

Solid-state carbon-13 n.m.r. studies of molecular motion in an aromatic copolyester

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Carbon-13 n.m.r. studies have been carried out on an oriented copolyester material comprising 73 mol% hydroxybenzoic acid (HBA) and 27 mol% hydroxynaphthoic acid (HNA). The $T_{1\rho}$ values for the carbonyl carbon, and non-protonated aromatic carbons of HBA and HNA rings have been measured over a range of temperature, and show minima at temperatures corresponding to the mechanical and dielectric relaxation transitions. The $T_{1\rho}$ –temperature plots have been fitted using the Cole–Davidson distribution, and indicate a broad distribution of correlation times. The activation energies obtained from the fits provide support for the association of the γ relaxation with the HBA ring, and the β relaxation with the HNA ring. Studies of the variation in chemical shift anisotropy indicate an increase in oscillations of both rings about the chain axis, with increasing temperature, and these motions appear not to be coupled with the motion of the carbonyl group. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The copolymerisation of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) results in a random thermotropic liquid crystalline copolyester. This material, produced by Hoechst Celanese under the name Vectra, has been the subject of much research over the last decade or so. The crystallinity^{1,2} and crystal structure^{3,4} have been examined, and there have been studies^{5–8} of the relaxation transitions using dynamic mechanical analysis and dielectric relaxation. These investigations have revealed three transitions, designated α , β and γ in order of decreasing temperature, which have been associated with the motion of the HBA ring (γ), the HNA ring (β), and with the α process displaying features similar to a glass transition. Since the γ and β processes are prominent in the dielectric relaxation studies^{6–8}, it has been suggested that the carbonyl group is associated in a cooperative motion with its adjacent aromatic ring. These assignments of the relaxation transitions are supported by n.m.r. studies, involving the variation in the proton second moments^{9,10} and proton $T_{1\rho}$ relaxation with temperature¹¹. Proton and carbon-13 n.m.r. experiments on poly-HBA^{12–14}, and deuterium n.m.r. work on the HBA/HNA copolymer¹⁵ have indicated the occurrence of substantial ring oscillation, or 180° phenyl ring flips about the 1,4 axis, while carbon-13 studies of a structurally similar aromatic polyester¹⁶ have shown that the ring motions are correlated with the adjacent carbonyl group motion.

In the present paper, we describe the results of carbon-13 n.m.r. studies of the molecular motions in the HBA/HNA copolymer. $T_{1\rho}$ is measured as a function of temperature, and the data analysed to extract activation energies, which are compared to those previously obtained from dielectric studies. Additional insight into the ring and carbonyl group motions is obtained from a study of the chemical shift anisotropy.

EXPERIMENTAL

Sample details

The HBA/HNA copolymer comprised 73 mol% HBA and 27 mol% HNA. It was supplied by Hoechst Celanese, in the form of an extruded, oriented monofilament of about 1 mm diameter. The sample was annealed at 250°C for 4 h, followed by 280°C for 15 h.

The structure of the copolymer is shown in *Figure 1*, where the carbon atoms of interest to the n.m.r. experiments are numbered.

N.m.r. measurements

Solid-state, carbon-13 n.m.r. spectra, recorded under conditions of cross-polarisation, magic-angle spinning and high-power proton dipolar decoupling (CP/MAS/DD) were obtained on a Chemagnetics CMX spectrometer, operating at approximately 200 MHz for protons, and 50.3 MHz for carbons. The standard CP pulse sequence was used, at a spinning speed of about 5 kHz, with a 2-ms contact time, and B_1 field strength of 62.5 kHz. For the $T_{1\rho}$ measurements, the spinlock was continued on the carbon channel without CP contact, for various times up to 25 ms. During this time, the r.f. to the proton channel was turned off. For measurements of the chemical shift anisotropy, a spinning speed of 1.05 ± 0.02 kHz was used, together with an interrupted decoupling pulse sequence whereby a delay of 60 μ s was inserted after the CP step before the dipolar decoupling. All spectra are the result of typically 3000 accumulations, with a recycle delay of 30 s. All chemical shifts are relative to TMS.

