values from T_c–M_w[7]. Atactic PMMA in MeCN is one of the cases where such large discrepancies are found[7]. The agreement between the values of equations (6) and (7) is therefore an important result.

We could have used equation (3) instead of equation (2) to estimate $(\mathrm{d}T_c\mathrm{d}x_2)_0$ from viscosity data. If we do so, with the values of χ_{13}, χ_{23}, χ_{12} determined previously by light scattering[22], and with $(\mathrm{d}\chi_{13}/\mathrm{d}T)_{T_{c1}}$ obtained from $(\mathrm{d}[\eta]/\mathrm{d}T)_{0,25^\circ\mathrm{C}}$ as:

$$(\mathrm{d}\chi_{13}/\mathrm{d}T)_{T_{c1}} \approx -(N_A V_1/1.02 M_w \bar{v}^2 \Phi)(\mathrm{d}[\eta]/\mathrm{d}T)_{0,25^\circ\mathrm{C}} \quad (8)$$

then we obtain an estimate for $(\mathrm{d}T_c/\mathrm{d}x_2)_0$ which is an order of magnitude larger than the experimental values, namely: 7.8×10^3K, and 2.0×10^3K, for MeCN = 1 and ClBu = 1, respectively. This does not mean that equation (3) is not adequate*, but, rather, that the temperature dependence of χ_{13} determined from $[\eta]$–T is, as discussed above, not compatible with T_c measurements.

However, agreement between cloud points and viscosity is found if we use the $[\eta]$ results twice: to estimate $\partial\chi/\partial x_2$ and $\partial\chi/\partial T$ simultaneously, as we have just done using equation (2). We reach the interesting conclusion that the comparison between the temperature and solvent composition variations of $[\eta]$ allows for a correct prediction of the cosolvent depression of the UCST. The comparison between cloud points and $[\eta]$–T gives, in general, inconsistent results, but the combination of $[\eta]$–T and $[\eta]$–φ corrects or compensates such an inconsistency and establishes a valid link between T_c and $[\eta]$.

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* It has been successfully applied to predict $(\mathrm{d}T_c/\mathrm{d}x_2)_0$ using solubility parameters[3,4].

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Proton-decoupled ^{13}C solid state n.m.r.: A lineshape study of molecular motion in a mesomorphic aryl-aliphatic polyester

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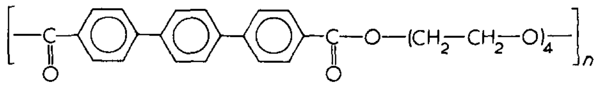
Introduction

High-power proton-decoupled ^{13}C nuclear magnetic resonance has proved to be a powerful tool for investigating molecular dynamics in solids. In this respect, attention has mainly been focused on measurements of the carbon spin-lattice relaxation times in the rotating frame ^{13}C $T_{1\rho}$ which are used to probe the density of motion of the C–H vectors in the tens of kilohertz region[1]. Interesting information about motional modes can also be provided by proton-decoupled ^{13}C n.m.r. lineshape analysis[2]: variations of these lineshapes can indeed be interpreted in terms of molecular reorientation or conformational processes[3]. In the particular case of mesomorphic polymers, they can be considered as a means for examining the dynamics of these compounds as a function of the structure or organization of their various states.

This communication gives some preliminary results obtained on the polyester:



(A)

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which gives an anisotropic phase according to[4]:

Solid ←→ Smectic C ←→ Isotropic liquid
112°C 247°C

Due to its very simple chemical formula, the proton-decoupled spectrum of this polymer consists of two well-resolved broad lines, and lineshape analysis therefore looks to be a particularly suitable tool for carrying out a separate study of the intramolecular motional processes affecting either the aromatic or the aliphatic part of the compound.

Experimental

The polyester was prepared in the Centre de Recherches des Carrières de Rhône-Poulenc, Saint-Fons, France, by standard methods as described elsewhere[4]. It has an inherent viscosity at 25°C of 0.6 dl/g at a concentration of 0.5 g/dl in dichloracetic acid. Besides the two first-order transitions at 112°C and 247°C, differential scanning calorimetry points out two glass-transitions for this polymer: the first one appearing between −40°C and −20°C, the second one in the range 40°–60°C.

