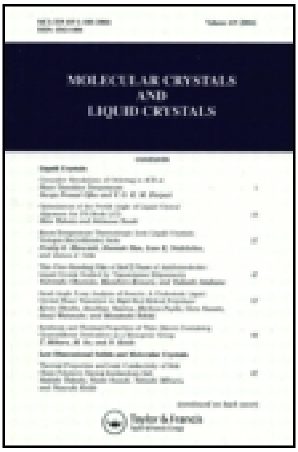

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NMR Studies of the Local Dynamics of Liquid Crystalline and Semicrystalline Aromatic Polyesters

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NMR STUDIES OF THE LOCAL DYNAMICS OF LIQUID CRYSTALLINE AND SEMICRYSTALLINE AROMATIC POLYESTERS

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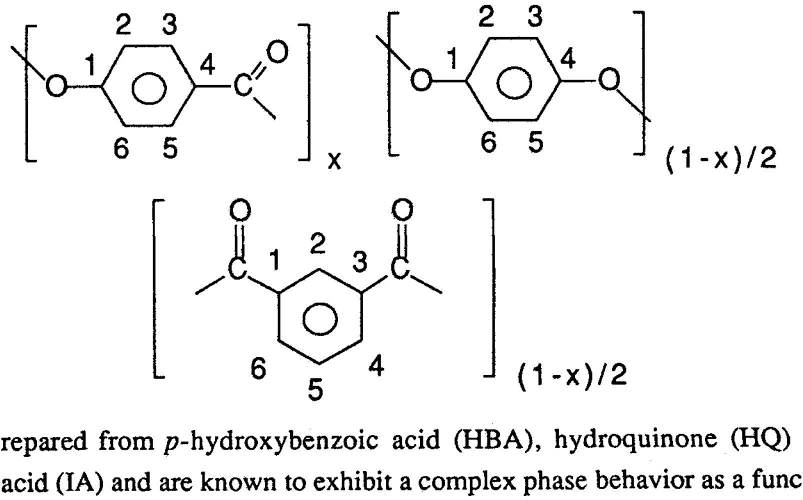
Abstract The local motions of terpolyesters based on varying amounts of hydroquinone, hydroxybenzoic acid and isophthalic acid units were investigated using high-resolution solid-state ^{13}C NMR. At temperatures below the glass transition temperature, the mesomorphic polymer having equal amounts of the three units demonstrates partial motional averaging of the chemical shift tensors of the aromatic carbons which indicates the existence of oscillations for both *para*- and *meta*-substituted rings. The oscillations of the *para*-substituted phenyl rings appear to be correlated with the motions of the adjacent carbonyl groups. At high temperature there also occurs small-amplitude main-chain reorientations which are likely to be involved in the glass-transition phenomenon. These motions were also observed in the amorphous phase of other compositions of the terpolyester leading to conventional semicrystalline polymers.

INTRODUCTION

The terpolyesters under study have the following stoichiometric formula:



They are prepared from *p*-hydroxybenzoic acid (HBA), hydroquinone (HQ) and isophthalic acid (IA) and are known to exhibit a complex phase behavior as a function of the HBA content[1,2]. Compositions containing low amounts of HBA ($x < 0.2$) are conventional semicrystalline polymers showing no mesomorphic characteristics.

Polymers in the range ($0.2 < x < 0.27$) are borderline cases between isotropic and liquid crystalline behavior. Compositions in the range ($0.3 < x \leq 0.5$) exhibit a large nematogenic temperature range. Terpolyesters with higher HBA contents ($x > 0.6$) tend to decompose at temperatures below their crystal-nematic transition[1,2].

Due to the existence of a nematic phase which favors the orientation of the chain axis along the stretching or flow directions, the thermotropic polyesters which belong to the above series have good mechanical properties. However, on decreasing the temperature below the glass-transition temperature, one observes secondary transitions, which induce a loss in the mechanical properties of the material. Since these secondary relaxations are known to originate from local motions, the identification and characterization of the different motional processes that may occur in these thermotropic polymers is of major interest for the understanding of their mechanical behaviour.

The present paper deals with the investigation of local motions in the above thermotropic and conventional semicrystalline terpolymers by high-resolution solid-state ^{13}C NMR experiments. Using the method of Herzfeld and Berger[3], the motional modulation of the chemical shift anisotropy of the different carbons has been determined at different temperatures above and below the glass transition temperature. In this way the dynamic behavior of the different aromatic units can be followed independently. Results will be shown first for the mesomorphic polymer with $x=0.33$ (HBA33), and then for the conventional semicrystalline polyesters with $x=0.27$ (HBA27) and $x=0.80$ (HBA80). Moreover, to obtain selective information on the *meta*-substituted ring motion, the *para*-substituted units of the HBA33 terpolyester have been selectively deuterated.

