# Nuclear magnetic resonance studies of selectively deuterated aromatic liquid crystalline copolyesters

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Deuterium n.m.r. has been used to follow the molecular dynamics of three polyester materials over a temperature range of −150°C to 150°C. Two of the materials are liquid crystalline copolymers, one of perdeuterated hydroxybenzoic acid and hydroxynaphthoic acid and the other of hydroxybenzoic acid, isophthalic acid and perdeuterated hydroquinone. The third sample is crystalline poly(ethylene terephthalate) (PET) in which the benzene rings are deuterated. At the lowest temperatures examined all three materials give n.m.r. lineshapes characteristic of little molecular motion. On heating the liquid crystalline materials, the onset of motion is observed, first in the form of 180° flips and then unrestricted rotation about the polymer axes. The PET spectra show a small degree of 180° ring flipping to be taking place above 100°C, but most of the motion is in the form of near random motion that comes to dominate at 150°C. The results confirm the relatively stiff rod-like nature of the liquid crystalline polymers in comparison to the more flexible PET.

**(Keywords: liquid crystalline; copolyester; n.m.r.; deuterium)**

## INTRODUCTION

In previous publications the mechanical and dielectric relaxation behaviour of a range of oriented thermotropic copolyesters based on hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) have been discussed[1,2]. In addition, proton n.m.r. studies of these polymers have been reported[3,4]. A general conclusion from these investigations is that there are three major relaxations, a glass transition at ~ 120°C, and two transitions at lower temperatures, relating to motion of the phenylene and naphthalene moieties, respectively.

The proton n.m.r. spectra of these polymers in the form of highly oriented tapes, is consistent with molecular motions, including those in the glass transition range, being limited to rotations within the molecular chains[4]. The present research was directed at confirming these previous conclusions and comparing the results for a crystalline polymer, poly(ethylene terephthalate) (PET), where previous n.m.r. studies[5] have shown that there is much more general molecular mobility associated with the glass transition.

In the present investigations deuterium n.m.r. has been used to observe the dynamic behaviour over a range of temperatures of selectively deuterated aromatic groups in two liquid crystalline copolymers and crystalline PET. This technique has a number of advantages. First, the sample can be selectively deuterated so that specific sites of interest are observed. This obviously simplifies analysis of the results. Second, the quadrupole interaction between the spin = 1 deuterium nucleus and the electric field gradient (EFG) of the C–D chemical bond dominates the n.m.r. spectrum. Other interactions, such as the dipole–dipole interaction are several orders of magnitude less than the quadrupolar interaction. Again, this simplifies interpretation of the spectra. Third, the shape of the quadrupole spectra are sensitive to orientation in the sample and to molecular motion involving the C–D bond. From the lineshapes obtained it is possible to identify, in general, the type of molecular motion taking place.

## EXPERIMENTAL

### *Materials*

Perdeuterated HBA and hydroquinone (HQ) were supplied by Dr R. W. Richards (formerly of Strathclyde University and now at Durham University). These monomers were incorporated into two copolymers by Dr A. Milburn in the Textiles Department, University of Leeds. The first is a copolymer of deuterated HBA and HNA in the ratio 25:75 and the second is a copolymer of HBA, isophthalic acid (IA) and deuterated HQ in the ratio 35:32.5:32.5. There is a general agreement that these polymers consist of randomly substituted chains, although there may be small regions of crystalline order[6–9]. The latter copolymer will henceforth be abbreviated to HIQ. Both samples are unannealed and in the form of coarse grained powders.

A sample of PET in which three positions on the aromatic ring are deuterated was also examined. This sample had originally been specially synthesized for examination by proton n.m.r.[5], where the interactions between protons on any one ring are eliminated by replacing three of the four protons by deuterium nuclei. The PET sample is in the form of an unoriented compressed rod.

