ferent carbazole/hydroxyl group molar ratios were synthesized similarly.

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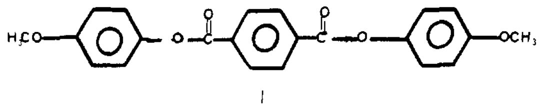
Two-Dimensional NMR and Proton Spin–Lattice Relaxation Studies of Thermotropic Homopolyesters Containing a Bicyclo[2.2.2]oct-2-ene Ring System

Due to their ordered nature, liquid crystals have been a subject of very intense scientific investigation.[1-5] It has been earlier reported[6-8] that several compounds that form a nematic mesophase contain a *p*-phenylene unit which serves a dual role: viz., (a) provides rigid linear grouping and (b) contributes to the polarizibility of the molecule. Dewar et al.[9] studied the factors influencing the stability of nematic liquid crystals by replacing the central benzene ring of bis(*p*-methoxyphenyl) terephthalate (I), with 1,4-bicyclo[2.2.2]octane. They observed that the introduction of a double bond into the bicyclooctane moiety led to an increase in mesophase stability.

In this paper, we describe the detailed proton nuclear magnetic resonance, homonuclear two-dimensional shift correlation (COSY) and proton spin–lattice relaxation studies to determine the structures of homopolyesters: poly[oxy(bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxyterephthaloyl] (II); poly[oxy(bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxycarbonyl(1,4-bicyclo[2.2.2]octylene)carbonyl] (III); poly[oxy(1,4-bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxycarbonyl(*trans*-1,4-cyclohexyl)carbonyl] (IV). We also show evidence for the influence of the electron density of the aromatic ring on bicyclo[2.2.2]oct-2-ene double bond in the homopolyester II by two-dimensional homonuclear dipolar correlated NMR (NOESY) studies.



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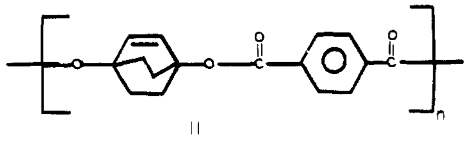

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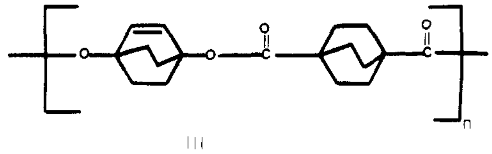

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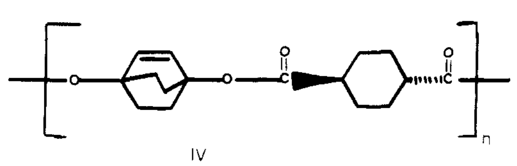

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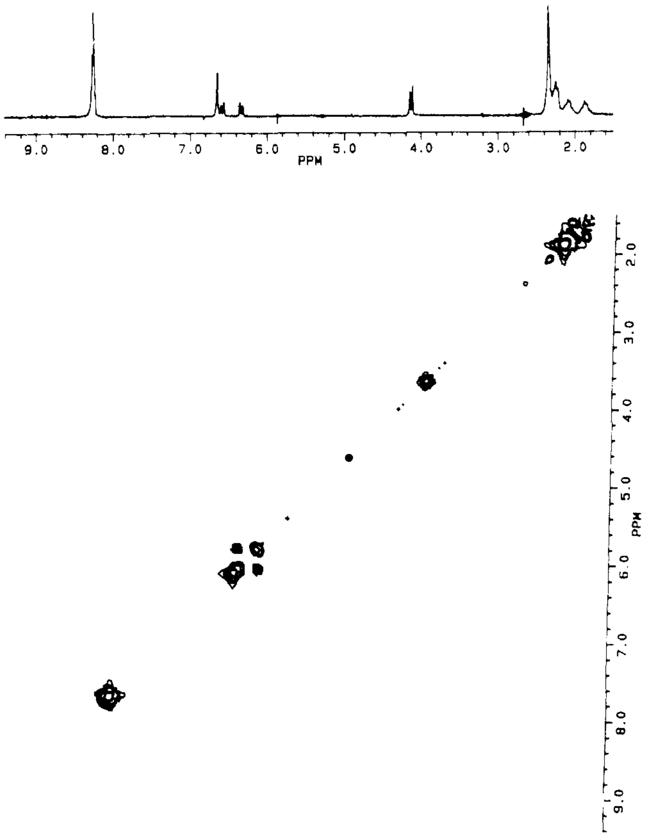

Figure 1. 250-MHz ^{1}H NMR 2D-COSY spectrum of poly[oxy(bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxyterephthaloyl] (II), recorded at 25 °C in CF$_3$COOD.