EXPERIMENTAL

The synthesis of the copolyesters was performed by W.A.MacDonald, N.Clough and F.Beaume at the I.C.I. Wilton Research Centre in Great Britain. The polymers were obtained in an unsheared quiescent state. The glass transition temperatures, Tg, of the copolyesters with $x=0.27$, 0.33 and 0.80 are 409, 405, and 425 K, respectively, as measured by DSC. The mesomorphic polymer with $x=0.33$ may be considered as being essentially glassy nematic below Tg. Prior to the NMR experiments, the HBA27 and HBA80 semicrystalline polyesters were annealed at 510K for about 20 hours under vacuum. They have a crystallinity of about 17 and 48%, respectively [4].

The high-resolution solid-state ^{13}C NMR experiments were carried out as a function of temperature on non-oriented powder samples at 75.47 MHz with a Bruker CXP 300 spectrometer and a DOTY probe. They were based on proton dipolar decoupling (DD), magic-angle sample spinning (MAS) and cross polarisation (CP) techniques. The spinning speed was around 4000 Hz. The matched spin-lock cross-polarization transfers were carried out with ^{13}C and ^{1}H magnetic field strengths of 64 kHz. Contact durations were either 1 ms (normal cross-polarization experiments) or 20 μs (cross-polarization experiments with very short contact times).

RESULTS AND DISCUSSION

Local dynamics of the HBA33 thermotropic terpolyester

The high-resolution solid-state ^{13}C NMR spectrum of the HBA33 copolyester at room temperature is shown in Figure 1. The 164 ppm peak represents the resonances of all the carbonyl carbons of the copolyester units. The 154 ppm line is characteristic of carbon 1 of the HBA unit. The 148 ppm line corresponds to carbons 1 and 4 of the HQ unit. The principal values σ_1, σ_2 and σ_3 of the chemical shift tensor for carbon 1 of the HBA unit, determined by measuring the relative intensities of the spinning side bands associated with the 154 ppm line and using the method of Herzfeld and Berger[3] are plotted in Figure 2 in the temperature range from 248 K to 510 K. Between 248 K and 425 K, σ_1 remains constant whereas σ_3 decreases and σ_2 increases until they reach a common value at about 425 K. At higher temperatures, the σ_1 value increases slightly and the common value of σ_2 and σ_3 decreases slightly.

Assuming that the least shielded element, σ_1, is in the aromatic plane pointing radially out from the ring whereas the most shielded one, σ_3, is perpendicular to the ring plane, results observed in Figure 2 at temperatures up to 425K are consistent with the existence of motions about the *para* axis of the ring. Indeed, motions about the *para* axis of the ring lead to a partial averaging of the σ_2 and σ_3 components, which are perpendicular to the axis of rotation, while the σ_1 principal component, parallel to the axis of rotation, is unchanged. Above 425 K, results reported in Figure 2 show a partial averaging of σ_1, which corresponds to a reorientation of the *para* axis of the ring.

The results obtained between 248 K and 425 K can be interpreted either in terms of rather slow motions with a constant amplitude and with an increasing rate as a function of temperature, or in terms of rapid motions with an increasing amplitude as a function of temperature. In the following, we will use the latter assumption and consider a motional model based on rapid oscillations about the *para* axis of the ring between increasing angles α and $-\alpha$, corresponding to a 2α amplitude of motion. One must also consider the possibility of dynamic heterogeneity. However, the HBA33 terpolyester is largely amorphous and there is no experimental evidence of dynamic

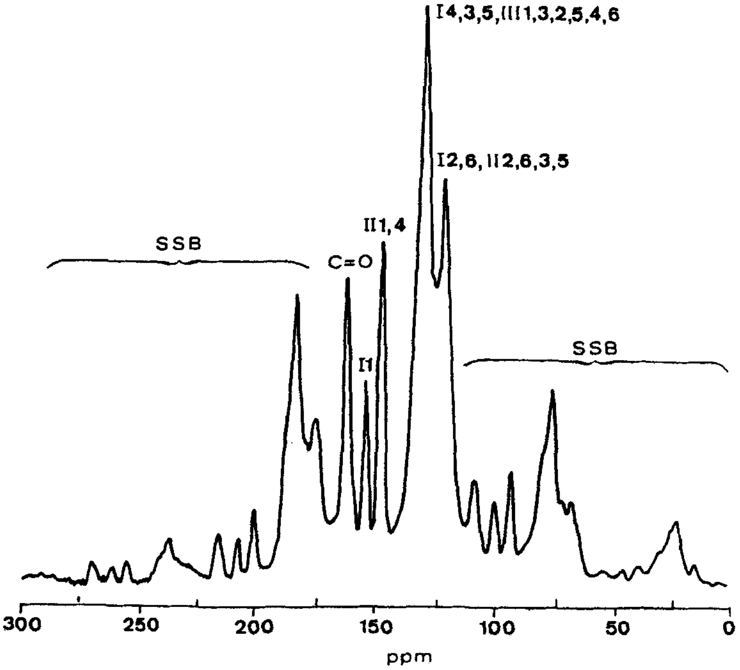


FIGURE 1 MAS/CP/DD ^{13}C NMR spectrum of the HBA33 polymer at room temperature (spinning speed: 4000 Hz, contact time: 1ms). I,II,II: HBA, HQ, IA rings, respectively. SSB: spinning side bands.

