha)}} = R_{(\alpha)} \cdot \sigma_{(x',y',z')} \cdot R_{(\alpha)}^{-1}$$

where $R_{(\alpha)}$ is defined as:

$$R(\alpha) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos \alpha \end{pmatrix}$$

hence at an angle α the chemical shift tensor of a protonated aromatic carbon becomes:

$$\sigma^{(\alpha)}_{(x',y',z')} = \begin{pmatrix} \frac{\sigma_1}{4} + \frac{3\sigma_2}{4} & \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\cos\alpha & \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\sin\alpha \\ \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\cos\alpha & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4}\right)\cos^2\alpha + \sigma_3\sin^2\alpha & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4}\right)\sin\alpha\cos\alpha \\ \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\sin\alpha & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} - \sigma_3\right)\sin\alpha\cos\alpha & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4}\right)\sin^2\alpha + \sigma_3\cos^2\alpha \end{pmatrix}$$

1.3.1. *Small angle oscillations*

If it is assumed that the phenyl rings undergo small angle oscillations between angles of $+\alpha$ and $-\alpha$, the chemical shift tensor for oscillating protonated aromatic carbons will be an average of all the tensors over the entire range of angles, hence:

$$\left\langle \sigma_{(x',y',z')^{(\alpha)}} \right\rangle_{\text{Oscil}} = \frac{1}{2\alpha}\int_{-\alpha}^{+\alpha} \sigma_{(x',y',z')^{(\alpha)}}\, d\alpha$$

The chemical shift tensor for protonated aromatic carbons undergoing small angle oscillation is therefore:

$$\left\langle \sigma_{(x',y',z')^{(\alpha)}} \right\rangle_{\text{Oscil}} = \begin{pmatrix} \frac{\sigma_1}{4} + \frac{3\sigma_2}{4} & \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\frac{\sin\alpha}{\alpha} & 0 \\ \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\frac{\sin\alpha}{\alpha} & \frac{1}{2}\left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} + \sigma_3\right) + \frac{\sin 2\alpha}{4\alpha}\left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} - \sigma_3\right) & 0 \\ 0 & 0 & \frac{1}{2}\left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} + \sigma_3\right) + \frac{\sin 2\alpha}{4\alpha}\left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} - \sigma_3\right) \end{pmatrix}$$

1.3.2. *Ring flips*

If, however, the phenyl rings are flipping between two positions, separated by an angle δ, the motionally averaged chemical shift tensor is given by:

$$\left\langle \sigma_{(x',y',z')^{(\delta)}} \right\rangle_{\text{flips}} = \frac{1}{2}\left(\sigma_{(x',y',z')} + \sigma_{(x',y',z')^{\delta}}\right)$$

The chemical shift tensor for protonated aromatic carbons that are flipping is therefore:

$$\left\langle \sigma_{(x',y',z')^{(\delta)}} \right\rangle_{\text{flips}} = \begin{pmatrix} \frac{\sigma_1}{2} + \frac{3\sigma_2}{2} & \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)(1 + \cos\delta) & \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\sin\delta \\ \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)(1 + \cos\delta) & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4}\right)(1 + \cos^2\delta) + \sigma_3\sin^2\delta & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} - \sigma_3\right)\sin\delta\cos\delta \\ \frac{\sqrt{3}}{4}(\sigma_1 - \sigma_2)\sin\delta & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4} - \sigma_3\right)\sin\delta\cos\delta & \left(\frac{3\sigma_1}{4} + \frac{\sigma_2}{4}\right)\sin^2\delta + \sigma_3(1 + \cos^2\delta) \end{pmatrix}$$

As can be seen from these models, both small angle oscillations and phenyl ring flips significantly alter the chemical shift tensor of the protonated aromatic carbons. It can therefore be seen that it is considerably easier to detect molecular motions in the protonated aromatic carbons than it is in the unprotonated aromatic carbons. It is, however, important to note that as with the unprotonated carbons, the chemical shift tensor is considerably more sensitive to small angle oscillations than it is to phenyl ring flips.

