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High-Resolution Solid-State ^{13}C NMR Investigation of Local Motions in a Mesomorphic Main-Chain Copolyester

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ABSTRACT: The local motions of a mesomorphic main-chain copolyester based on hydroquinone, hydroxybenzoic acid, and isophthalic acid units were investigated by using high-resolution solid-state ^{13}C NMR. The ^{13}C chemical shift tensor parameters were determined from the spinning side band intensities. The rigid-lattice behavior was obtained from the study of model molecules in the crystalline state. At temperatures below the glass transition temperature, partial motional averaging of the chemical shift tensors of the aromatic carbons has shown the existence of oscillations for both para- and meta-substituted rings. The amplitude of these oscillations increases with increasing temperature. Results obtained from the chemical shift anisotropy of the carbonyl carbons have been interpreted in terms of correlated motions of the para-substituted phenyl rings and adjacent carbonyl groups. Above 425 K one also observes small-amplitude main-chain reorientations which are likely to be involved in the glass-transition phenomena.

Introduction

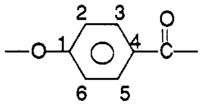
Thermotropic polymers with mesogenic units in the main chain have good mechanical properties that are related to the existence of a nematic phase which favors the orientation of the chain axis along the stretching or flow directions. However, on decreasing the temperature below the glass-transition temperature, 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 behavior.

Among the various techniques that provide information on local dynamics, high-resolution solid-state ^{13}C NMR spectroscopy is one of the most powerful. Unlike fluorescence anisotropy or electron spin resonance techniques, it does not require any labeling and yields direct information on the compound under study. It selectively allows the observation of one signal per magnetically inequivalent carbon, and therefore the dynamic behavior of different parts of a molecule can be followed independently. Moreover, there is a large number of NMR parameters which are sensitive to molecular motions. They include the different relaxation times as well as the spectrum line shape, the strength of the dipolar coupling, or the chemical shift anisotropy. For thermotropic main-chain polymers that are mainly made of aromatic units, the latter parameter is of particular interest since aromatic carbons have a large chemical shift anisotropy that can be averaged by both ring and chain motions whose frequencies are in the range of 10^2–10^5 Hz.

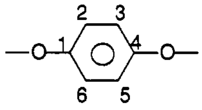
In principle, the chemical shift tensor parameters can be obtained from the proton-decoupled ^{13}C NMR spectra recorded without magic-angle sample spinning. However, as the absence of magic-angle sample spinning strongly reduces the selectivity of the technique, other methods have been proposed, based on either spinning out of the magic angle,[1] slow magic-angle spinning,[1–3] or two-dimensional spectroscopy.[4–14] The two-dimensional techniques place the anisotropic information into a second frequency dimension, while maintaining the isotropic spectrum in the first. In the case of slow magic-angle sample spinning, by referring to the theoretical calculations performed by Herzfeld and Berger,[15] it is possible to determine the values of the principal elements of the shielding tensor from the relative intensities of the spinning side bands (SSB) of different orders.

In this paper, we have used high-resolution solid-state ^{13}C NMR experiments and determinations of ^{13}C chemical shift parameters by the method of Herzfeld and Berger[15] to investigate the motional behavior of the thermotropic copolyester (A) based on the following three units in equal proportions:

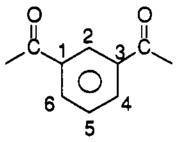
unit I:



unit II:



Unit III:



The mesogenic groups are the type I and II units with para-substituted rings. Type III units act as chain disruptors. For a quantitative analysis of motional averaging, rigid-lattice chemical shift parameters are needed. They have been determined either from crystalline model molecules or from low-temperature spectra of the polymer A. Moreover, to obtain selective information on the type III ring motion, the copolyester A has been selectively deuterated on the type I and II units, leaving the type III rings protonated. The resulting polyester will be called polymer AD in the following sections.

Experimental Section

1,4-Diacetoxybenzene (1205-91-0) and methyl 4-acetoxybenzoate (24262-66-6) were purchased from Lancaster Synthesis. Dimethyl isophthalate (19,423-9) and phenyl benzoate (14,271-9) were purchased from Aldrich.