Two-dimensional COSY[10-16] and two-dimensional NOESY[10,15,17-20] techniques have been applied extensively to the interpretation of proton spectra of biological macromolecules and synthetic macromolecules such as poly(vinylbutyral),[21] poly(methyl methylacrylate),[22] poly(vinyl alcohol),[23] and a vinylidene chloride–isobutylene copolymer.[24]

Experimental Section. The homopolyesters II, III, and IV were synthesized[25] by the polycondensation of bicyclo[2.2.2]oct-2-ene-1,4-diol with terephthaloyl chloride, bicyclo[2.2.2]octane-1,4-dicarbonyl chloride, and *trans*-1,4-cyclohexanedicarbonyl chloride, respectively.

All the NMR spectra were acquired on a Bruker WM250 spectrometer, equipped with an Aspect 3000 computer, operating at the frequency 250 MHz for proton. The routine ^{1}H NMR, two-dimensional NMR, and proton spin–lattice relaxation studies were done in deuteriotrifluoroacetic acid with tetramethylsilane (TMS) as internal standard at 25 °C. In the ^{1}H NMR spectrum, the peak at 4.1 ppm is due to an impurity in the solvent (CF$_3$COOD), and the peak at 4.12 is due to moisture (Figure 1). Homonuclear 2-D correlated spectroscopy (COSY) was performed by using the standard pulse sequence RD–90°–t_1–90°–t_2.[26] It was obtained by collecting an initial time domain spectrum ($S(t_1,t_2)$), consisting of 1024 × 256 complex data points for t_2 and t_1, respectively. The initial delay time, in which the spin system comes to equilibrium, was kept at 5 s. Each increment of t_1 was scanned 64 times. The spectral windows in f_1 and f_2 dimensions were ±1350 Hz each, so that the total sweep width was 2700 Hz. A sine-bell filtering function was used in both dimensions, prior to Fourier transformation, to improve resolution. Homonuclear 2-D spectra were all symmetrized to eliminate the bands of "t_1 noise" arising from spectrometer instabilities during the extended acquisition time associ-

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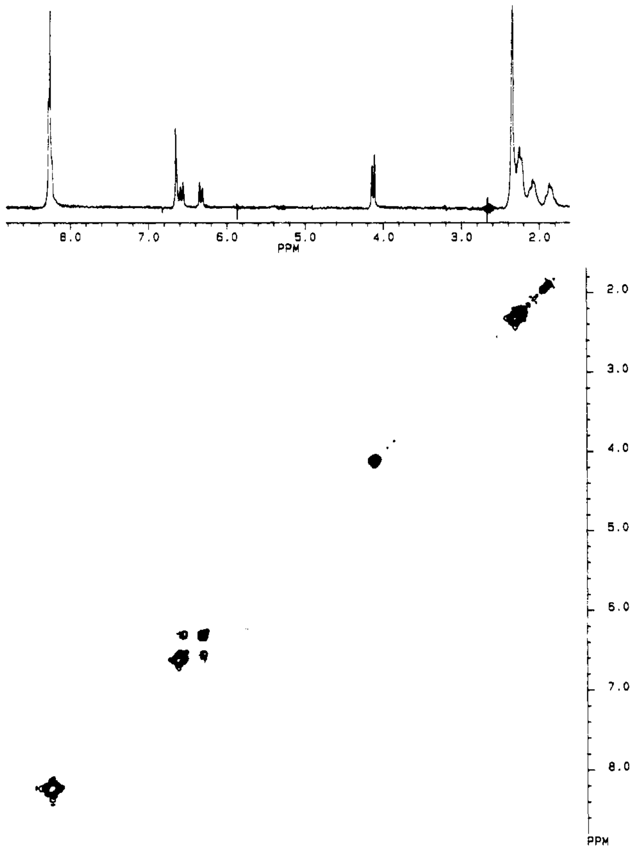