^{13}C n.m.r. spectra were recorded at 12 MHz on a home-built spectrometer. The following pulse sequence was used: first a low level proton irradiation enabled Nuclear Overhauser enhancement of the ^{13}C nuclei. Then, following the $\pi/2$ ^{13}C pulse, a higher proton decoupling irradiation ($H_1 = 10$ Gauss) was established during the ^{13}C free induction decay observation. Therefore dipolar broadening was suppressed and only the anisotropies of the chemical shift tensors were observed[2]. It is noticeable that the low values (~ 1 ms) of the ^{1}H $T_{1\rho}$ of the polymer under study do not allow multiple contacts to be performed. The repetition time was equal to 1 s and kept constant over the whole range of temperature.

A special quartz dewar was home-built and allowed the heating of the samples in the range 0°–400°C.

Results and Discussion

In *Figure 1* the ^{13}C spectra of the polyester at various temperatures between 25° and 205°C are shown. *Figure 2* presents the comparison between the solid and solution spectra at 25°C. Owing to their long relaxation times, T_1, the carbonyl and quaternary phenyl carbon absorptions can be neglected. Reported in *Figures 3* and *4* are the widths Δ_{CH_2} and Δ_ϕ of each line, and the line intensity ratio

$$R = \frac{h_{CH_2}}{h_\phi} \cdot \frac{\Delta_{CH_2}}{\Delta_\phi}$$

where h_{CH_2} is the height of the aliphatic peak and h_ϕ the height of the aromatic peak.

From the dependence of the lineshapes on temperature, it appears that the spectra of the aromatic carbons of the polymer are those of the rigid lattice until 120°C. They are comparable with that of hexamethylbenzene at low temperature[5]. At 120°C, the linewidth of the aromatic part strongly decreases and the lineshape is modified, pointing out a dynamic process of the phenyl rings. Moreover the increasing intensity of the aromatic pattern as compared with that of the $-CH_2-$ region in the range 25°–120°C seems to indicate a variation of the ^{13}C spin-lattice relaxation times and/or nuclear Overhauser effects.

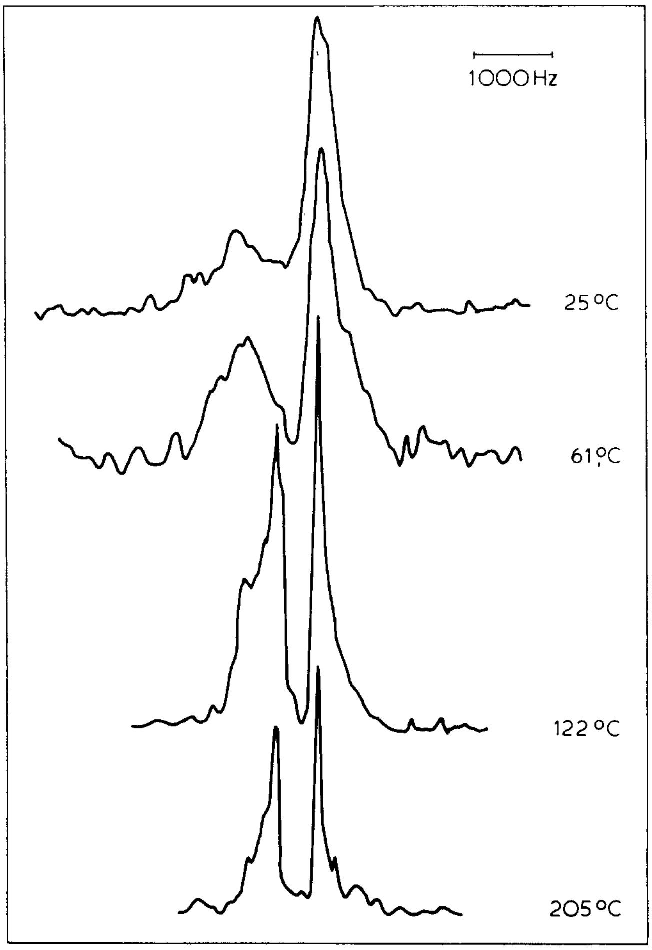


Figure 1 Proton-decoupled ^{13}C n.m.r. spectra of polyester A in bulk as a function of temperature