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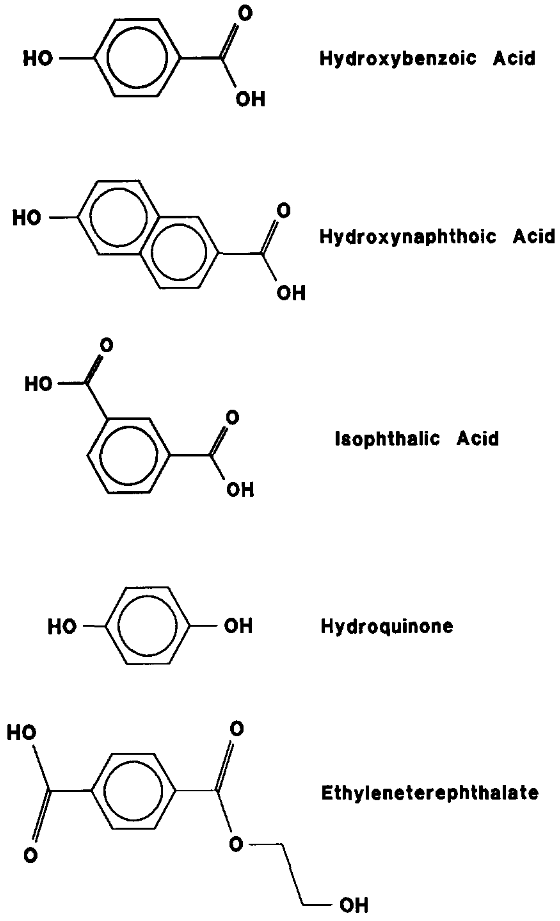

**Figure 1** Molecular structure of the monomer units

The structures of the monomer units are given in *Figure 1*.

*N.m.r. measurements*

N.m.r. deuterium spectra were recorded on a Bruker MSL-300 Fourier transform spectrometer using a high power broad band probe fitted with a 10mm diameter solenoid coil. On this spectrometer, the n.m.r. frequency of deuterium is ~46.073 MHz. Because the deuterium quadrupolar spectra are around 285kHz wide, the composite pulse sequence developed by Raleigh *et al.*[10] has been used. This gives a relatively flat excitation of the magnetization over a frequency range of $5/4D$, where $D$ is the $\pi/2$ pulse length, centred on the spectrometer frequency. A value of $D = 5.0\,\mu s$ was achieved, giving an undistorted spectrum over 250kHz. $T_1$ relaxation times were measured at a limited number of temperatures in order to determine the approximate values involved. These govern the rate at which the macroscopic magnetization reassumes its equilibrium orientation in the spectrometer magnetic field after being disturbed. From these measurements a recycle delay of 6s between data acquisitions was decided upon in order to ensure that all components in the n.m.r. spectra had sufficient time to recover. Spectra were recorded over the temperature range −100°C to 150°C in the case of the HBA:HNA and HIQ copolymers and over 20°C to 150°C in the case of PET.

*Lineshape modelling*

As already mentioned, the deuterium n.m.r. spectra are dominated by the quadrupolar interaction. Other effects are small in comparison. Therefore, in calculating the spectra expected from the deuterated samples only the quadrupolar interaction for the spin = 1 nucleus will be examined in detail and all other interactions will be dealt with by a general line broadening of the spectra.

When the EFG tensor is defined in the principle axis system (PAS) the n.m.r. quadrupolar frequency for a spin = 1 nucleus is given by:

$$\nu = (\nu_Q/2)[3\cos^2(\theta) - 1 - \eta\sin^2(\theta)\cos(2\phi)] \qquad (1)$$

where $\nu_Q$ is the quadrupolar coupling constant, $\eta$ the EFG asymmetry parameter, and $\theta$ and $\phi$ are the second and third Euler angles describing the orientation of the C–D bond with respect to the spectrometer magnetic field $B_0$.

Equation (1) is sufficient for considering samples exhibiting no molecular motion, but is limited when dynamic behaviour has to be incorporated. For the polymers of interest here, it is desirable to express the EFG tensor in the laboratory frame of reference containing the spectrometer magnetic field $B_0$. Locally the rotation axis of the monomer and the polymer chain axis are parallel and in future discussion the two terms will be used interchangeably. The change of coordinate system involves first a transformation of the PAS containing the C–D bond to the coordinate system of the monomer unit containing its rotation axis. A second transformation is then required to convert from the monomer frame of reference to the laboratory frame containing the spectrometer field $B_0$. The first transformation involves two Euler angles $\beta'$ and $\gamma'$ that are assumed constant at $\beta' = 60°$ and $\gamma' = 90°$ for a deuterium atom covalently bonded to an aromatic ring. With this condition, the orientation of the C–D bond is specified only by the Euler angles $\beta$ and $\gamma$ describing the orientation of the monomer unit to the magnet field $B_0$. After performing the transformations, the n.m.r. frequency is given by:

$$\begin{aligned}\nu = (\nu_Q/16)[&(9-5\eta)\sin^2(\beta)\cos(2\gamma)\\ &-\sqrt{3}(6+2\eta)\sin(2\beta)\cos(\gamma)\\ &-(1+3\eta)(3\cos^2(\beta)-1)]\end{aligned} \qquad (2)$$

where $\beta$ and $\gamma$ are the second and third Euler angles describing the orientation of the polymer chain axis relative to the spectrometer magnetic field, $B_0$ (see *Figure 2*). An outline of the mathematics involved is given in the Appendix.