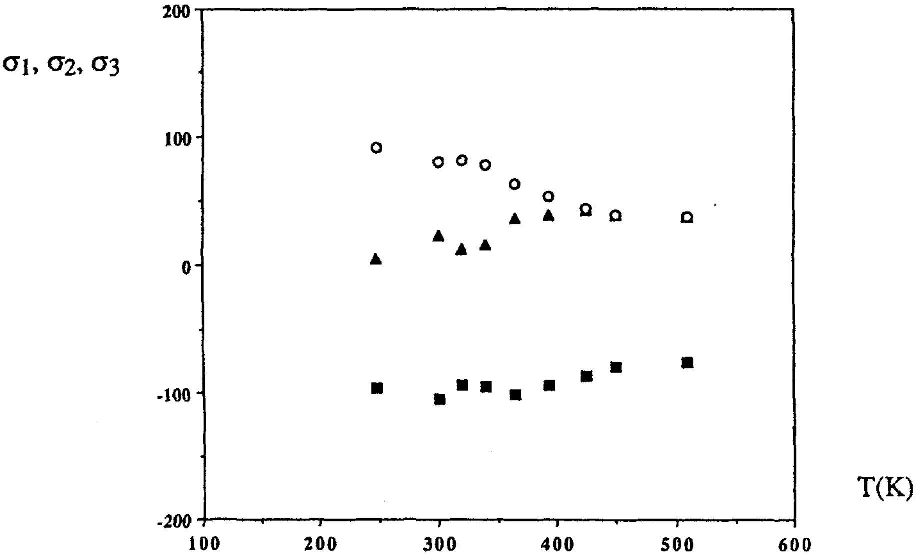


FIGURE 2 Temperature dependence of the principal values σ_1 (■), σ_2 (▲), σ_3 (o), (expressed in ppm) of the chemical shift tensor for the carbon 1 of the HBA ring in the HBA33 polymer

heterogeneity within the accuracy of our experiments. Therefore, we have considered that the dynamic heterogeneity of the HBA33 terpolyester is negligible as a first approximation and, therefore, we have characterized the motional behavior of the HBA ring in terms of an average oscillation amplitude that increases with increasing temperature. The same assumptions will be used throughout this paper for the different rings and types of motions considered.

For carbon 1 of the HBA unit, the rigid-lattice values (α=0) were taken to be equal to those measured at 248 K, an assumption corroborated by the fact that the 248 K chemical shift parameters are quite similar to those determined for the corresponding carbon of the small model molecule methyl 1-4 acetoxybenzoate in its crystalline state[5]. Calculated amplitudes of rapid oscillations about the *para* axis of the ring between increasing angles α and $-\alpha$ are plotted in Figure 3. They show a regular increase in α from 248 K up to a complete ring flip (α=90°) at 425 K.

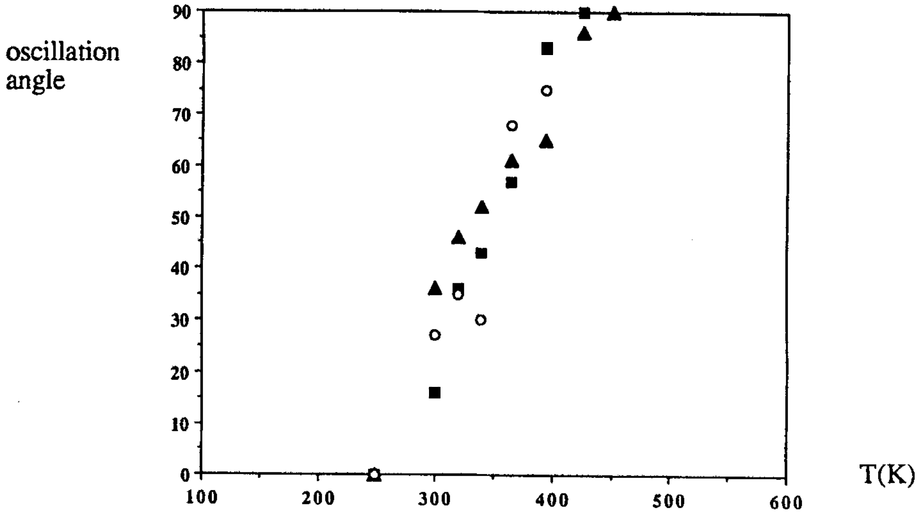


FIGURE 3 Variation of the amplitude of oscillation of the HBA aromatic units (■), HQ aromatic units (▲) and C=O groups (o) as a function of temperature in the HBA33 polymer.

Above 425 K, the dynamics of the local symmetry axis of the ring can be described in terms of an oscillation about an axis perpendicular to the σ_1 direction. Taking into account the fact that σ_1 has already slightly increased below 425 K, the analysis shows that the amplitude of this oscillation varies from 20° at 425 K to 35° at 510 K.