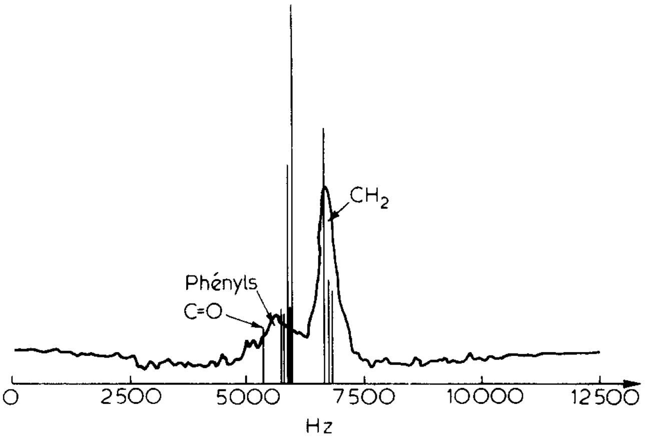


Figure 2 Comparison between solid and solution spectra of polyester A at 25°C

Results concerning the aliphatic part of the molecule are summarized in *Figure 3*. The motion of the methylene carbons is already obvious at 40°C. The linewidth regularly decreases until 140°C and then remains unchanged above this temperature.

The chemical shift tensors of the aliphatic and aromatic carbons of the molecule have not been yet determined. However, both the chemical formula and solution spectra of hexamethylbenzene and diethylether suggest that the

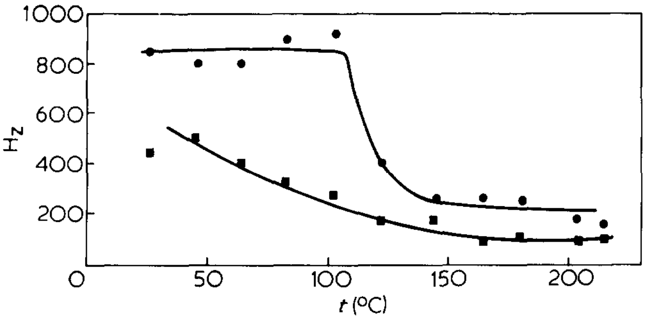


Figure 3 Linewidths Δ_{CH_2} and Δ_ϕ of aliphatic and aromatic lines of polyester A as a function of temperature: ΔCH_2, (■); $\Delta\phi$, (●)

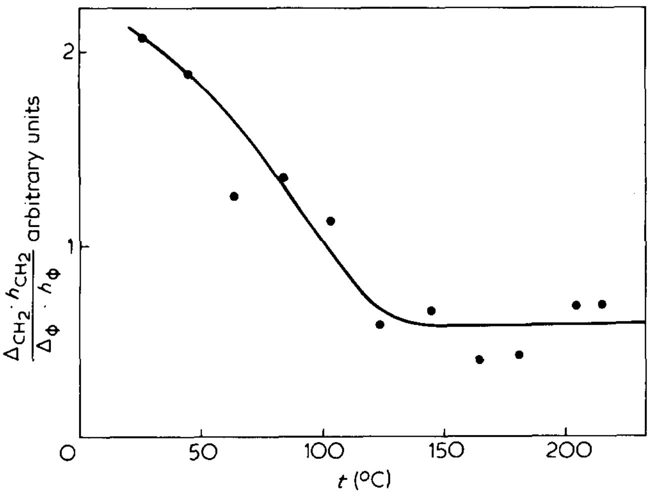


Figure 4 Intensity ratio $R = h_{CH_2}/h_\phi \cdot \Delta_{CH_2}/\Delta_\phi$ for the polyester A as a function of temperature

simulation of the polymer spectrum can be carried out using the ^{13}C chemical shift tensors of these two model compounds[5,6] taken as parameters for the two parts, aromatic and aliphatic, of the polymer chain.

In the case of a powder, the asymetric lineshape function $I(\sigma)$ has been calculated by Bloembergen and Rowland as[7]:

$$I(\sigma)=\pi^{-1}(\sigma-\sigma_{11})^{-1/2}(\sigma_{33}-\sigma_{22})^{-1/2}K(m)$$

with:

$$m=(\sigma_{22}-\sigma_{11})(\sigma_{33}-\sigma)/(\sigma_{33}-\sigma_{22})(\sigma-\sigma_{11})$$

for $\sigma_{33}\geqslant\sigma>\sigma_{22}$

and $I(\sigma)=\pi^{-1}(\sigma_{33}-\sigma)^{-1/2}(\sigma_{33}-\sigma_{11})^{-1/2}K(m)$

with $m=(\sigma-\sigma_{11})(\sigma_{33}-\sigma_{22})/(\sigma_{33}-\sigma)(\sigma_{22}-\sigma_{11})$

for $\sigma_{22}>\sigma\geqslant\sigma_{11}$

and: $I(\sigma)=0$ in case $\sigma>\sigma_{33}$ and $\sigma<\sigma_{11}$

σ_{11}, σ_{22} and σ_{33} are the principal values of the shielding tensor $\sigma(\sigma_{11}\leqslant\sigma_{22}<\sigma_{33})$ and $K(m)$ is the complete elliptic integral of the first kind.

