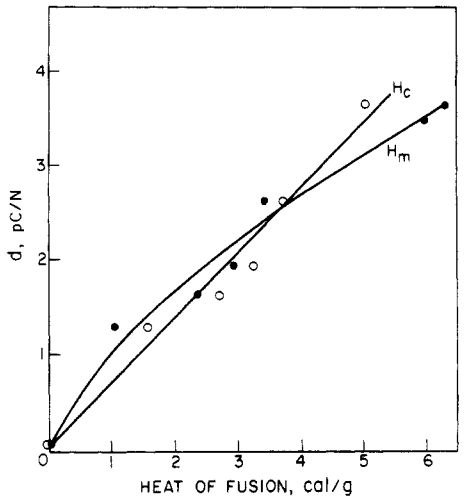

Figure 5. Plots of piezoelectric strain coefficient d as a function of heat of fusion either at the melting, H_m (●), or at the Curie transition, H_c (○).

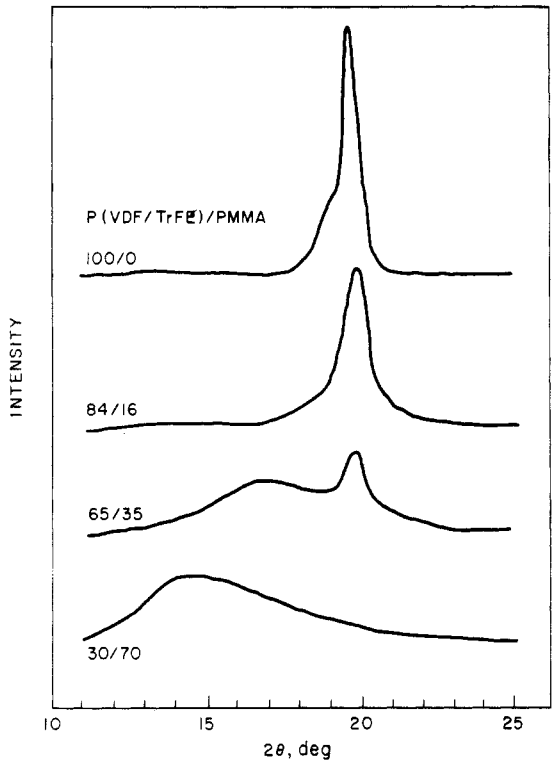

Figure 6. X-ray scans of P(VDF/TrFE)/PMMA mixtures with various compositions.

tivity is not proportional to the total crystalline content of the mixture. On the other hand, a linear relationship is observed (Figure 5) when we plot the d value as a function of H_c, the area under the curie transition peak in Figure 1. This result strongly suggests that the crystalline region contains both ferroelectric and paraelectric phases, but only the ferroelectric fraction contributes to polarization.

The above conclusion is also supported by the X-ray data (Figure 6), which show a peak corresponding to the ferroelectric phase at 19.7 2θ and a shoulder corresponding to the paraelectric phase at 18.8 2θ for the copolymer sample. As PMMA is added to the copolymer, both the ferroelectric and paraelectric peak diminished, but the suppressing effect is much stronger in the paraelectric than in the ferroelectric phase. (The peak near 16.5 2θ for the 65/35 mixture corresponds to the amorphous halo, which is seen to shift to a lower angle as ϕ_w is increased, e.g., the bottom curve of the figure.) This selective suppression is also evident in Figure 5, where the d–H_m plot crosses over the d–H_c plot as the heat of fusion decreases, i.e., as the PMMA fraction in the mixture increases.

In summary, our study showed that PMMA is compatible with P(VDF/TrFE) above the melting point of the copolymer; however, while PMMA depressed both the T_m and the rate of crystallization of the copolymer, it did not affect the Curie point. We also found that the piezoelectric activity of the copolymer did not depend on the total degree of crystallinity but only on the ferroelectric fraction of crystals.

Registry No. (VDF)·(TrFE) (copolymer), 28960-88-5; PMMA, 9011-14-7.

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Homo- and Heteronuclear Two-Dimensional Correlated Nuclear Magnetic Resonance Spectra of Cellulose

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A substantial recent effort has been devoted to the investigation of cellulose solutions by NMR spectroscopy.[1-4] Difficulties arise in the application of the technique because of (i) the problem of dissolving cellulose, (ii) the high viscosity of the polymer solutions and hence the lack of spectral resolution, and (iii) the inadequacy of the classical assignment techniques.