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The synthesis of copolyesters A and AD was performed by MacDonald and Clough of the I.C.I. Co. The chemical composition of these products was established by high-resolution solution ^{13}C NMR. The high-resolution solid-state ^{13}C NMR spectrum of the AD copolyester, obtained by using a 20-μs contact time to select only the protonated carbons, shows small signals from residual protonated carbons of type I and II units, indicating an incomplete (~80%) deuteration of these units.

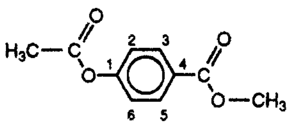
The copolyester A has a glass transition temperature, T_g, of 405 K as measured by DSC. The morphology of a sample annealed for 30 min at 543 K has been investigated by Blundell et al. by using X-ray diffusion.[16] Below the T_g both nematic regions frozen in the glassy state and crystalline regions coexist. The latter regions are associated to sequences formed by units II and III, and their extent is of the order of 16%. Since the sample studied in this paper has not been annealed at high temperature, it may be considered as being largely glassy nematic below T_g, as also indicated by the DSC traces.

The high-resolution solid-state ^{13}C NMR experiments were carried out on nonoriented powder samples of copolyesters A and AD. The experiments were conducted at 75.47 MHz with a Bruker CXP 300 spectrometer, with quadrature detection and a single rf coil which was double tuned for both ^{13}C and ^{1}H. Proton dipolar decoupling (DD) and magic-angle sample spinning (MAS) were used. The samples were contained in Al_2O_3 rotors. The spinning speed was around 4000 Hz. The pulse sequence consisted of a cross polarization (CP) proton dipolar decoupling sequence. 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). The Opella pulse sequence[17] was used to select carbons with weak proton dipolar coupling, i.e., quaternary and methyl carbons. Variable-temperature experiments at 75.47 MHz were made using a DOTY probe. Spin-temperature inversion techniques allowed the minimization of base line noise and roll.[18] Flip-back[19] was also used to shorten the delay between two successive pulse sequences.

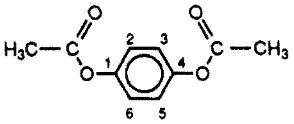
The spinning side bands were identified by using a TOSS pulse sequence, which permits the suppression of the spinning side bands.[20,21] The chemical shift parameters were calculated from the relative intensities of the spinning side bands by referring to the theoretical calculations of Herzfeld and Berger.[15]

Results and Discussion

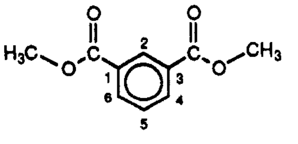
High-Resolution Solid-State ^{13}C NMR Spectrum of Crystalline Model Molecules. The formulas and numbering of the different carbons are depicted below:



methyl 4-acetoxybenzoate



1,4-diacetoxybenzene



dimethyl isophthalate

The high-resolution solid-state ^{13}C NMR spectra of the three cystalline model molecules recorded at room temperature are shown in Figure 1 together with the line assignment. The assignment of the aromatic resonances is based on empirical additivity rules for aromatic ring carbons.[22] It is in agreement with results obtained by using an Opella pulse sequence[17] which discriminates against the protonated CH and CH_2 carbons. The two lines observed for the 3,5 carbons of methyl 4-acetoxybenzoate indicate that these two carbons are magnetically inequivalent, which implies that there exists no ring motion in the crystalline state that renders the two sites equivalent.