The same analysis has been carried out for carbons 1 and 4 of the HQ units[5]. The variation of the calculated amplitude of the motion about the *para* axis as a function of temperature is plotted in Figure 3. Furthermore, data recorded in the high-temperature region show that the amplitude of the chain motion increases from 25° at 450 K to 40° at 510 K, similar to what is observed for carbon 1 of the HBA unit.

The selective information on the ring motion of the IA units has been obtained from the selectively deuterated copolyester[5]. The evolution of the σ_3-σ_1 difference for the 4,6 carbon pair as a function of temperature is shown in Figure 4. This difference is a decreasing function of temperature that can be interpreted in terms of motions that partially average the chemical shift anisotropy.

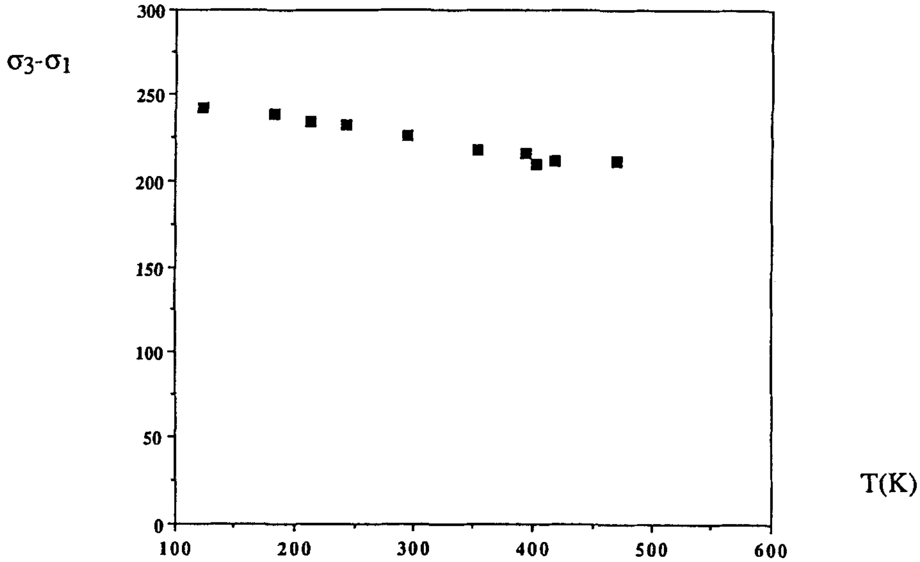
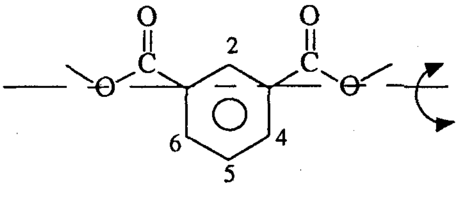


FIGURE 4 Temperature dependence of the σ_3 - σ_1 difference (expressed in ppm) for the carbons 4,6 of the deuterated HBA33 polymer.

Different types of motions for this *meta*-substituted ring may be considered such as, for example, oscillations about some of the covalent single bonds. However, ^{13}C NMR studies of local dynamics, carried out in solution and based on the comparison of the values of the spin-lattice relaxation times, T_1, measured for carbons 2,5 and 4,6, of the IA units have led to the conclusion that the IA units are involved in stochastic jumps about the axis joining carbons 1 and 3 as represented below[6]:



In the following, we have assumed that the local motions in solution and in bulk differ by their amplitudes and rates, but that they share the same axis of preferred reorientation. This assumption is in agreement with the consideration of molecular models. The oscillation amplitudes, γ, about the local axis represented above, have been determined by using, as rigid-lattice parameters, chemical shift parameters measured for the 4,6 carbon pair either for the deuterated polymer at 123 K, or for crystalline dimethylisophthalate at room temperature[5]. These calculations show that γ increases regularly from 0° at 123 K to a limiting value of 40° at 400 K.

The local dynamics of the carbonyl groups have been investigated by analyzing the spinning side band intensities of the 164 ppm peak. As shown in Figure 5, the temperature dependence of σ_1, σ_2 and σ_3 derived from these data shows a motional averaging, the extent of which increases with increasing temperature.