When rapid rotation about one axis of the molecule occurs, a partial averaging of the shielding tensor ensues[2]. The average shielding tensor displays axial symmetry about the rotation axis and the motionally narrowed anisotropy may be written as:

$$\overline{\Delta\sigma}=\sigma_{\parallel}-\sigma_{\perp}$$
$$=\tfrac{1}{2}(3\cos^2\beta-1)[\Delta\sigma(1+\tfrac{3}{4}\eta\sin^2\beta\cos 2\alpha)]$$

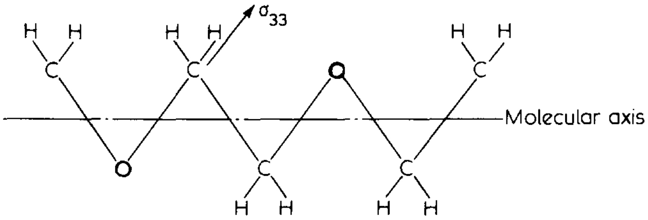
with: $\Delta\sigma=\sigma_{33}-\tfrac{1}{2}(\sigma_{11}+\sigma_{22})$

$$\eta=(\sigma_{11}-\sigma_{22})/\Delta\sigma$$

Here the Euler angles (α, β) define the transformation from the principal axes of the tensor (1, 2, 3) to the molecular rotating frame ($\bar{1}$, $\bar{2}$, $\bar{3}$).

Results of the simulation are shown in *Figures 5* and *6*. For the phenyl carbons, agreement with a rigid lattice behaviour is observed at 25°C, and with a rapid axis rotation at 120°C. In the latter case, the best fit is obtained for $\alpha=60°$, $\beta=90°$. As the observed phenyl absorption is mainly due to the protonated carbons, this result shows that the motional process of the phenyl rings above 120°C is a rotation about their C_1–C_4 axis.

As regards to the $^{13}CH_2$-spectrum, the best fit is obtained for an angle β of about 30° between the principal component σ_{33} and the axis of rotation. This is in good agreement with a model in which the 'mean rotation axis' is directed along the molecular axis and the σ_{33} component of the shielding tensor for a CH_2–O group is parallel to the C–O bond:



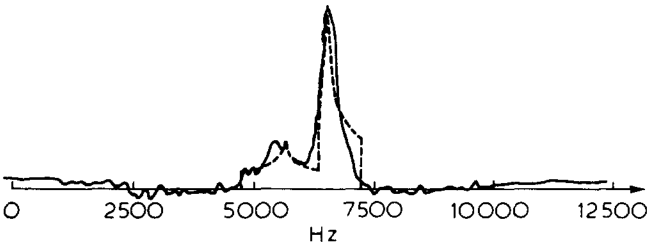


Figure 5 Comparison of experimental and simulated spectra, assuming rigid lattice behaviour at 25°C. (———) experimental spectrum; (— — —) simulated spectrum

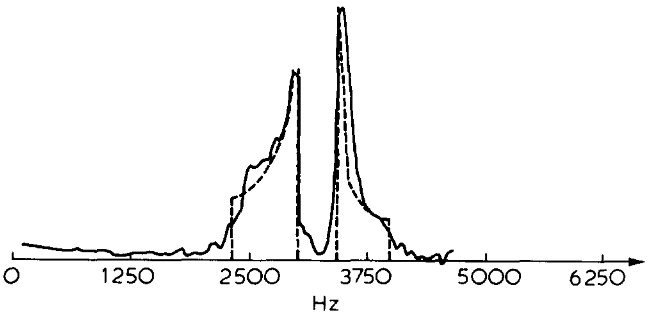


Figure 6 Comparison of experimental and simulated spectra at 120°C. Euler Angles for the simulation: Aromatic spectrum: $\alpha=60°$, $\beta=90°$; Aliphatic spectrum: $\alpha=0°$, $\beta=30°$; (———) experimental spectrum; (— — —), simulated spectrum

In reference 6, the orientation of the chemical shift tensor of the carbons of diethylether with respect to the molecular bonds is not given. In the present study, the reasonable assumption of a symmetrical distribution of the C–0 bonds about the molecular axis leads to an orientation of the shielding tensor. It is different in a CH_2–0 group and in a –CH_2– one[8]. The strongly electronegative oxygen atom plays a determinant role. This is a good illustration of how motional effects can help for assigning orientation of chemical shift tensors.