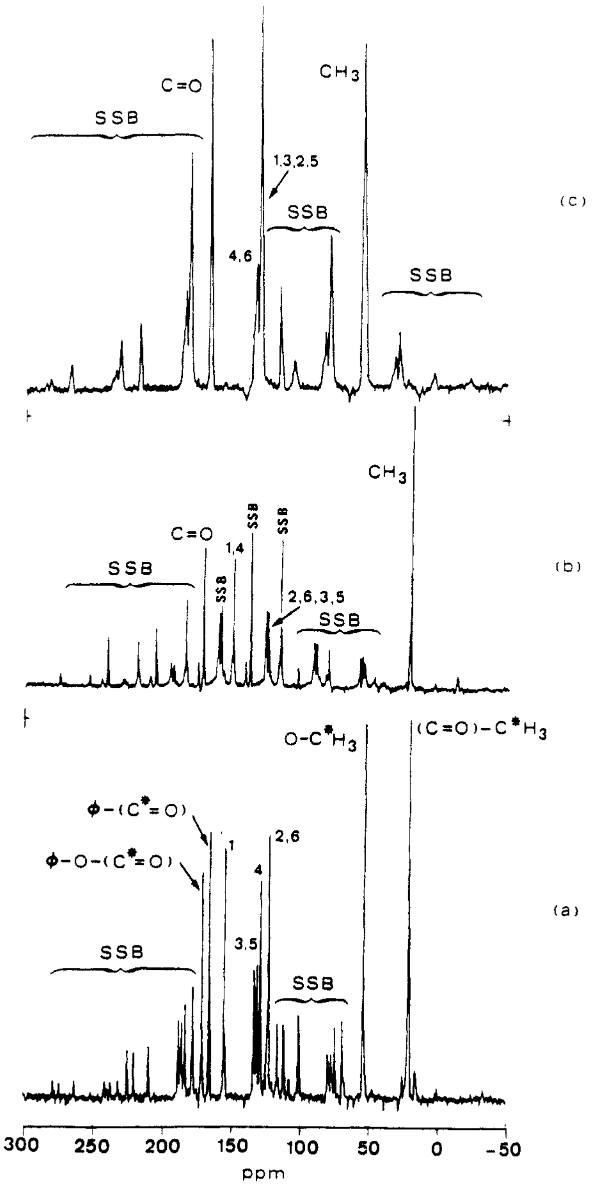


Figure 1. MAS/CP/DD ^{13}C NMR spectra at room temperature of (a) methyl 4-acetoxybenzoate (spinning speed: 4000 Hz, contact time: 1 ms), (b) 1,4-diacetoxybenzene (spinning speed: 2600 Hz, contact time: 1 ms), and (c) dimethyl isophthalate (spinning speed: 3850 Hz, contact time: 1 ms).

Similarly, the 2,6,3,5 carbons of 1,4-diacetoxybenzene are characterized by two distinct lines, indicating the absence of large amplitude ring motions.

The chemical shift parameters σ_1, σ_2, and σ_3 of the aromatic and carbonyl carbons have been derived from the spinning side band intensities by referring to Herzfeld and Berger calculations.[15] They are listed in Table I for the three crystalline model molecules considered. The chemical shift anisotropy of the substituted carbons of the rings and the carbonyl carbons depends on the chemical nature of the ring substituents. On the other hand, the protonated ring carbons have comparable chemical shift parameters, whatever the ring substituents.

High-Resolution Solid-State ^{13}C NMR Spectrum of Polyester A. The high-resolution solid-state ^{13}C NMR spectrum of copolyester A at room temperature is shown in Figure 2. The line assignment is based on the study of the model molecules described above. It is also supported by the observation of short contact time CP spectra which discriminate against the unprotonated carbons and methyl carbons. The line assignment is also given in Table II. The 164 ppm peak represents the resonances of all the carbonyl carbons of the copolyester units. The 154 ppm

Table I. Principal Values σ_1, σ_2, and σ_3 of the ^{13}C Chemical Shift Tensors in the Different Model Molecules ($\sigma_1 + \sigma_2 + \sigma_3 = 0$)

carbon	σ_1	σ_2	σ_3
I1	-100	30	70
I2,6	-88	-20	108
I3,5	-89	-30	119
I4	-94	-14	108
II1,4	-121	20	101
II2,6,3,5	-92	-23	115
III1,3,2,5[a]	-95	-20	115
III4,6	-98	-29	127
C=O of I (C=O-Φ)	-72	-26	98
C=O of I (C=O-O-Φ)	-87	24	63
C=O of II	-118	50	68
C=O of III	-92	26	66

[a] The resonances of carbons 1, 3, 2, and 5 are not resolved.