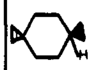
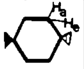
Figure 2. 250-MHz ^{1}H NMR 2D-NOESY spectrum of poly[oxy(bicyclo[2.2.2]oct-2-enen-1,4-diyl)oxyterephthaloyl] (II), recorded at 25 °C in CF_3COOD.

ated with these experiments (24 h).[27,28] In the NOESY experiment a RD–90°–t_1–90°–T_m–90°–t_2 pulse sequence[29,30] was employed. The initial delay time was 7 s and the mixing time T_m was 100 ms. The time domain parameters and the number of scans were similar to those for the COSY experiment. The proton spin relaxation (T_1) times were measured by using an inversion–recovery pulse sequence, with a total of 15 evolution delays. To minimize changes in homogenity during the course of the experiment, the evolution values were repetitively cycled.

Result and Discussion. The homopolyesters containing the bicyclo[2.2.2]oct-2-ene ring system as a mesogenic unit and *p*-phenylene, bicyclo[2.2.2]octane, and 1,4-cyclohexane ring moieties, respectively II, III, and IV, have been synthesized and their thermal behavior investigated.[25]

The proton NMR spectrum of homopolyester II in deuteriotrifluoroacetic acid is shown in Figure 1. It is of interest to note that the olefinic protons of bicyclic[2.2.2]oct-2-ene appear as a singlet (δ 6.64) and also as a double doublet centered at δ 6.45 (J = 5.2, 1.4 Hz). The fact that the doublet centered at δ 6.55 is coupled to the doublet centered at δ 6.34 is confirmed by a two-dimensional shift correlation experiment (Figure 1). This suggests that there are two sets of vinyl protons, one being equivalent (δ 6.64) and the other being nonequivalent. The presence of a double-doublet peak in the homopolyester II suggests that the nonequivalent chemical environment may probably be due to the proximity of an olefin proton to the aromatic ring of the molecule. It has been observed by two-dimensional nuclear Overhauser spectroscopy (NOESY) (Figure 2) that the aromatic protons appearing at δ 8.25 interact with the protons at δ 6.64. This indicates the proximity of the aromatic rings to the olefinic protons. However, the close proximity of the aromatic rings causes the olefinic protons to be nonequivalent and gives rise to two doublets at δ 6.55 and 6.45 instead of the singlet at δ 6.64. Hence, one would expect the magnitude of the NOE to be larger between the aromatic protons and one of the doublets representing nonequivalent protons than to the singlet due to the equivalent methylenes. The absence of cross-peaks due to this interaction in the 2D NOESY spectrum is attributable to two effects:[31] (1) this effect is more difficult to observe for the nonequivalent protons due to the lower relative intensity of each doublet as compared to the singlet and (2) there is a very large NOE between the two doublets due to nonequivalent protons and this reduces the intensities of the expected cross-peaks.

Table I
Proton Spin–Lattice Relaxation Time (T_1) Measurements of Homopolyesters

Homopolyester	Ring systems				
					
II	1.21sec 1.26	0.26sec 0.29	1.36sec	–	–
III	1.07	–	–	–	–
IV	1.02	0.33	–	0.70	0.58^a 0.60^e

Due to the poor solubility of the homopolyester II, in trifluoroacetic acid the formation of an organized mesophase could not be detected. The polyester II is completely insoluble in solvents such as dioxane, *o*-chlorophenol, *m*-cresol, etc. However, it is surprising to observe a narrow and sharp resonance for the double doublets appearing at δ 6.55 and 6.45 and the singlet at δ 6.64 (Figure 2), for the conformational isomers, even if the conformers are in slow exchange on the NMR time scale. At higher temperature, the polyester II in trifluoroacetic acid undergoes hydrolysis, and so further study could not be carried out. The ester group can conjugate with the phenylene rings, thus enhancing the anisotropic polarizability.[32] This serves to increase the molecular length and maintains rigidity. Hsu et al.[32] have shown that the ester group is also effective in maintaining rigidity by confering double bond character on the C–O linkage. Exposure of homopolyester II to deuteriotrifluoroacetic acid in an NMR tube for 2 weeks results in its hydrolysis. The hydrolysis product of homopolyester II showed an additional acid peak in the NMR spectrum, and the olefinic proton resonance appearing as a double doublet also disappeared.