To overcome these difficulties, spectral assignment can be made easier by means of two-dimensional NMR. The dissolution of cellulose is a difficult operation, owing to the existence of strong intra- and intermolecular hydrogen bonds of this highly hydroxylated polymer in its solid state. Among the new solvent systems for cellulose, *N*,*N*-dimethylacetamide (DMA) containing 5–8% lithium chloride is an aprotic solvent, which, in turn, allows observation by proton NMR spectroscopy of individual labile hydroxyl resonance signals.[5] These signals can then be used as a source of new information concerning the nature and the conformation of the polymer in solution.

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Experimental Section

Cellulose Solutions. Cellulose was dissolved according to a published method[3] by activating in water and exchanging twice with DMA at 60 °C. For NMR study, the last traces of water were eliminated by freeze-drying the activated cellulose. The freeze-dried sample was then dissolved in a fresh 8% LiCl solution in DMA-d_9 by stirring 30 min at 60 °C.

^{13}C-enriched cellulose was extracted from ^{13}C-enriched poplar wood grown under air containing $^{13}CO_2$ enriched to 10%.[6] Cellulose was extracted from ball-milled wood by a classical delignification method.[7] It was uniformly labeled at an approximately 5% level at each position.

NMR Spectroscopy. NMR spectra were obtained on a Bruker AM400 spectrometer using the standard DISNMRP software.

A 2% solution of cellulose was used to obtain the COSY homonuclear ^{1}H spectrum with a $SW_1 = SW_2 = 2000$-Hz sweep width. The pulse sequence used was D_1–90°$_x$–D_0–45°$_x$–FID.

The delays were $D_1 = 2$ s for relaxation and D_0 variable from 5 μs in 256 increments of 500 μs. The resulting data matrix of 256 × 2K points was multiplied by a "pseudo-echo" function and zero-filled in each dimension to build up a 1K × 2K symmetrized matrix with a digital resolution of 1.95 Hz/point in both dimensions. Quadrature detection was used. The 90° observe pulse was 5 μs, and the acquisition time was 515 ms.

The ^{13}C–^{1}H correlation experiment was conducted on a 2% solution of ^{13}C-enriched cellulose at a frequency of 100 MHz. The chemical shift range shown here (enlargement) is $\delta_C = 56.6$–109.6 ppm (spectral width = ±11 kHz in the F_2 dimension for acquisition) and $\delta_H = 2.6$–4.8 ppm (spectral width = ±440 Hz in the F_1 dimension for acquisition). The pulse sequences used were as follows:

^{1}H: D_0–90°$_x$–D_0–D_0–D_3–90°$_x$–D_4–BB

^{13}C: D_1–(90x 180y 90x)–90°$_x$–FID
composite pulse

The delays were $D_1 = 1.5$ s (for relaxation), $D_3 = {}^1/_2J_{CH} = 4$ ms, $D_4 = {}^1/_4J_{CH} = 2$ ms, and D_0 variable from 5 μs in 64 increments of 454 μs. The resulting data matrix (4K × 64) was multiplied by a "pseudo-echo" function and zero-filled in the F_1 dimension to build up a 4K × 512 matrix with an apparent digital resolution of 2.1 Hz/point in the F_1 dimension and 5.4 Hz/point in the F_2 dimension. The 90° pulse widths were 15 μs for ^{13}C (observation pulse) and 25 μs for ^{1}H (decoupler pulse).

The Bruker standard DISNMRP software version for the Aspect 3000 was used.

Homonuclear ^{1}H 2D Correlated Spectrum of Cellulose (COSY). COSY[8] gives correlation maps showing the connectivity of spin–spin coupled protons. In the case of cellulose, each repeating D-glucopyranosyl unit is independent of the two adjacent ones. COSY spectra will thus give information on the connectivity of protons with scalar coupling along the C–C chemical bonds, ranging from C-1 to C-6, within the D-glucopyranosyl ring.