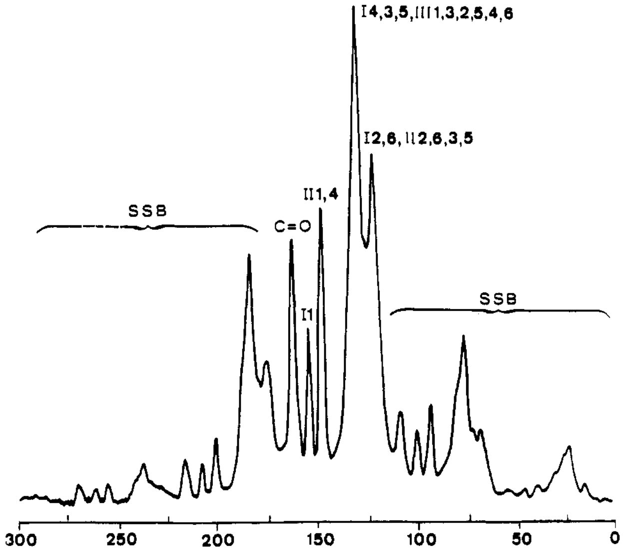


Figure 2. MAS/CP/DD ^{13}C NMR spectrum of polymer A at room temperature (spinning speed: 4000 Hz, contact time: 1 ms).

Table II. Experimental and Calculated Isotropic Chemical Shifts of the Different Carbons of Polymer A Expressed in ppm with Respect to the ^{13}C of TMS

carbon	calcd[a] chemical shift	expl chemical shift
I1	156	154
I2,6	122.6	122
I3,5	130.5	131
I4	128.6	127
II1,4	149.5	148
II2,6,3,5	123.5	122
III1,3	130.7	131
III2	130.7	131
III4,6	134.1	134
III5	128.7	127
C=O	163	164

[a] The calculation is based on empirical additivity rules for aromatic ring carbons.[22]

line is characteristic of carbon 1 of the type I unit (I1). The 148 ppm line corresponds to carbons 1 and 4 of the type II unit (II1,4). Analysis of the spinning side bands associated to these two main lines will thus provide specific information on the motional behavior of rings I and II, respectively. On the other hand, all the resonances from carbons of the type III unit belong to composite lines, so that no specific information on the motion of the meta-substituted ring can be derived from the spectrum of the protonated copolyester A. Therefore, for the type III unit, motional information can only be obtained from the study of the selectively deuterated copolyester AD discussed below.

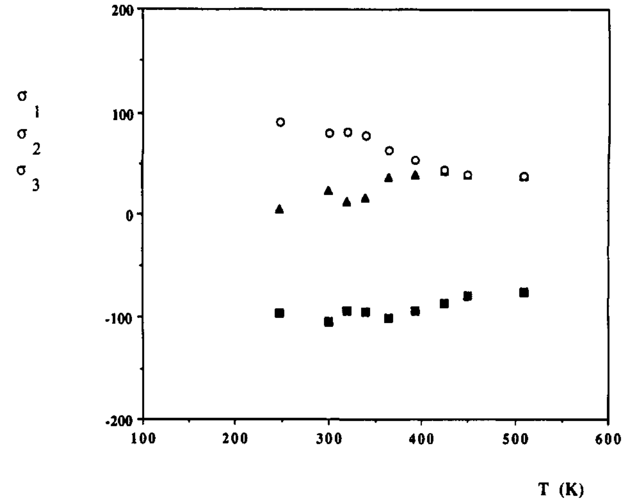


Figure 3. Temperature dependence of the principal values σ_1 (■), σ_2 (▲), and σ_3 (○) (expressed in ppm) of the chemical shift tensor for the carbon I1 of polymer A.

The MAS/CP/DD ^{13}C NMR spectra of copolyester A were recorded in the temperature range from 248 to 520 K. The peak positions are independent of temperature, whereas the relative intensities of the spinning side bands decrease on increasing temperature, indicating a progressive averaging of the chemical shift tensor and, as a consequence, the occurrence of local motions. The quantitative analysis of spinning side bands will be described in the next sections.