The methylene protons of the homopolyester II absorb in the region δ 1.87–2.33. All the protons are deshielded due to the use of a polar solvent (deuteriotrifluoroacetic acid). The proton NMR spectrum of II in deuteriochloroform is similar to the proton NMR in deuteriotrifluoroacetic acid, but all the protons absorb at relatively higher field.

The results of proton spin–lattice relaxation time (T_1) measurement are presented in Table I. The proton T_1 values for the olefinic protons appearing as a singlet and as a double doublet are very similar (1.21–1.26 s), whereas the aromatic protons relaxes slower (1.36 s) than the olefinic protons.

Comparison of the proton NMR of III, which is devoid of any aromatic groups, with II indicates a distinct dif-

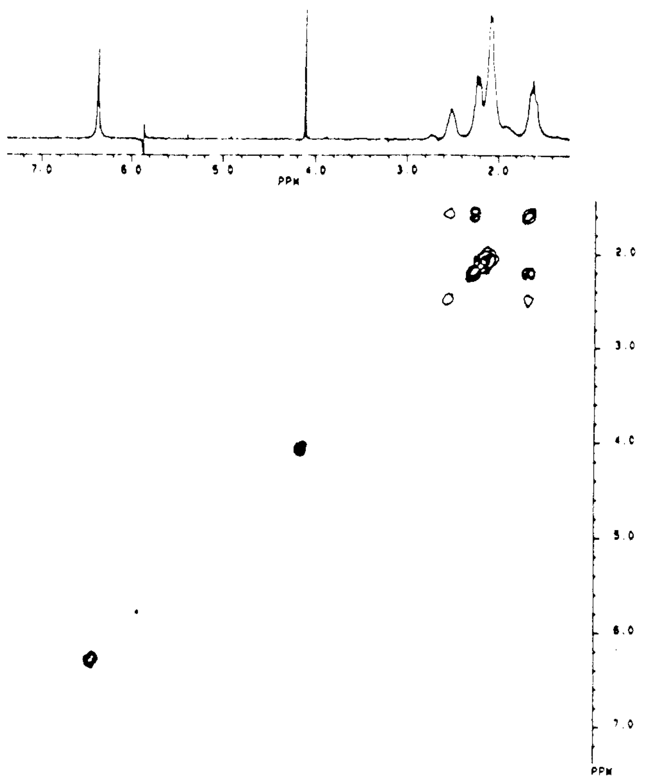


Figure 3. 250-MHz ^{1}H NMR 2D-COSY spectrum of poly[oxy-(1,4-bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxycarbonyl(*trans*-1,4-cyclohexyl)carbonyl] (IV), recorded at 25 °C in CF_3COOD.

ference in the olefinic region. The olefinic protons appear as a singlet at δ 6.33, as expected, with complete absence of the double-doublet peak observed in the case of homopolyester II. The methylene protons of the saturated and unsaturated bicyclic ring appear as a broad singlet δ 2.00.

Unlike the homopolyester II, the homopolyester IV, containing the bicyclo[2.2.2]oct-2-ene system and *trans*-1,4-cyclohexane moieties, does not exhibit thermotropic behavior.[26]

The proton NMR spectrum of IV (Figure 3) exhibits exhibits a singlet for the olefinic proton. The methylene region (δ 1.2–2.8) indicates a complex broad signal, and to differentiate the methylene protons of the bicyclo[2.2.2]-oct-2-ene system from the cyclohexane methylene protons is rather difficult from the proton NMR spectrum. Due to the broadness of the peaks, a single-frequency proton decoupling study does not result in a clear understanding of the coupling involved. Hence, we opted for a homonuclear two-dimensional shift correlations study (COSY) (Figure 3), which resulted in the complete assignment of methylene and methine protons of polyester IV.