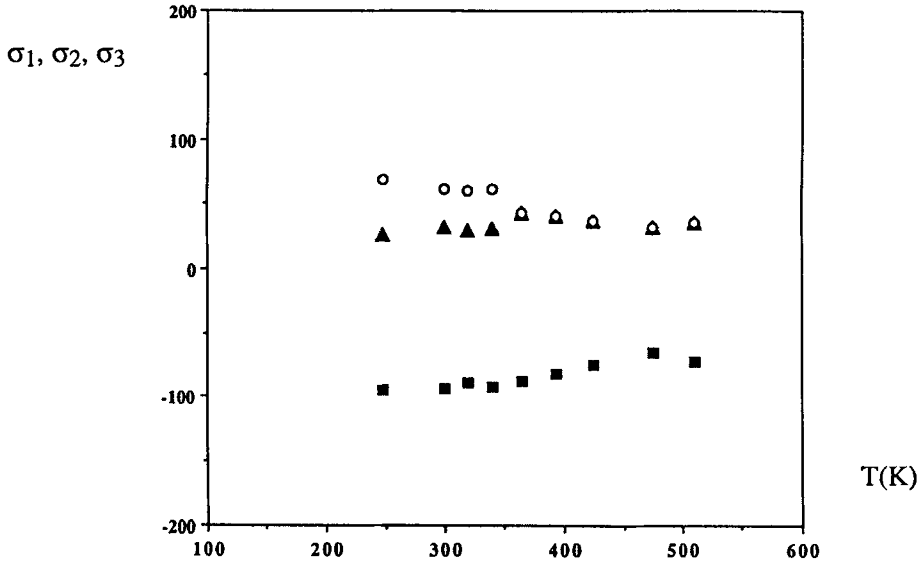


FIGURE 5 Temperature dependence of the principal values σ_1 (■), σ_2 (▲), σ_3 (o), (expressed in ppm) of the chemical shift tensor for the C=O carbons of the HBA33 polymer.

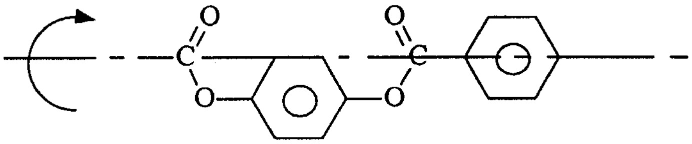
The principal axis orientations of the carbonyl carbons depend on the chemical nature of the neighboring groups. In the following, we have used results reported for acetophenone and benzophenone[7,8] in which the most shielded axis is perpendicular to the sp^2 plane, and the intermediate axis is along the C=O bond[9].

To interpret the results obtained from the carbonyl carbons, one has first to consider the different types of carbonyl carbons that are found in HBA33 polymer.

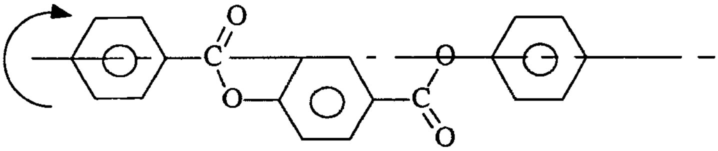
About two thirds of these carbons belong to an IA unit, the remainder sitting between HBA or HQ units. The former carbonyl carbons are involved in the oscillatory motion of the IA unit described in the previous section. However, calculations carried out at the investigated temperatures show that the amplitude of these oscillations is too small to be responsible for the experimental motional averaging observed above 320K. This result implies the existence of a second type of motion which involves at least part of the carbonyl carbons.

Consideration of molecular models and local geometries points to the likely existence of motions about the axes as schematized below:

(a)



(b)



Such motions induce a translation of the *para* axis of the HBA or HQ rings. They can only occur if the carbonyl carbons are in a given *cis* (a) or *trans* (b) configuration with respect to the phenyl ring depending on the unit considered. However, it is interesting to note that if one unit is in the correct configuration allowing this type of motion to occur, then the motion of the considered unit will induce a *cis-trans* conformational change of the next unit which might in turn be placed into the right configuration. The configuration that favors these processes corresponds to the maximum extension of the chain, which is consistent with the nematic character of the polymer. Due to the lack of information about the actual conformations of the polymer under study and in order to simplify further calculations, we assume that all the C=O carbons are involved in such a reorientation.

To estimate the amplitude of this process, we have assumed that the 248K NMR spectrum corresponds to a *quasi* rigid-lattice behavior and that the measured chemical shift anisotropy at higher temperatures is the average of the contributions of the two types of carbonyl carbons. Motional amplitudes calculated under these assumptions are plotted in Figure 3 together with the temperature dependence of the amplitudes of the oscillations of the HBA and HQ rings about their *para* axes. It has to be noted that the three motional amplitudes have similar values and temperature dependences until 425K.

Such a result indicates that the motions of the rings and C=O groups are correlated, which is consistent with the motional model that we have adopted. Above 425 K, an additional chain reorientation occurs, which increases the complexity of the data analysis. However, data obtained on the whole temperature range are in at least qualitative agreement with the present discussion.

At this point, it is interesting to relate these conclusions to the glass-transition phenomenon and β and γ secondary relaxations as observed by dynamic mechanical experiments performed in our laboratory[10]. It must be noticed that the comparison of the two techniques requires the extrapolation of the lower frequency data of the dynamic mechanical experiments to the higher frequencies of the NMR experiments. However, in spite of the inherent inaccuracy of the extrapolation, there is a close similarity between the temperatures at which the glass-transition manifests itself in the 10^3-10^5 Hz range, as extrapolated from the results of dynamic mechanical measurements, and the temperature at which the reorientation of the main-chain axis is first observed by NMR. The β and γ secondary relaxations are observed by viscoelastic techniques at about 340K and 265K, respectively, for an experimental frequency of 10^3 Hz. Comparing these results with the NMR results described above, it seems that the β process can be identified with the coupled motions of the *para*-substituted rings and carbonyl carbons, and the γ-process with the oscillations of the *meta*-substituted rings.