Local Dynamics of Type I Units. For aromatic carbons, the directions of the principal axes of the chemical shift tensor have been determined from single-crystal studies.[23] 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. Orientations of the ^{13}C principal elements in different single aromatic crystals differ only from 1 to 2°.[24]

The principal values σ_1, σ_2, and σ_3 of the chemical shift tensor for carbon I1 were 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[15] in the temperature range from 248 to 510 K. Results thus obtained are plotted in Figure 3. Between 248 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, there occurs a slight increase in the σ_1 value and a decrease in the common value of σ_2 and σ_3.

Assuming that the principal axes of the chemical shift tensor of carbon I1 are identical to those of aromatic carbons previously studied and described above, results observed in Figure 3 at temperatures up to 425 K are consistent with the existence of motions about the para axis of the ring. Indeed, processes 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 leaving the σ_1 principal value, which is parallel to the axis of rotation, unchanged. Above 425 K, results reported in Figure 3 show a partial averaging of σ_1, which corresponds to a reorientation of the para axis of the ring.

The results obtained between 248 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 text, we will use the latter assumption and consider a motional model based on rapid oscillations about

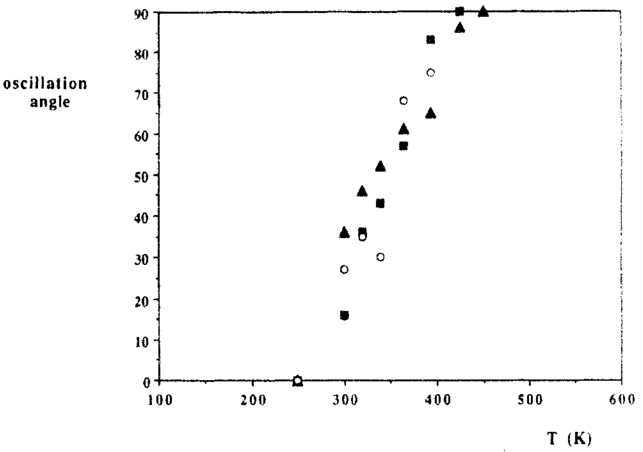


Figure 4. Variation of the amplitude of oscillation of the type I aromatic units (■), type II aromatic units (▲), and C=O groups (○) as a function of temperature.

the para axis of the ring between increasing angles α and $-\alpha$, corresponding to a 2α amplitude of motion. Besides, in most mesomorphic main-chain systems, dynamic heterogeneity is expected. However, as noted in the Experimental Section, the extent of the crystalline parts is very small, and the copolyester under study is largely amorphous. It must also be noticed that there is no experimental evidence of dynamic heterogeneity within the accuracy of our experiments. Therefore, we have considered that the dynamic heterogeneity of the copolyester A is negligible as a first approximation, and therefore, we have characterized the motional behavior of carbon I1 in terms of an average oscillation amplitude that increases with increasing temperature. The same assumptions will be used throughout this paper for the different carbons and types of motions considered.

For carbon I1, the rigid-lattice values ($\alpha = 0$) 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 4-acetoxybenzoate in its crystalline state. Calculated amplitudes of rapid oscillations about the para axis of the ring between increasing angles α and $-\alpha$ are plotted in Figure 4. They show a regular increase of α from 248 K up to a complete ring flip (α = 90°) at 425 K.

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.

Local Dynamics of Type II Units. The dependence on temperature of σ_1, σ_2, and σ_3 for the carbons 1 and 4 of unit II, determined from the method of Herzfeld and Berger, is plotted in Figure 5. From comparison with Figure 3 one can conclude that the behavior of σ_1, σ_2, and σ_3 is essentially the same as that of the principal values of the shielding tensor of carbon I1. Therefore, the results can be interpreted in terms of the same type of local motions, i.e., an oscillation about the local symmetry axis of the phenyl ring that is completed about 425 K and a reorientation of this axis at high temperature. The variation of the calculated amplitude, β, of the motion about the para axis as a function of temperature is plotted in Figure 4. Furthermore, the analysis of the high-temperature region in Figure 5 shows 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 I1.