APPENDIX 2

2.1. *Cross-polarisation model*

2.1.1. *Modulation of $t_{1/2}$*

Cross-polarisation is a technique by which magnetisation is transferred from the proton nuclei to neighbouring carbon nuclei. To determine the rate at which this transfer occurs, the contact time that is required for the magnetisation in the carbon nuclei to reach half its maximum value is measured ($t_{1/2}$). The contact time required depends upon both the dipolar interactions between the spins of the carbon and proton nuclei M_2, and the number of protons to which each carbon is directly bonded, hence:

$$t_{1/2} = \frac{\pi}{\sqrt{n}\sqrt{M_2}}$$

where, M_2 is the second moment of the dipolar interaction, and n is the number of directly bonded protons.

When molecular motions occur in the polymer the dipolar interactions between the carbon and proton nuclei (M_2^{rigid}) are reduced (M_2^{mobile}), with the result that longer cross-polarisation contact times are required to magnetise the carbon nuclei:

$$\frac{t_{1/2}^{\text{rigid}}}{t_{1/2}^{\text{mobile}}} = \sqrt{\frac{M_2^{\text{mobile}}}{M_2^{\text{rigid}}}}$$

For a particular orientation the dipolar interaction M_2, between two nuclei of spins I and S is given by:

$$M_2 = \frac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left[F_{o(r)}\right]^2$$

where,

$$F_{o(r)} = \frac{1-3\cos^2\theta_{IS}}{r^3}$$

θ_{IS} is the angle between the magnetic field $\vec{\mathrm{H}}_{\mathrm{o}}$ and the IS vector.To determine the effect that molecular motions have upon the cross-polarisation, M_2 is placed into a more convenient frame of reference, so that H_{o} is parallel to the z-axis about which the molecule rotates (*Figure 18*). Thus, α is the direction of the IS vector in the xy plane, β is the angle between the IS vector and the z-axis about which the molecule rotates and γ is the angle between magnetic field H_{o} and the z-axis. It can therefore be seen that it is possible to define the angle θ_{IS} in terms of the angles α, β and γ:

$$\cos\theta_{IS} = \cos\beta\cos\gamma - \sin\beta\sin\gamma\sin\alpha$$

2.1.2. Cross-polarisation in a rigid powder

In a powder in which there is no motion the direction of the IS vector is randomly distributed, therefore M_2 must be averaged over all values of α and γ:

$$\left\langle M_2^{\text{rigid}}\right\rangle_{\text{powder}} = \frac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left\langle\left[F_{o(r)}\right]^2\right\rangle_{\text{powder}}$$

where

$$\left\langle\left[F_{o(r)}\right]^2\right\rangle_{\text{powder}} = \frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\alpha\int_0^{\pi}F_{o(r)}^2\sin\gamma\,\mathrm{d}\gamma$$

Therefore M_2 in a rigid polymer powder is given as:

$$\left\langle M_2^{\text{rigid}}\right\rangle_{\text{powder}} = \frac{4}{15}\frac{\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{r^6}$$

2.1.3. Small angle oscillations

2.1.3.1. Single orientation. To examine the effect that small angle oscillations have on the cross-polarisation contact time, a single orientation of the IS vector is considered. In this case the angle α varies with time, t, from $\alpha+\delta$ to $\alpha-\delta$. M_2 therefore becomes:

$$M_2^{\text{oscil}} = \frac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left[\left\langle F_{o(r,t)}\right\rangle_{\text{oscil}}\right]^2$$

where,

$$\left\langle F_{o(r,t)}\right\rangle_{\text{oscil}} = \frac{\displaystyle\int_{\alpha-\delta}^{\alpha+\delta}F_o(r,\alpha)\mathrm{d}\alpha}{\displaystyle\int_{\alpha-\delta}^{\alpha+\delta}\mathrm{d}\alpha} = \frac{1}{2\delta}\int_{\alpha-\delta}^{\alpha+\delta}F_{o(r,\alpha)}\mathrm{d}\alpha$$