RESULTS AND DISCUSSION

Chemical shift assignments

The CP/MAS spectrum of the copolymer is shown in *Figure 2*. The peaks at 152 and 157 ppm are assigned to the non-protonated aromatic carbons 4 and 2, respectively,

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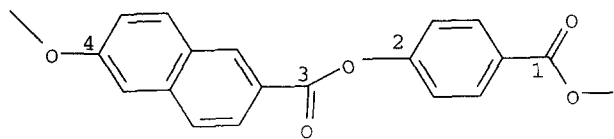


Figure 1 A typical sequence of the HBA-HNA copolymer

labelled in *Figure 1*. These assignments can be supported by the use of simple chemical shift additivity rules and, furthermore, we have also observed systematic changes in these peak intensities in different compositions of the copolymer. The peaks in the range 110–140 ppm are due to the other aromatic carbons. The different possible sequence distributions in the copolymer will give rise to a number of carbonyls of theoretically different chemical shifts, but in the solid-state n.m.r. spectrum these are not resolvable, a single carbonyl peak appearing at 165 ppm. In the structure of the copolymer (*Figure 1*) the two carbonyls labelled 1 and 3 are representative of carbonyl carbons bonded to naphthyl and phenyl rings, respectively. Since *Figure 2* demonstrates that it is possible to resolve peaks uniquely associated with carbons on the HBA and HNA moieties, we can use the relaxation times of these carbons as a probe of the molecular motion of these moieties as a function of temperature, which can be compared with the mechanical and dielectric studies.

Carbon-13 $T_{1\rho}$ results

Representative $T_{1\rho}$ decays for the HBA and HNA ring carbons, and the carbonyl carbon are shown in *Figure 3*. Hardware limitations restricted the maximum spin lock time to 25 ms, but the data are well described by a single $T_{1\rho}$ in each case. *Figure 4* shows the plots of $T_{1\rho}$ versus reciprocal temperature for each of the three carbons. It can be seen that each plot displays a minimum, which is indicative of the onset of a relaxation transition process in the polymer. At this point, it should be mentioned that, during the extended spin-lock on the carbon channel, the proton r.f. was turned off, and therefore it is possible that the $T_{1\rho}$ measured under such conditions may contain a contribution from carbon-proton spin diffusion, rather than reflecting a purely motional process. However, when the spectral density at the B_1 field is significant, it is usually the case that the $T_{1\rho}$ reflects predominantly the local dynamics¹⁷. The spectral density would appear to be significant in the present work, because we observe the $T_{1\rho}$ minima. Thus, in the analysis of the $T_{1\rho}$ behaviour, we will assume that this parameter is predominantly spin-lattice in nature and reflecting molecular motion.

The temperature of the HNA minimum is difficult to discern with any accuracy, but is in the region of 140°C, and the HBA minimum appears at about 125°C. Previous dielectric relaxation and dynamic mechanical work^{5–8} has