The methylene protons of the bicyclic ring, with no indication of a corresponding cross-peak, appear at δ 2.08 (Figure 3). The methine protons appearing at δ 2.51 are strongly coupled to the axial protons of the cyclohexane ring, appearing at δ 1.60 (see Figure 3 for cross-peaks), which in turn is coupled to the equatorial methylene protons appearing at δ 2.23. The difference in chemical shift between the axial and equatorial protons is found to be δ 0.63. In the case of proton NMR of 100% *trans*-hexahydroterephthalic acid a difference in axial and equational proton chemical shifts has been reported to be 0.59 ppm.[33]

From the proton spin–lattice relaxation studies of homopolyester IV (Table I), it can be observed that the methylene protons of bicyclo[2.2.2]oct-2-ene relax twice as fast as the methylene protons of cyclohexane. The olefinic protons relax much slower compared to the methylene protons.

Conclusion. Our results obtained from proton NMR, two-dimensional homonuclear shift correlation (COSY), dipolar correlated two-dimensional NMR (NOESY), and proton spin–lattice relaxation studies resulted in the structure analysis of the homopolyesters II, III, and IV. Further work is in progress in the NMR study of liquid-crystalline copolyesters having a flexible spacer and bicyclo[2.2.2]oct-2-ene as a mesogenic unit.

Acknowledgment. This research was supported in part by Office of Naval Research (Grant No. 0014-84-K-0404) and the NIH-RCMI (Grant G12 RR03062). We thank Dr. Y. H. Mariam for helpful discussions.

Registry No. II (copolymer), 113779-34-3; II (SRU), 113792-91-9; III (copolymer), 113779-35-4; III (SRU), 113792-92-0; IV (copolymer), 113779-36-5; IV (SRU), 113792-93-1.

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Determination of the Chain Conformation in Fast-Spun Polypropylene Fibers by Small-Angle Neutron Scattering[†]

In the melt spinning process filaments (fibers) are formed by extruding a polymer melt through a capillary and simultaneously applying an extensional force to the extrudate. The filaments are taken up by a winder with a constant take-up velocity. Along the spinning path the fluid extrudate is deformed, cooled, solidified, and transformed into a filament with a highly anisotropic supramolecular structure. For crystalline polymers such as polypropylene (PP), it is well-known[1-3] that for sufficiently high take-up velocities, the solidification along the spinning line is due to a stress-induced crystallization process. For fast spun fibers Vassilatos et al.[4] suggested that the crystallization takes place in the highly oriented, affinely deformed melt. One of the interesting questions with respect to such an orientation-induced crystallization process is the way a single molecular chain is incorporated into the semicrystalline structure of the fiber.

Small-angle neutron scattering (SANS) on deuterium labeled molecules, dissolved in a nondeuterated matrix, is the ideal tool to investigate this problem. Scattering experiments yield the scattering form factor of a single labeled molecule and, therefore, its morphology. This report gives first results of such scattering experiments on fast-spun fibers, spun from a blend of perdeuteriated PP and nondeuteriated PP, for two take-up velocities.

As Ziabicki[3-5] has shown, the stress σ_s at the solidification point is strongly dependent on the take-up velocity v_a. In the velocity range considered in our experiments, the relation $\sigma_s = \text{const} \times v_a^2$ is valid to a good approximation. Consequently, the take-up velocity is expected to influence strongly the morphology; as will be shown, this cannot be concluded from our measurements. For comparison, we have also investigated fibers spun, without take-up, and mechanically cold-drawn by a necking process.