Now, if the aromatic rings undergo 180° flips about the chain axis such that they occupy orientations $\psi + 90°$ and $\psi - 90°$ with equal probability over the lifetime of the n.m.r. experiment, then the n.m.r. frequency for particular values of $\beta$ and $\gamma$ is given by:

$$\begin{aligned}\nu = (\nu_Q/16)[&(9-5\eta)\sin^2(\beta)\cos(2\psi)\\ &+(1+3\eta)(3\cos^2(\beta)-1)]\end{aligned} \qquad (3)$$

At higher temperatures, free rotation of the aromatic rings might be expected. In this case there is complete averaging over $\psi$ and the quadrupolar frequency for a single deuteron is given by:

$$\nu = (\nu_Q/16)(1+3\eta)[3\cos^2(\beta)-1] \qquad (4)$$

Complete n.m.r. lineshapes are obtained from equations (2), (3) and (4) by summing over all possible angles $\beta$ and $\gamma$ or $\beta$ and $\psi$ or $\beta$, respectively.

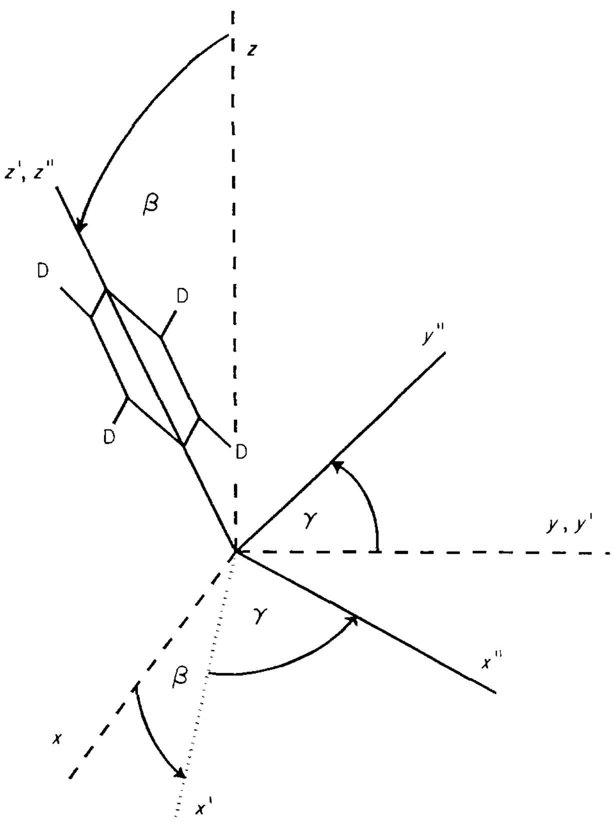

**Figure 2** Definitions of orientation angles $\beta$ and $\gamma$

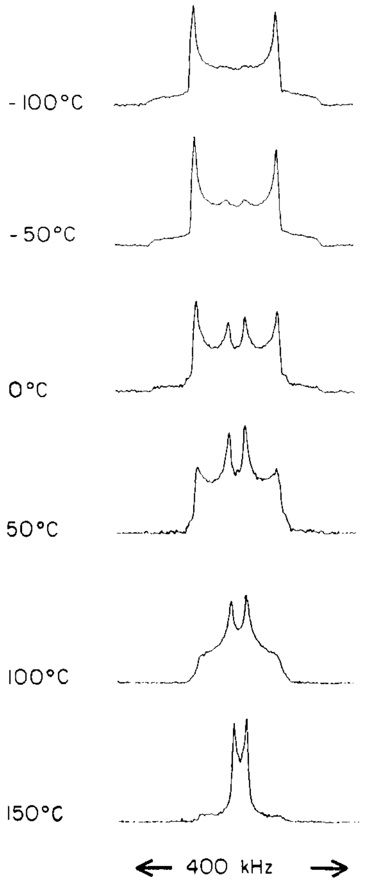

**Figure 3** Deuterium n.m.r. spectra of the HIQ copolymer

Lineshape analysis has been based on that of Greenfield *et al.*[11] and Vold and Vold[12]. Programs have been written in the C computer language on a Silicon Graphics Personal Iris model 4D-20-G. The model currently allows the aromatic rings to be either static, performing rapid 180° flips about the polymer chain axis, or undergoing rapid rotational motion about the chain axis. From equations (2), (3) and (4) we can find the average angular frequency of rotation of a deuterium nucleus in the laboratory frame of reference from any given polymer chain orientation $\beta$, $\gamma$. Using this frequency we can follow the time evolution of the orientation of the spins with respect to the laboratory frame. By summing all such time responses over all possible $\beta$s and $\gamma$s, an n.m.r. time domain signal (free induction decay, f.i.d.) can be constructed. An f.i.d. is computed from each of equations (2), (3) and (4). The f.i.d.s are then multiplied through by an exponential function that broadens the eventual spectrum and accounts somewhat for the other n.m.r. interactions that are omitted from the more detailed model calculations. The process of line broadening is not easily accomplished in the frequency domain and accounts for the construction of the time domain signal. The f.i.d.s are then fast Fourier transformed to yield a frequency spectrum. Finally the spectra may be added together in various proportions to simulate the experimental spectra.