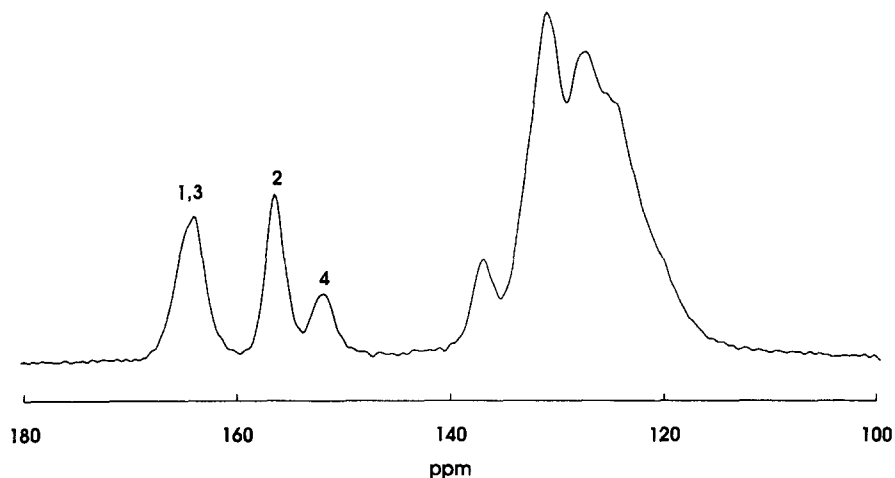


Figure 2 Carbon-13 CP/DD/MAS spectrum of the copolymer. The numbered peaks relate to the carbons labelled in *Figure 1*

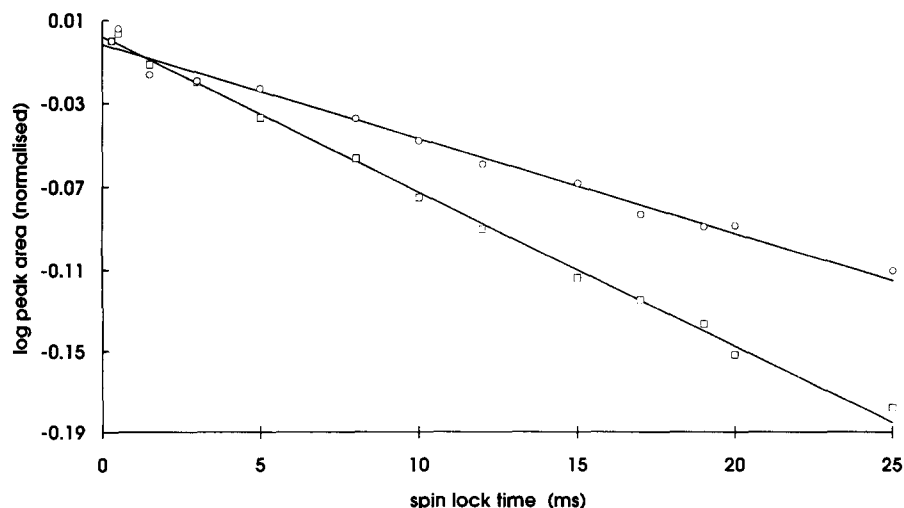


Figure 3 Typical rotating frame relaxations at room temperature for carbonyl (O) and HBA (□) carbons

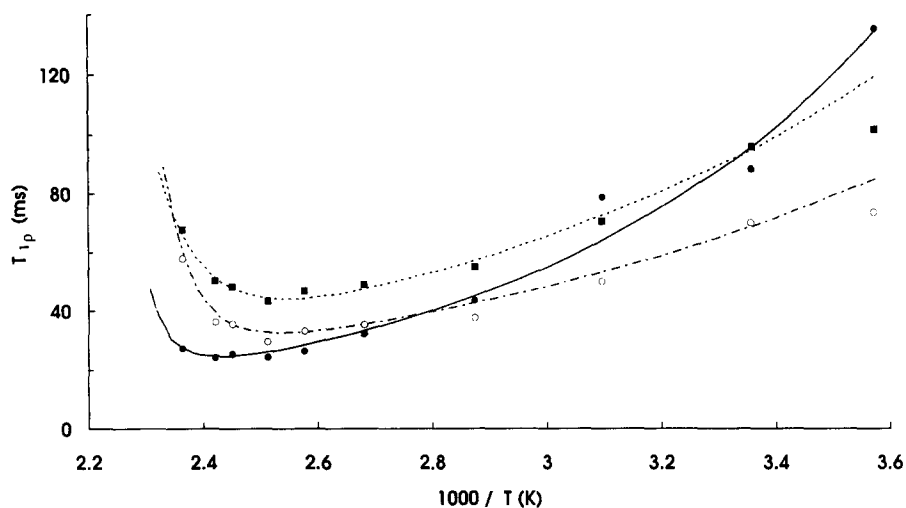


Figure 4 $T_{1\rho}$ versus temperature for carbonyl (■), HBA (○) and HNA (●) carbons. The lines through the data are fits to the Cole–Davidson spectral density function (equations (1)–(3))