Local Dynamics of Type III Units. As mentioned in the first part of the discussion, the only way to obtain selective information on the ring motion of the type III unit is to study the selectively deuterated copolyester AD. Figure 6 shows representative variable-temperature ^{13}C NMR spectra of polymer AD recorded between 123 and 520 K in the absence of magic-angle sample spinning. The contact time has been taken as being equal to 20 μs in order to observe only the contribution from the protonated 2, 4, 5, and 6 carbons of the type III unit. The observed 20-μs chemical shift anisotropy pattern is different from that obtained with a much longer contact time. Indeed, the polarization acquired by a given carbon during a very short contact time depends on the carbon orientation with

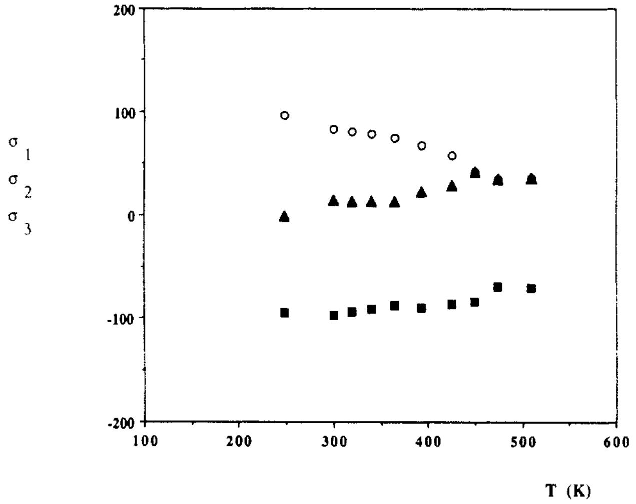


Figure 5. Temperature dependence of the principal values σ_1 (■), σ_2 (▲), and σ_3 (○) (expressed in ppm) of the chemical shift tensor for the carbon II1,4 of polymer A.

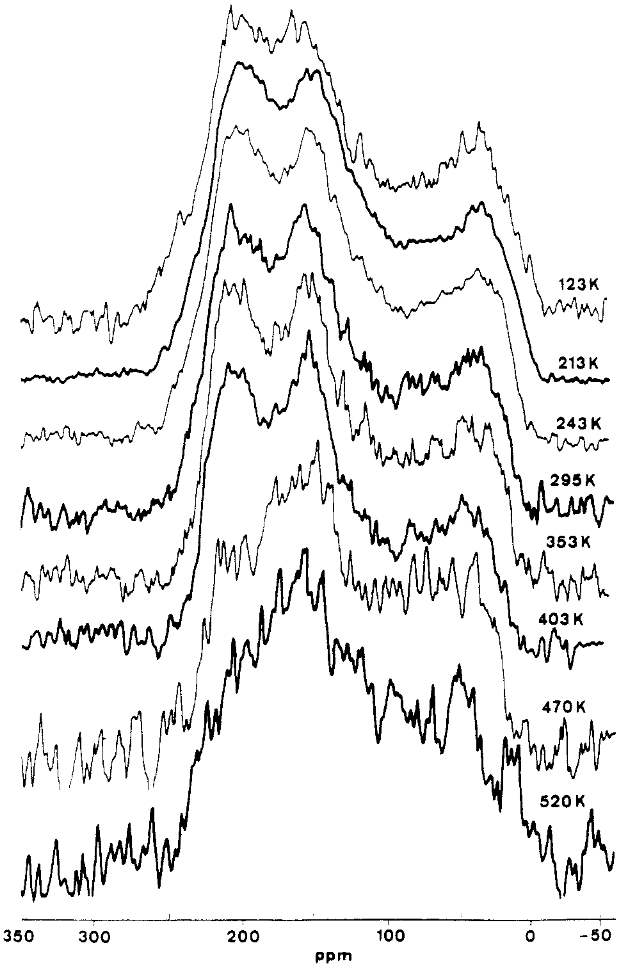


Figure 6. Variable temperature CP/DD ^{13}C NMR spectra of polymer AD (contact time = 20 μs).