## RESULTS

Experimental deuterium n.m.r. spectra from the HIQ and HBA–HNA copolymer and crystalline PET are given in *Figures 3*, *4* and *5*, respectively. Computed lineshapes for different ratios of rigid and 180° flipping rings are given in *Figure 6*. A further sequence for different ratios of 180° flipping and rapidly rotating rings is given in *Figure 7*.

At the lower temperatures, the spectra of all three samples approximate to the Pake doublet expected for the situation where little molecular motion is present. As the temperature is raised, the spectra develop narrower doublet components that are associated with rotational motion. To a good approximation the splitting is reduced by a quarter which is consistent with 180° ring flips about the chain axis as shown in *Figure 6*. This result is consistent with the observation of a low temperature $\gamma$-relaxation in all three polymers which has been attributed to motion of the phenyl residues[13]. The narrow doublet becomes progressively more pronounced in the HBA–HNA and HIQ materials as the temperature is raised. However, in the PET the proportions of narrow and broad doublets appear to maintain approximately equal proportions and a central peak develops with increasing temperature. This latter component is typical of more random motion. At the highest temperatures examined (150°C) the HBA–HNA and HIQ materials still give doublets, although the whole spectra are now considerably narrowed. The splitting is about an eighth that of the immobile rings. The lineshapes are closely modelled by rings performing rapid unrestricted rotational motion. In comparison the PET is almost entirely dominated by the singlet derived from near random motion. It is important to comment here that studies of the dynamic mechanical behaviour of all these polymers show major relaxations above 100°C which in PET is associated with the glass transition. The glass transition