detected transitions labelled γ and β in order of increasing temperature, which have been associated with the motions of the HBA and HNA units, respectively. These transitions have activation energies, determined from the dielectric work⁶, of 50.2 (γ) and 105 (β) kJ mol⁻¹, and so as the frequency of the measurement increases the processes tend to converge. Using these activation energies, and extrapolating to the present n.m.r. frequency of 62.5 kHz, the γ transition would be predicted to be located at 72°C, and the β at 120°C, which do not correspond in absolute terms to the temperatures of the $T_{1\rho}$ minima in Figure 4. A major problem in extrapolating to the n.m.r. frequency in this system is the possibility of merging with the α process, which displays features of a glass transition, having a very high apparent activation energy⁵ (~850 kJ mol⁻¹). It is quite possible that the high temperature sides of the broad minima seen in the n.m.r. encompass part of the α process in addition to the γ or β transition. However, the fact that the HNA minimum appears at a higher temperature than the HBA minimum is consistent with the association of these moieties with the β and γ transitions observed mechanically and dielectrically.

Correlation time distribution

Further insight into the comparison between mechanical/dielectric data, particularly the activation energies, and the carbon-13 $T_{1\rho}$ relaxation, can be obtained by analysing the shape of the $T_{1\rho}$ -temperature plots, which are the result of the distribution of molecular correlation times that exist in this polymer. The full expression for the $T_{1\rho}$ under conditions of heteronuclear (carbon–proton) dipolar interaction is given by¹⁸ equation (1).

$$\frac{1}{T_{1\rho}} = \frac{1}{9} M_2 \{ 4J(\omega_1) + J(\omega_0 - \omega_2) + 3J(\omega_2) + 6J(\omega_0) + 6J(\omega_0 + \omega_2) \} \quad (1)$$

where M_2 is the carbon–proton second moment, and J the spectral density function, with ω_0 the proton Larmor frequency, ω_2 the carbon Larmor frequency, and ω_1 the frequency of the spin locking field. M_2 is not available directly, because the techniques used to acquire the spectrum by necessity remove the carbon–proton dipolar interactions. However, the proton second moment, as a function of

temperature, has been measured¹⁰ on the same material, and these values can be used to obtain¹⁹ approximate values for the carbon–proton second moment, via equation (2).

$$M_2^{\text{CH}} = M_2^{\text{HH}} \left\{ \frac{4}{9} \left(\frac{\gamma_S}{\gamma_I} \right)^2 \left[\frac{S(S+1)}{I(I+1)} \right] \right\} \quad (2)$$

where γ_S and γ_I are the gyromagnetic ratios of carbon and proton, respectively, and $S = I = 1/2$. The carbon–proton second moment is therefore smaller than the proton–proton second moment by a factor of about 36. This results in a room temperature carbon–proton M_2 of $8.853 \times 10^7 \text{ s}^{-2}$. Several expressions²⁰ are available for the spectral density function, incorporating a molecular correlation time, τ , and parameters that attempt to quantify the correlation time distribution. The location of the minimum of the distribution should be unaffected by the distribution, but a broad distribution of correlation times is reflected in a broad $T_{1\rho}$ -temperature curve. We have examined several models for the distribution, all of which give very similar results. We discuss here the use of the Cole–Davidson²⁰ spectral density function, which we have successfully applied¹¹ to the analysis of proton $T_{1\rho}$ relaxation in similar materials. The Cole–Davidson expression for the spectral density is given by equation (3).