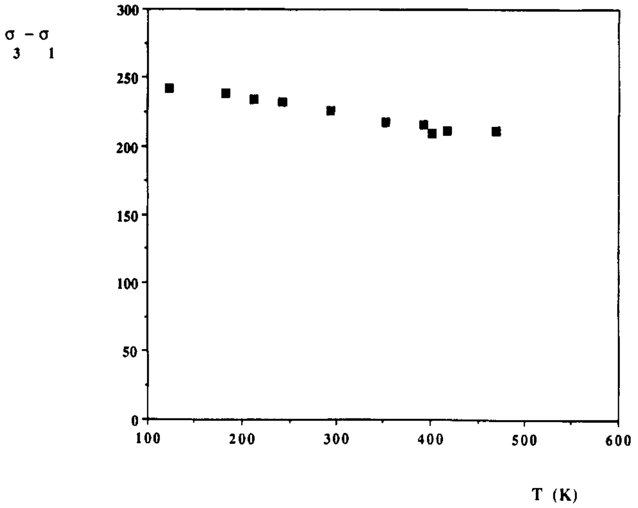
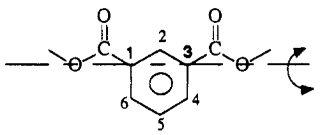


Figure 7. Temperature dependence of the $\sigma_3 - \sigma_1$ difference (expressed in ppm) for the carbons III4,6 of polymer AD.

respect to the static magnetic field. This phenomenon will be discussed in more detail in a further paper. In the absence of magic-angle sample spinning, the obtained spectrum is the sum of the chemical shift patterns of the four magnetically inequivalent protonated carbons of ring III. However, use of data listed in Table I shows that the total spectrum width is due to the $\sigma_3 - \sigma_1$ difference for the 4,6 carbon pair. The evolution of the $\sigma_3 - \sigma_1$ difference as a function of temperature is shown in Figure 7. It is a decreasing function of temperature that can be interpreted in terms of motions that partially averaged the chemical shift anisotropy. For this meta-substituted ring different types of motions 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 the carbons III2,5 and III4,6, have led to the conclusion that the type III units are involved in stochastic jumps about the axis joining the carbons III1 and III3 and represented below:[25]



In the following text, 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 amplitudes of oscillations, γ, about the local axis represented above, have been calculated by using as rigid-lattice parameters chemical shift parameters measured for the 4,6 carbon pair either for the polymer AD at 123 K or for crystalline dimethylisophthalate at room temperature. Variation of γ as a function of temperature is shown in Figure 8. γ increases regularly from 0° at 123 K to a limiting value of 40° at 400 K.

Local Dynamics of the Carbonyl Groups. Investigation of the local dynamics of the carbonyl groups has been performed by analyzing the spinning side band intensities of the 164 ppm peak of the CPMAS spectrum of polymer A. The temperature dependence of σ_1, σ_2, and σ_3 derived from these data is plotted in Figure 9. It shows a motional averaging whose extent increases with increasing temperature.

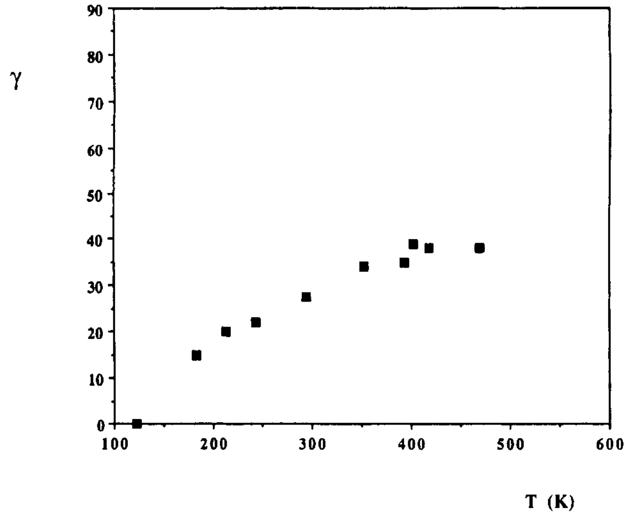


Figure 8. Variation of the amplitude of oscillation, γ (deg), of the type III aromatic units as a function of temperature.