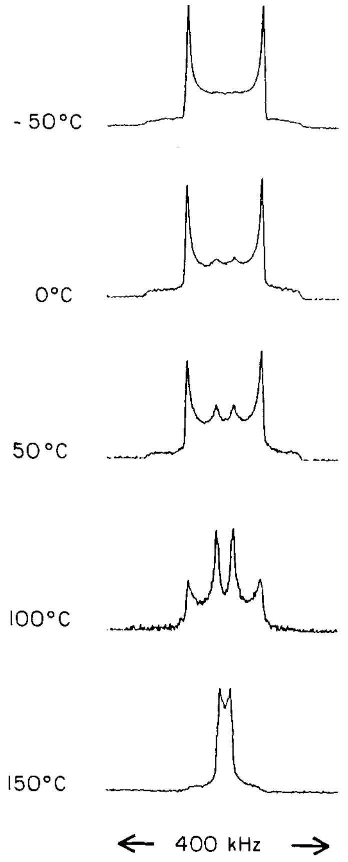

**Figure 4** Deuterium n.m.r. spectra of the HBA–HNA copolymer

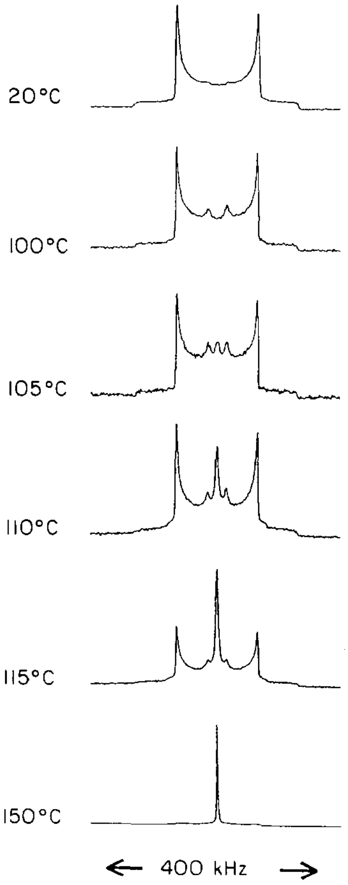

**Figure 5** Deuterium n.m.r. spectra of PET

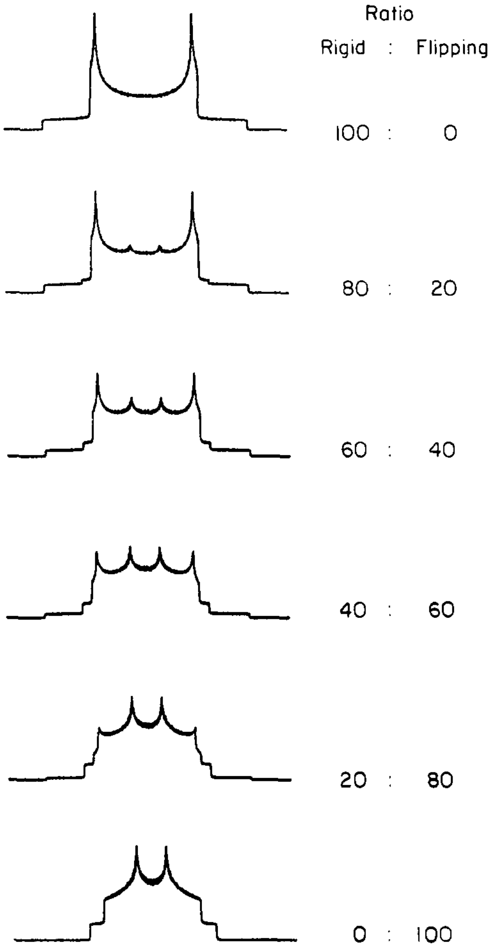

**Figure 6** Computed lineshapes for different ratios of rigid and 180° flipping rings

temperature of crystalline PET is ~120°C[14], and for the HBA–HNA and HIQ liquid crystalline polymers the α-relaxation, which has a very high apparent activation energy[1] akin to that of a glass transition, has been observed at ~120°C[15] and 140°C[16], respectively.

The liquid crystalline nature of the copolyesters relates to the stiff and rod-like nature of the molecular chains, which in turn relates to the restricted molecular mobility within the chain. In contrast, PET has the relatively flexible ethylene glycol units between the aromatic rings which permits a high degree of molecular mobility at high temperatures. The n.m.r. spectra presented here support the rigid rod-like nature of the liquid crystalline copolyesters and the greater flexibility of the PET.

The calculated lineshape for the rigid rings fits closely the equivalent broad component in the experimental data, as would be expected in this relatively simple case. However, the lineshape computed for the rings performing 180° flips bears only a qualitative similarity to the narrow doublet component observed at intermediate temperatures. The central doublet arising from rings having predominantly rotational motion is somewhat sharper in the experimental spectra from the HBA–HNA material than in the computed spectra. A possible explanation could be the effect of the spectrometer magnetic field on the motion or alignment of the polymer chains. It has been shown that when raised above the solid to liquid crystalline phase transition temperature such materials can be oriented in a strong magnetic