Local dynamics of the HBA80 semicrystalline terpolyester

The principal elements, σ_1, σ_2 and σ_3, of the chemical shift tensor of carbon 1 of the HBA units and carbons 1 and 4 of the HQ units, derived from the relative intensities of the spinning side bands, are plotted as a function of temperature in Figure 6. For carbon 1 of the HBA units only a very weak temperature dependence can be observed. Whereas σ_1 remains constant a slight increase in σ_2 and a slight decrease in σ_3 can be detected which is more pronounced between the two highest temperatures. On the other hand, a pronounced temperature dependence is found for the motional behavior of the HQ units. For carbons 1 and 4 the values of σ_2 and σ_3 become equal for temperatures above 400 K. At the highest temperature the common value of σ_2 and σ_3 decreases and σ_1 starts to increase. As for the HBA33 polymer, the partial averaging of σ_2 and σ_3 for the HBA units can be interpreted in terms of an increasing mobility of the phenyl rings about the *para* axis. The complete averaging in the case of the HQ unit above 400 K indicates complete ring flips or very fast rates of motion. The averaging of σ_1 and the common value of σ_2 and σ_3 for the HQ unit at the highest temperature corresponds to an additional motion involving reorientations of the *para* axis of the ring.

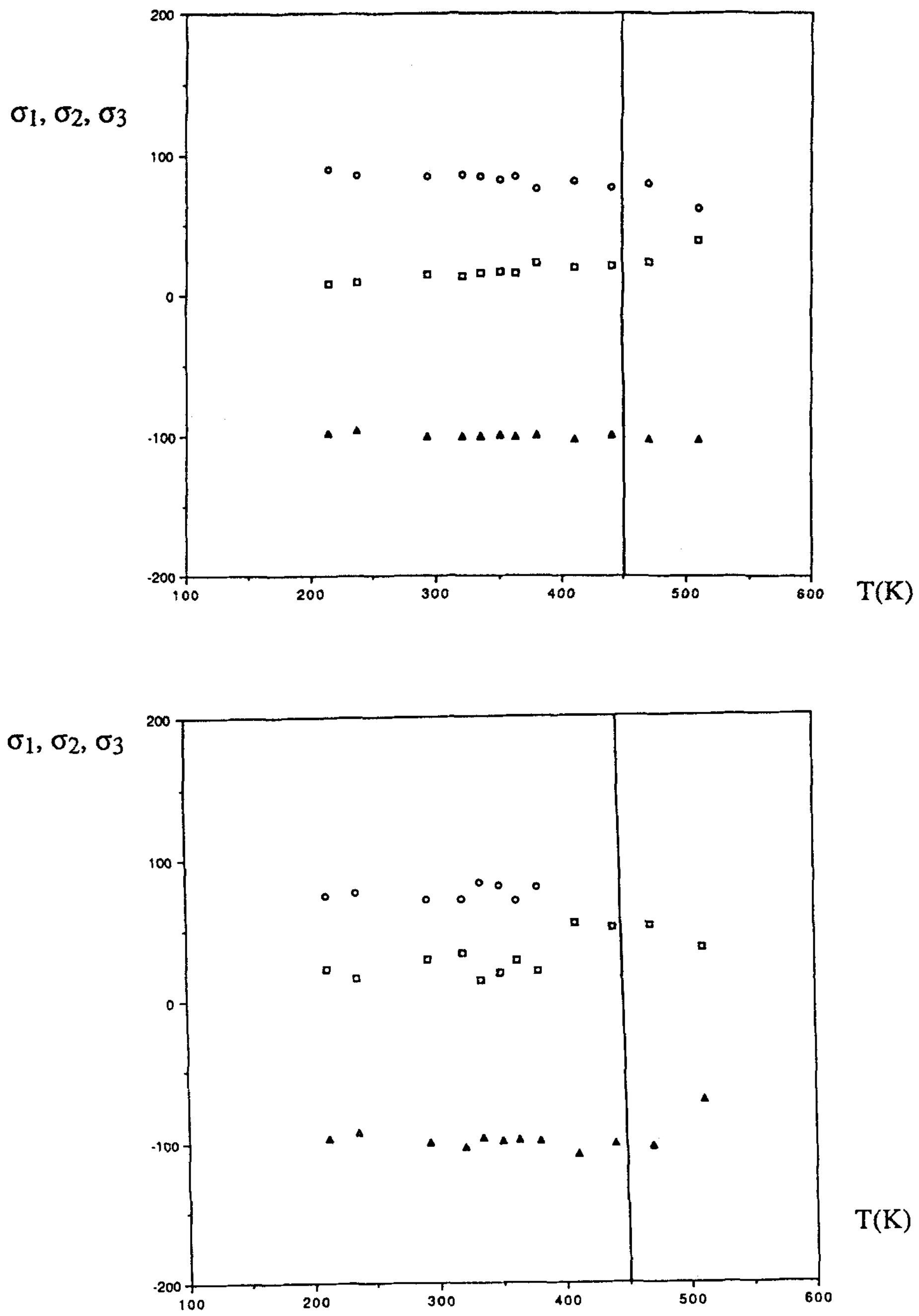


FIGURE 6 The principal elements σ_1 (Δ), σ_2 (□) and σ_3 (o) (expressed in ppm) of the chemical shift tensor of carbon 1 of the HBA unit (upper figure) and carbon 1 and 4 of the HQ unit (lower figure) as a function of temperature for the HBA80 polymer. The extrapolated T_g of HBA80 is indicated as a vertical line.