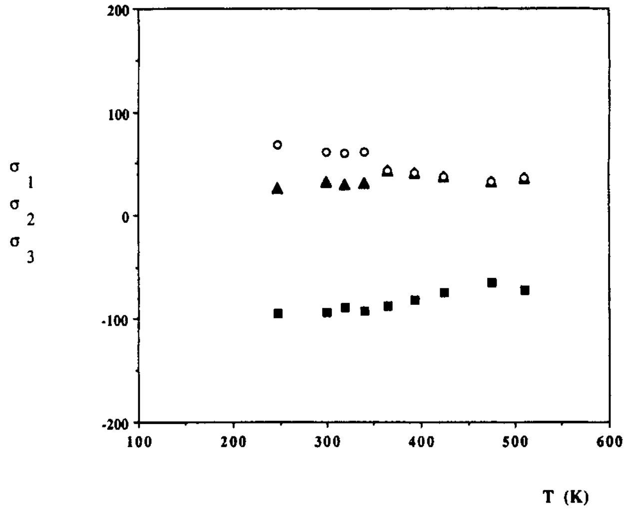


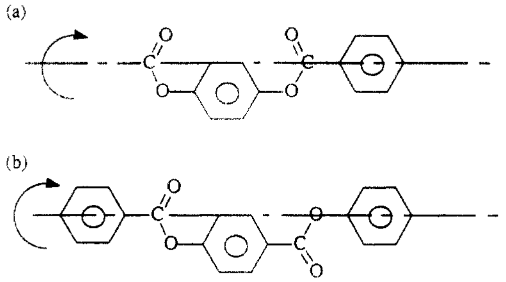
Figure 9. Temperature dependence of the principal values σ_1 (■), σ_2 (▲), and σ_3 (○) (expressed in ppm) of the chemical shift tensor for the C=O carbons of polymer A.

For carbonyl carbons, the principal axis orientations depend on the chemical nature of the neighboring groups. In the following, we have used results reported for acetophenone and benzophenone[26,27] in which the most shielded axis is perpendicular to the sp^2 plane and the intermediate one is along the C=O bond.[24]

To interpret the results reported in Figure 9 one has first to consider the different types of carbonyl carbons that are found in polymer A. About two thirds of these carbons belong to a type III unit. The remaining carbonyl carbons sit between type I or II units. In the first case, the carbonyl carbons are involved in the oscillatory motion of the type III unit described in the previous section. However, calculations carried out at the investigated temperatures show that the amplitude of these oscillations, given in Figure 4, is too small to be responsible for the motional averaging evidenced in Figure 9 above 320 K. This result indicates that there exists 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 on the top of the next page.

Such motions induce a translation of the para axis of the type I or II 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 of interest to notice 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 polymer A and in order to simplify further calculations, we have assumed in the following text that all the C=O carbons are involved in such a reorientation.

To estimate the amplitude of this process, we have assumed that the 248 K 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. The assumption that this type of motion is frozen at 248 K is likely in terms of the activation energy such a process would require. Motional amplitudes obtained under these assumptions are plotted in Figure 4 together with the temperature dependence of the amplitudes of the oscillations of the type I and II rings about their para axis. It has to be noted that the three motional amplitudes have similar values and temperature dependences until 425 K. 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, there occurs an additional chain reorientation, 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.

Conclusion

The analysis of the motional averaging of the ^{13}C chemical shift tensors has pointed out the existence of different types of motions in the aromatic copolyester under study. At low temperature, only small-amplitude oscillations of the meta-substituted rings occur. Above 300 K, the two para-substituted rings exhibit identical reorientations about their local symmetry axis, which are coupled with the motions of the neighboring carbonyl carbons. The amplitude of these processes increases regularly until 425 K where the para-substituted rings are involved in full ring flips. Finally, above 425 K, one observes, in addition to the previous modes, a reorientation of the main-chain axis.

At this point, it is of interest 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.[28] 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 introduced by the extrapolation, one observes 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 340 and 265 K, 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. To confirm this assignment, further NMR and dynamic mechanical experiments on copolyesters made of the same three reccurring units with different proportions are now in progress in our laboratory.

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