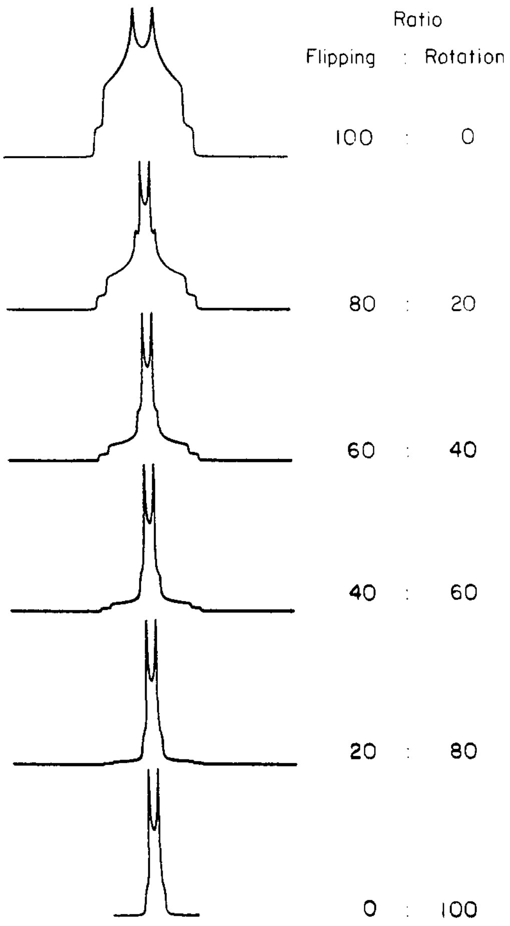

**Figure 7** Computed lineshapes for different ratios of 180° flipping and rapidly rotating rings

field[17,18]. This could possibly produce the sharpened experimental curves obtained from the HBA–HNA material.

In the case of PET a narrow singlet is observed above the glass transition. It is considered that this arises from near random motion and therefore may be simply modelled, to first approximation, by a Lorentzian curve.

## CONCLUSIONS

The experimental results obtained so far clearly demonstrate the usefulness of deuterium n.m.r. to the study of polymer chain dynamics. Even at a qualitative level, the onset of motion in the particular groups studied (d-HBA in the HBA–HNA and d-HQ in the HIQ copolymers and d-phenyl in the PET) can easily be followed over an extended range of temperatures. The PET is the only sample that gave evidence of random-like motion from the rings. This can be traced to the relatively long and flexible $-CO-O-CH_2-CH_2-O-CO-$ linkage between the phenyl rings that allows a large degree of both rotational and lateral motion. The copolyester materials, in contrast, do not show the isotropic motion. The motion is essentially rotational only. This confirms the rigid rod-like nature of the aromatic copolyesters that can be traced to the short, inflexible ester spacer groups between the rings.

The lineshapes computed for rings performing 180° flips about the chain axis are qualitatively similar to the corresponding components in the experimental spectra. It appears therefore that this forms the basis for the type of motion taking place. However, the differences suggest that further refinements are necessary. In particular, some molecular alignment in the spectrometer magnetic field may be taking place.

A further sample of HIQ is now available that has been annealed. This process has been found to induce crystallization. It will therefore be interesting to compare the results that this new sample gives with those obtained already from the unannealed sample.

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## APPENDIX

The energy of the quadrupolar interaction is given by:

$$H = I^{\mathrm{T}}\mathbf{Q}I \qquad \text{(A1)}$$

where $I$ is a column vector representing nuclear spins, $I^{\mathrm{T}}$ its transpose and $\mathbf{Q}$ is a second rank tensor describing the EFG. In Cartesian coordinates equation (A1) can be expressed as:

$$H = \sum_{ij} I_i Q_{ij} I_j \qquad \text{(A2)}$$

and in spherical polar coordinates equation (A1) becomes:

$$H = \sum_{k=0}^{2} \sum_{q=-k}^{+k} (-1)^q Q_{k,q} T_{k,-q} \qquad \text{(A3)}$$

The relationship between $Q_{ij}$ and $Q_{k,q}$ and between $I$ and $T$ can be found in reference 19.

If the EFG tensor $\mathbf{Q}$ is defined in the PAS of the C–D bond then the Wigner rotation matrix $D$ must be applied twice to $\mathbf{Q}$ to express it first in the coordinate system of the monomer unit by a rotation through Euler angles $\phi$,

$\theta$, $\chi$ and then in the coordinate system of the laboratory frame containing $B_0$ by rotation through Euler angles $\alpha$, $\beta$, $\gamma$. The elements of the Wigner rotation matrix can be found in reference 20.

The deuterium atoms are covalently bonded to the monomer units and so angles $\phi$, $\theta$ and $\chi$ are constant ($\phi=0$, $\theta=60°$, $\chi=90°$). Also, in computing the n.m.r. frequencies it is necessary only to tilt the polymer chain an angle $\beta$ away from the spectrometer field $B_0$ and rotate the polymer chain an angle $\gamma$ about its axis so angle $\chi$ can be held fixed at $\alpha=0°$. The n.m.r. frequency is a function of $\beta$ and $\gamma$ only and is given in equation (2).