Comparison of the NMR results with the thermal behavior of the HBA80 polymer[4] shows that, for the HQ unit, the T_g at the NMR experimental frequency lies in the temperature range above which an averaging of σ_1 and the common value of σ_2 and σ_3 of carbons 1 and 4 of this polymer segment set in. Therefore, the glass transition observed by DSC can be assigned to motions of the *para* axis of the phenyl rings in the amorphous HQ-rich regions of the polymer.

In analogy to the results obtained from NMR and dynamic mechanical measurements on the HBA33 terpolyester, the averaging of σ_2 and σ_3 of carbons 1 and 4 of the HQ unit around 400 K has been assigned to a β secondary relaxation involving a coupled motion of the *para*-substituted rings and carbonyl carbons.

From the NMR results one can conclude that the HBA units are preferentially found in the crystalline regions of the polymer since their mobility is very restricted in the investigated temperature range whereas the HQ units are preferentially located in the amorphous regions showing greater mobility above the glass transition temperature. These observations correlate very well with results of X-ray diffraction experiments on the HBA80 polymer[1,4], since only those reflections were observed that are associated with sequences of the HBA unit. If the 48% crystallinity obtained after a long annealing is entirely due to crystals involving this unit, there is still about 30% of this segment in non-crystalline regions of the HBA80 polymer. The reason why no contribution of these mobile segments above the T_g can be observed in Figure 6 may be due to the use of the CP technique in the NMR experiments. This technique discriminates against the more mobile parts of the sample, the main contribution to the detected signal originating from the carbons in the rigid crystalline parts. Actually, a pronounced decrease in the signal to noise ratio passing T_g was detected not only for the peak at 148 ppm representing the HQ units, but also for the peak at 154 ppm originating from the HBA segments.

Local dynamics of the HBA27 semicrystalline terpolyester

The principal elements σ_1, σ_2 and σ_3 of the chemical shift tensor of carbon 1 of the HBA units and carbons 1 and 4 of the HQ units are plotted as a function of temperature in Figure 7. For the HBA unit carbon, at temperatures up to about 450 K, σ_2 slowly increases and σ_3 slowly decreases whereas σ_1 stays unchanged. Above 450 K σ_2 and σ_3 become equal and their common value decreases with increasing temperature whereas σ_1 increases. For carbons 1 and 4 of the HQ unit the only significant evolution in the behavior of the principal elements of the chemical shift tensor can be observed somewhat below 400 K where σ_2 and σ_3 approach. Above this temperature, and until the highest temperature investigated, the three elements are nearly constant.