$$J(\omega) = \frac{2}{\omega} \left\{ \frac{\sin[\delta \tan^{-1}(\omega\tau)]}{(1 + \omega^2\tau^2)^{\delta/2}} \right\} \quad (3)$$

The parameter δ varies from 0 to 1, and indicates the width of the distribution; δ equal to 1 implying a single correlation time. In the present work, we have measured the $T_{1\rho}$ as a function of temperature, and since previous dynamic mechanical and dielectric work^{5–8} has established that the β and γ processes are well described by an Arrhenius expression, we can relate the correlation time to temperature via equation (4).

$$\tau = \tau_0 \exp(E_a/RT) \quad (4)$$

where E_a is an activation energy, and R the gas constant. The curves through the data sets in Figure 4 are fits (obtained using the least-squares fitting procedure in Microsoft Excel) to the Cole–Davidson model in this form, and δ , τ_0 and E_a are obtained from the fits; their values are given in Table 1. The small values of δ indicate a broad distribution

Table 1 Parameters obtained from the Cole–Davidson distribution function fits to carbon-13 $T_{1\rho}$ data for carbonyl, HBA and HNA ring carbons

Structural unit	E_a (kJ mol ⁻¹)	δ	τ_0 (s)
Carbonyl	126	0.066	6.47×10^{-22}
HBA ring	88.1	0.099	3.29×10^{-17}
HNA ring	173	0.075	2.48×10^{-27}

of correlation times. The distribution is greater for the HNA ring than for the HBA ring, a result consistent with the previous proton $T_{1\rho}$ study¹¹. Comparing the activation energies with the dielectric results, we find that the n.m.r. activation energies due to the motion of the HBA and HNA rings, 88.1 and 173 kJ mol⁻¹, respectively, compare with the dielectric activation energies of 50.2 and 105 kJ mol⁻¹ for the γ and β processes, respectively. It is not surprising that the absolute magnitudes of the activation energies do not agree since the relaxation of nuclear magnetisation on the one hand, and dielectric or mechanical relaxation on the other hand, are fundamentally different physical phenomena. However, the fact that the ratio of the two activation energies obtained by each method is almost exactly 2:1 suggests that the n.m.r. is monitoring the same basic motional processes as the dielectric and dynamic mechanical experiments, and provides further support for the association of these processes with the motion of specific structural units in the copolymer. The results for the carbonyls are less easy to interpret, as there are several different types. A carbonyl carbon can have four different permutations of nearest neighbours, considering the HBA and HNA groups, and whether the in-chain oxygen is bonded to a phenyl or naphthyl ring. The mechanism for the $T_{1\rho}$ relaxation of the carbons will be by dipolar interactions with the adjacent protons, which in the case of the carbonyl carbons will involve interactions with both HBA and HNA ring protons. Hence the $T_{1\rho}$ behaviour of the carbonyl will in fact be reflecting the motion of the HBA and HNA rings rather than the motion of the carbonyl group itself. This is reflected by the results in *Table 1* where the activation energy and pre-exponential factor for the carbonyl is midway between the values obtained for the HBA and HNA units.

Chemical shift anisotropy

In order to obtain more information on the nature of the carbonyl carbon motion, and the extent to which this is