Conclusions

These preliminary results clearly demonstrate the value of proton-decoupled ^{13}C n.m.r. lineshape analysis for the description of intramolecular dynamics in polymer solids. It is particularly noticeable that the increasing rate of rotation of the phenyl rings about their C_1–C_4 axis is closely related to the apparition of the smectic phase of the polyester.

However, it also appears that ^{13}C lineshape investigation is complementary to ^{13}C $T_{1\rho}$ measurements. When the interpretation of ^{13}C $T_{1\rho}$ data in terms of molecular motions is valid[1], ^{13}C lineshape analysis gives more information about the nature of the motional processes, although less about their rates. But, in some cases, such as anisotropic reorientation and low *rf* fields, the molecular motion contribution to the ^{13}C $T_{1\rho}^{-1}$ may be hidden by spin–spin depolarization effects[1]. In such a case, a ^{13}C lineshape study becomes an attractive alternate to ^{13}C $T_{1\rho}$ measurements.

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Chemical modification of chloromethylated crosslinked polystyrene *via* phase transfer catalysed Wittig reactions

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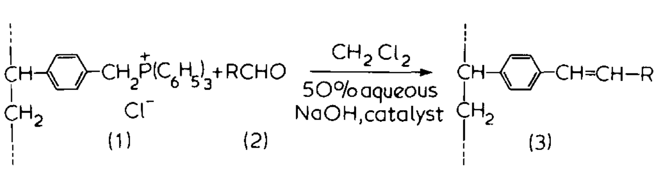
Introduction

The recent considerable interest in polymer-supported reagents, catalysts, and protecting groups[1] and in chemically active stationary phases for chromatography[2] has, in turn, led to renewed interest in the preparation of chemically modified crosslinked polystyrenes[3]. One method of obtaining a polymer with the required functional groups is to attach appropriate small molecules by covalent bonds to a preformed polystyrene[4]. We wish to report a method of this type which proceeds at ambient temperatures and which results in the small molecules being attached to the polymer by bonds which are stable to both acid and base. The key step is a phase transfer catalysed Wittig reaction between a polymer containing phosphonium salt residues (1) and an aldehyde (2) to give a polymer containing residues (3). Until recently phase transfer catalysed reactions have only occasionally been used in polymer chemistry[5,6], although they have been used extensively in organic chemistry for several years[7].



Experimental

The following procedures are typical.

Preparation of the polymer containing phosphonium salt residues (*1*). Chloromethylated 2% crosslinked polystyrene[8] (10.09 g, 3.57 mmol of Cl per g) was treated with triphenylphosphine (15.01 g) in chlorobenzene (50 ml) at reflux temperature for 60 h. After cooling the polymer was filtered off, washed successively with benzene and ether, then dried to constant weight (19.50 g). By phosphorus analysis it contained 1.81 mmol of phosphorus per g. Chloromethylated polystyrene has strong infra-red bands as 1270 and 680 cm^{-1} but the product had only very weak bands at these positions; it had new strong bands at 1440 and 1000 cm^{-1}.

Wittig reaction with ferrocene-carboxaldehyde. The above polymer (2.00 g), ferrocene-carboxaldehyde (784 mg), methylene chloride (8 ml), 50% aqueous sodium hydroxide (8 ml), and cetyltrimethylammonium bromide (150 mg) were vigorously stirred under nitrogen at 20° for 36 h. The polymer beads were filtered off and washed successively with aqueous tetrahydrofuran, tetrahydrofuran, and ether then dried. The red-brown product (1.39 g) had a strong infra-red band at 960 cm^{-1}, but no bands at 1440 and 1000 cm^{-1}. By elemental analysis it contained 9.0% iron, corresponding to 1.61 mmol per g of residues (9).

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