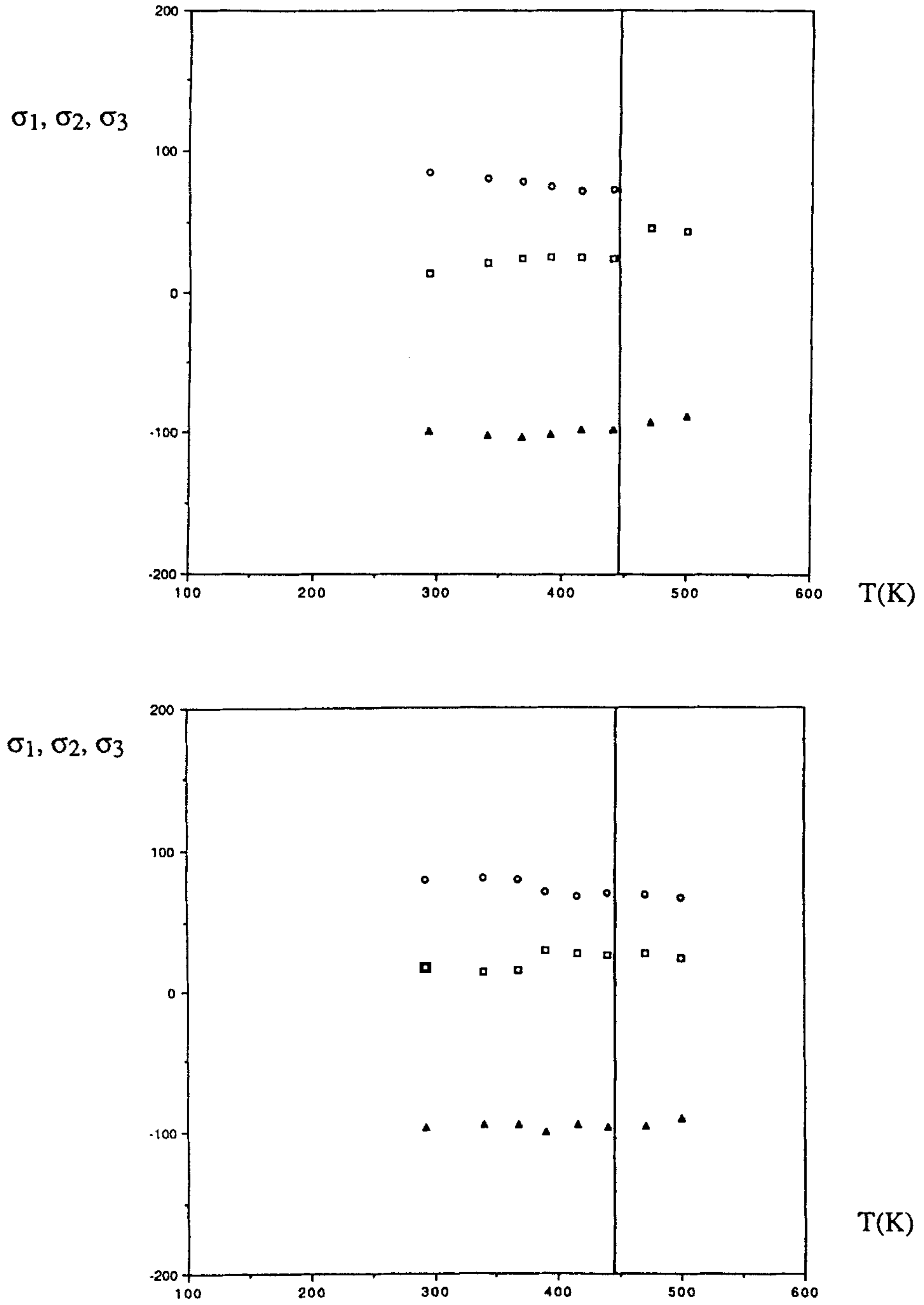


FIGURE 7 The principal elements σ_1 (Δ), σ_2 (□) and σ_3 (o) (expressed in ppm) of the chemical shift tensor of carbon 1 of the HBA unit (upper figure) and carbon 1 and 4 of the HQ unit (lower figure) as a function of temperature for the HBA27 polymer. The extrapolated T_g of HBA27 is indicated as a vertical line.

These observations may be interpreted in terms of the same local motions as those discussed for the HBA33 and HBA80 polymers, that is, a rotational motion about the local symmetry axis of the phenyl ring and a reorientation of this axis at temperatures above 450 K in the case of the HBA unit.

The glass transition temperature of the HBA27 polymer at a frequency of 10^5Hz is indicated on Figure 7[4]. In the case of the HQ unit of the HBA80 polymer, it lies in the temperature range above which an averaging of σ_1 and the common value of σ_2 and σ_3 of carbon 1 of the HBA unit set in. For temperatures above the T_g the onset of motion of the *para* axis of the phenyl ring can be detected for this unit, indicating an increasing segmental mobility of the polymer chain. Thus, the glass transition observed by DSC can be related to motions of the *para* ring axis in the amorphous HBA-rich regions of the polymer.

As for the HBA unit in HBA80, passing the T_g has no significant effect on the values of the chemical shift tensor of carbons 1 and 4 of the HQ unit. Nevertheless, as in the former case, there occurs a pronounced decrease in the signal to noise ratio for the corresponding peaks of both units above the transition. The origin of the step observed in the motional behavior of the HQ unit somewhat below 400 K is not yet fully understood. It indicates an onset of mobility and seems to be a general phenomenon for the semicrystalline terpolyester.

From the results obtained in the NMR investigation of the HBA27 polymer it can be concluded that the more mobile HBA units are preferentially located in the amorphous regions of this polymer whereas the more rigid HQ segments are preferentially found in the crystalline regions. This again correlates nicely with the results of the X-ray diffraction experiments on this polymer where only those crystal forms could be found that are associated with $(IA\text{-}HQ)_n$ sequences [1,4].

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REFERENCES

1. D.J. Blundell, W.A. MacDonald and R.A. Chivers, High Performance Polymers, 1, 97 (1989)
2. A. B. Erdemir, D. J. Johnson, I. Karacan and J. G. Tomka, Polymer, 29, 597 (1988)

3. J. Herzfeld and A. Berger, J. Chem. Phys., 73, 6021 (1980)
4. U. Wiesner, F. Lauprêtre and L. Monnerie, submitted to Macromolecules
5. A. Gérard, F. Lauprêtre and L. Monnerie, Macromolecules, 26, 3313 (1993)
6. A. Gérard,F. Lauprêtre and L. Monnerie, L. to be published
7. J. Kempf, H.W. Spiess, U. Haeberlen and H. Zimmermann, Chem.Phys.Lett., 17, 39 (1972)
8. J. Dongen Torman, W.S. Veeman and E. De Boer, J.Magn.Res., 32, 49 (1978)
9. W.S. Veeman, Progress in NMR Spectroscopy, 16, 193 (1984)
10. L. Monnerie and J.L. Halary , private communication