linked to the motion of its associated ring, we have examined the chemical shift anisotropy (CSA) of the three carbons as a function of temperature. The technique involves relatively slow MAS, and the components of the chemical shift tensor can be calculated from the relative intensities of the spinning side bands using the methodology of Herzfeld and Berger²¹. As can be seen from *Figure 2*, the intensities of the three peaks we need to focus on are much less than the other peaks at 110–140 ppm, so that under conditions of slow spinning the sidebands from these peaks tend to obscure the peaks of interest. To circumvent this problem, the spectra have been obtained using an interrupted decoupling pulse sequence, where the high-power proton decoupling is delayed for a short time following the CP. The magnetisation from protonated carbons is rapidly dephased during this period, such that the resulting spectrum is comprised principally of the non-protonated carbons. It was found that a delay of 60 μ s removed virtually all the protonated carbon peaks without significantly attenuating the carbonyl and non-protonated aromatic peaks. An example of a spectrum obtained using the interrupted decoupling sequence and a MAS speed of 1.05 kHz is shown in *Figure 5*. It was found that this spinning speed gave reasonable sideband intensity without causing significant overlap between peaks. CSA analysis using sideband intensities has been used by Gérard et al.¹⁶ in a study of the molecular motion in a related aromatic copolyester, and we follow their principal axis assignments of the chemical shift tensors. For aromatic carbons, the least shielded element, σ_1 , is in the aromatic ring plane pointing along the chain axis, and the most shielded element, σ_3 , is perpendicular to the ring plane. For carbonyls, σ_3 is perpendicular to the sp^2 plane, and σ_2 is along the C=O bond. The results of the Herzfeld–Berger analysis for the carbonyl, HBA and HNA peaks are shown in *Table 2*. In the case of the HBA and HNA carbons, there is observed a partial and gradual averaging of the σ_3 and σ_2 components with increasing temperature, which corresponds to an increase in amplitude and/or rate of oscillation of the rings about the chain axis. The motion of the carbonyls appears to be very different, involving significant averaging, above about 75°C, of σ_1 with both σ_2 and σ_3 . Although, from these results alone, the precise nature of the carbonyl motion is unclear, the important conclusion is that it appears not to be linked to the motion of the aromatic ring, unlike in similar

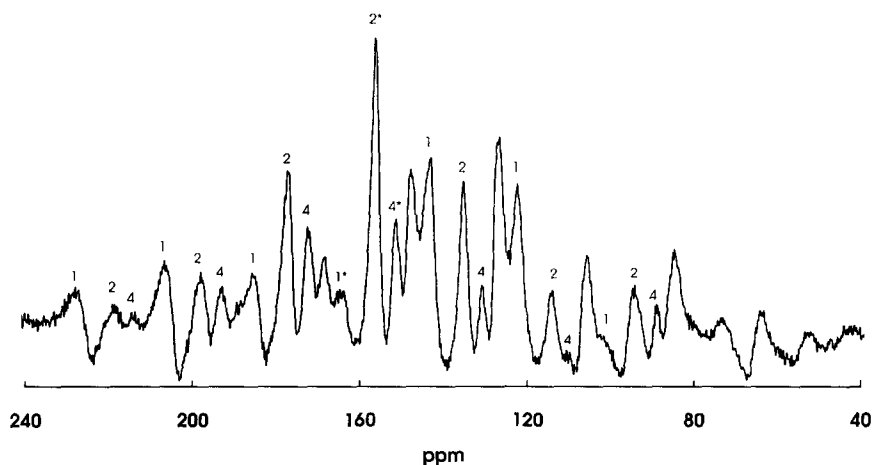
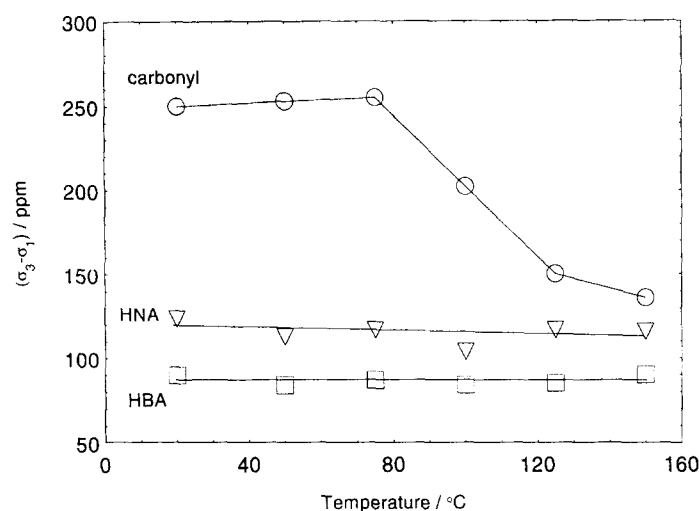