Experiments. As nondeuteriated matrix material, a degraded isotactic homo-PP has been used with a molecular mass M_w = 210 000 g/mol and M_w/M_n = 2. The perdeuteriated material was prepared in a 1000-cm^3 autoclave by using a gas-phase polymerization technique. A normal Ziegler catalyst was used. Experience shows that with the procedure used, a value M_w/M_n of about 7 is obtained. In view of the great amount of PP-*d* sample material required (1 kg for each deuterium concentration studied!) a fractionation has not been performed. D6-Propen was bought from IC-Chemicals. The molecular mass was M_η = 130 000 g/mol as determined by viscosimetry. The deuteriated and nondeuteriated PP were mixed mechanically. In order to achieve a homogeneous distribution of the components the mixture was extruded twice at 200 ± 5 °C. Fibers with two concentrations of the perdeuteriated material, c_D = 0.5% and 1.9%, were spun at take-up velocities v_a = 2500 and 4000 m/min. For each velocity, a nondeuteriated fiber was spun as a reference. In addition, samples with c_D = 0%, 0.5%, and 1.9% were extruded without applying an extensional force and afterward slowly cold-drawn by a necking process; the macroscopic draw ratio was $\lambda = 4$.

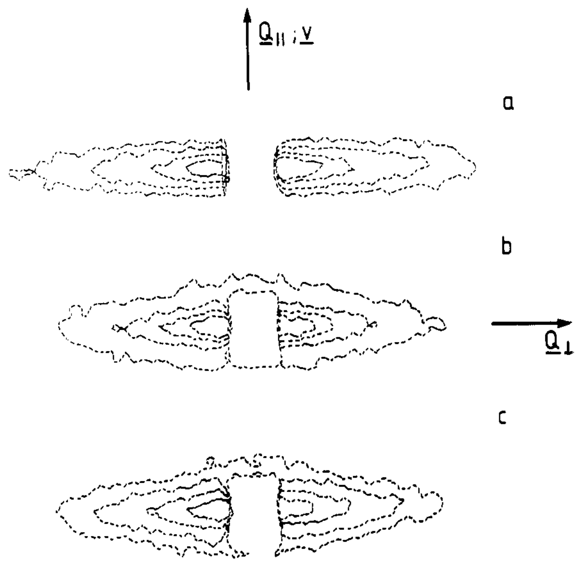

Figure 1. Contour plots for neutron small-angle scattering on polypropylene fibers (c_D = 1.9%): (a) cold-drawn sample; (b) fast-spun sample with take-up velocity v_a = 2500 m/min; (c) take-up velocity v_a = 4000 m/min. The fiber axis is parallel to the vertical axis in the diagrams.

The small-angle scattering experiments were carried out by using the diffractometer D 17 at the high-flux reactor in the ILL Grenoble. The wavelength was λ = 1.2 nm and the range of scattering vectors 0.09 nm^{-1} $\leq Q \leq$ 0.6 nm^{-1}, with $Q = (4\pi/\lambda)\sin\theta/2$ (θ = scattering angle). Figure 1 shows typical contour plots for the sample, cold-drawn by a necking process, and for the two fast-spun samples. The pictures demonstrate the elongation of the labeled molecules in the stretching direction: The meridional width of the intensity profile (parallel to the fiber axis) is so narrow that it disappears in the primary beam spot. The longitudinal extension of the contours is caused by the strongly reduced lateral dimension of the molecules.

For the further evaluation we used the radially averaged equatorial data; they were integrated over sectors with a half-width of 22.5°. The incoherent scattering background for all samples was individually determined by using the meridional intensities at large Q, where the coherent scattering has practically decayed to zero. After subtraction of the incoherent background, the coherent intensities were normalized by the measured sample transmission. In order to correct for the different sample volumes, these scattering intensities were finally normalized by means of the measured incoherent scattering of the samples. This procedure introduces uncertainties as high as 20% caused by irregularities in the packing density of the sample coils.

Parasitic coherent scattering at small Q was corrected for by subtracting the coherent scattering of the corresponding unlabeled samples. In each case the coherent scattering from the unlabeled samples was less than 20% of the scattering from the labeled samples. Under these conditions, the above-mentioned uncertainties with respect to the scattering volume should not lead to significant errors as concerns the correction for parasitic coherent scattering. A comparison of the corrected data for c_D =

[†] Dedicated to Professor Dr. Helmut Dörfel on the occasion of his 60th birthday.

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