2.1.3.2. Oscillations in a powder. To determine the effect that small angle oscillations have on cross-polarisation in a powder, it is necessary to expand the expression for a single orientation to cover all possible angles of α and γ:

$$\left\langle\left[\left\langle F_{o(r,t)}\right\rangle_{\text{oscil}}\right]^2\right\rangle_{\text{powder}}$$

$$= \frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\alpha\int_0^{\pi}\left[\left\langle F_{o(r,t)}\right\rangle_{\text{oscil}}\right]^2\sin\gamma\,\mathrm{d}\gamma$$

The effect that the oscillations of $\pm\delta$ have upon the cross-polarisation are therefore given by the following reduction factor:

$$\frac{\left\langle M_2^{\text{oscil}}\right\rangle_{\text{powder}}}{\left\langle M_2^{\text{rigid}}\right\rangle_{\text{powder}}} = 1 - 3\sin^2\beta\left[1-\left(\frac{\sin\delta}{\delta}\right)^2\right]$$

$$+\frac{9}{4}\sin^4\beta\left[1-\frac{4}{3}\left(\frac{\sin\delta}{\delta}\right)^2+\frac{1}{3}\left(\frac{\sin 2\delta}{2\delta}\right)^2\right]$$

2.1.4. Phenyl ring flips

2.1.4.1. Single orientation. When phenyl rings undergo rapid flips of an amplitude δ, at time t, they are just as likely to be found in their original position as their flipped position. The value of M_2 for a single IS vector can therefore be obtained from the following expression:

$$M_2^{\text{flips}} = \frac{1}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left[\left\langle F_{o(r,t)}\right\rangle_{\text{flips}}\right]^2$$

where,

$$\left\langle F_{o(r,t)}\right\rangle_{\text{flips}} = \frac{1}{2}\left[F_o(r,\alpha)+F_o(r,\alpha+\delta)\right]$$

2.1.4.2. Ring flips in a powder. To expand the above expression to examine the effect that phenyl ring flips have in a powder, it is necessary to expand the above expression to cover all possible angles of α and γ, as shown below:

$$\left\langle\left[\left\langle F_{o(r,t)}\right\rangle_{\text{flips}}\right]^2\right\rangle_{\text{powder}}$$

$$= \frac{1}{4\pi}\int_0^{2\pi}\mathrm{d}\alpha\int_0^{\pi}\left[\left\langle F_{o(r,t)}\right\rangle_{\text{flips}}\right]^2\sin\gamma\,\mathrm{d}\gamma$$

The effect that phenyl ring flips have upon the cross-polarisation of the carbon nuclei is therefore given by the reduction factor:

$$\frac{\left\langle M_2^{\text{flips}}\right\rangle_{\text{powder}}}{\left\langle M_2^{\text{rigid}}\right\rangle_{\text{powder}}} = 1 - 3\sin^2\beta\left(\frac{1-\cos\delta}{2}\right)$$

$$+3\sin^4\beta\left(\frac{1-\cos\delta}{2}\right)^2$$

where, β is the angle between the vector of the carbon–hydrogen bond and the axis about which the molecule rotates, and δ is the angle through which the rings flip.

In the case of PET it can be seen from *Figure 19* that β is 60° and that as the rings are believed to undergo complete flips δ must be 180°. Substituting these values of β and δ into the above equation gives a value for the reduction factor of phenyl rings undergoing ring flips of 0.4375. If it is therefore assumed that the number of rings undergoing flips is 'x', then the reduction factor for the whole polymer is:

$$\frac{\left\langle M_2^{\text{flips}} \right\rangle_{\text{powder}}}{\left\langle M_2^{\text{rigid}} \right\rangle_{\text{powder}}} = x \times 0.4375 + (1-x) \times 1 = 1 - 0.5625x$$

From this equation it is possible to determine the number of rings that are flipping in a polymer from the cross-polarisation contact time $t_{1/2}$.

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