Figure 5 Carbon-13 CP/DD/MAS spectrum, recorded at room temperature using interrupted decoupling at a spinning speed of 1050 Hz. The first three sidebands for the HBA, HNA and carbonyl carbons are indicated, where the numbers relate to the carbons in *Figure 1*. The isotropic peaks are indicated by an asterisk in each case

Table 2 Values (in ppm) of the principal components of the shielding tensor as a function of temperature for the carbonyl carbon, and non-protonated aromatic carbons on the HBA and HNA rings

T (°C)	Carbonyl			HBA			HNA		
	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}
20	-164	78	86	-45	-0.9	46	-58	-8.4	67
50	-160	68	92	-42	-1.4	43	-58	2.6	56
75	-156	58	99	-44	0.3	43	-6.1	4.1	57
100	-113	23	90	-43	2.3	41	-55	4.6	50
125	-82	14	68	-44	3.7	41	-6.4	10	54
150	-74	12	62	-51	11	40	-68	19	49

**Figure 6** Width of the CSA versus temperature for the carbonyl, HBA and HNA carbons

systems¹⁶. This is further borne out by *Figure 6* which shows the change in the full width of the CSA pattern ($\sigma_3 - \sigma_1$) for each carbon. This width decreases only slightly for HBA and HNA, but decreases significantly above 75°C for the carbonyl. Similar conclusions about the lack of cooperation between carbonyl and ring motions have been made recently on a study of PET^{22,23}. Here, a combination of ²H lineshapes and ¹³C CSA studies, and dynamic mechanical and dielectric investigations have shown that the phenyl group and carbonyl group both undergo small-angle oscillations, but the phenyl ring can undergo 180° ring flips independently.

CONCLUSIONS

Our objective in this paper has been to attempt to relate solid-state carbon-13 $T_{1\rho}$ behaviour to the dynamic mechanical and dielectric relaxation transitions in the HBA-HNA copolymer. The $T_{1\rho}$ values of the carbonyl carbon and non-protonated aromatic carbons on the phenyl and naphthyl rings, measured over a wide temperature range, all show a minimum, but it is difficult to relate the temperature of a minimum unambiguously to a specific relaxation transition because of the convergence of the α , β and γ processes at frequencies corresponding to the n.m.r. measurement. A greater insight has been acquired by analysing the $T_{1\rho}$ -temperature curves in terms of a distribution of molecular correlation times, and the parameters obtained from using the Cole-*Davidson* spectral density indicate a broad correlation time distribution for all types of carbon. The activation energies obtained from this analysis are of a similar magnitude to those obtained from dielectric studies⁶⁻⁸, and are consistent with the association of the γ processes to the motion of HBA units and the β

process to HNA units. The limitation of both techniques is that they produce only a single average activation energy, whereas in reality there is most likely to be a distribution of relaxation processes (indicated by the broad correlation time distribution) with different activation energies. It would appear, then, that the dielectric and n.m.r. relaxations are sensitive to different types of motion. The CSA analysis has indicated an increase in oscillations of the phenyl and naphthyl rings about the chain axis, with increasing temperature, which appears to be separate from a more complex motion of the carbonyl group. A previous deuterium n.m.r. study¹⁵ indicated that a substantial number of the phenyl rings in this copolymer are undergoing 180° ring flips at 150°C, whereas it would appear that the carbon-13 CSA is more sensitive to the ring oscillations. In this respect it would be interesting to perform the CSA analysis at higher temperatures to observe when the complete averaging of σ_2 and σ_3 occurs, which, by this technique, would be indicative of ring flipping.

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