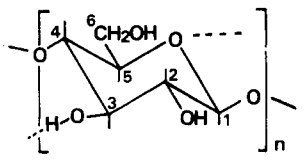

Figure 1 shows the 400-MHz COSY spectrum of cellulose at 70 °C dissolved in N,N-dimethylacetamide-d_9–LiCl solvent. The F_2 axis represents the 1D ^{1}H NMR spectrum of cellulose. Starting from the H-1 anomeric signal at $\delta = 4.6$—being the only low-field signal insensitive to temperature—a unique transverse connectivity with H-2 at $\delta = 3.05$ is then possible. Hence H-2 is correlated both with H-3 and with OH-2. From H-3 on, the same mechanism reveals connectivities with H-4, H-5, and H-6′. Because of the high peak resonance of water, connectivity between the two methylene H-6 protons cannot be observed.

^{1}H/^{1}H connectivity through the H–CO–H moieties is observed only for the OH-2 hydroxyl group. On a slice in the *F2* direction, it is possible to observe the OH-6/H-6 connectivity, which is too weak to be seen at the chosen level for the contour plot. Figure

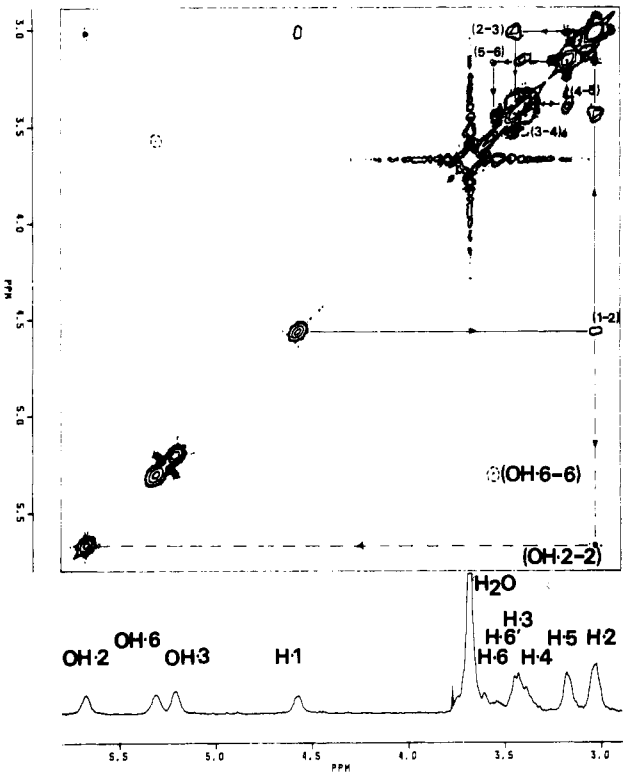

Figure 1. 400-MHz 2D homonuclear ^{1}H correlated NMR spectrum (COSY-45) of cellulose in N,N-dimethylacetamide-d_9–LiCl solution at 70 °C (contour plot). On the F_2 axis (horizontal) is given the 1D proton NMR spectrum of cellulose in the same solvent, showing the specific signals of each hydroxyl group. The connectivities between the protons are indicated.

1 shows with a dashed line the OH-6/H-6 connectivity. It has not been possible to observe the same connectivity for OH-3, probably owing to the small coupling constant, $^3J_{H\text{-}CO\text{-}H}$ being less than 1 Hz (as compared to 4 Hz found for the other hydroxyl groups), a value that has been found for methyl-β-D-cellobioside, the cellulose dimer. As already observed,[3] the OH-3 hydroxyl signals for cellulose and cellulose oligomers present a specific behavior: (i) a low δ value, (ii) a low $^3J_{H\text{-}CO\text{-}H}$ value, and (iii) a small temperature dependence. This has been related to the existence of an intramolecular hydrogen bond between this hydroxyl proton and the heterocyclic oxygen atom of the neighboring unit in the case of cellulose dissolved in this aprotic solvent.

Heteronuclear ^{13}C–^{1}H 2D Correlated NMR Spectrum of Cellulose. ^{13}C NMR spectroscopy can yield interesting information in cellulose chemistry, especially concerning the degree and positions of substitution of cellulose derivatives.[9-11] Despite the simplicity of the ^{13}C NMR spectra, important problems are always encountered with regard to signal assignment.

2D ^{13}C–^{1}H correlated NMR spectroscopy[12-14] is particularly useful for signal assignment as a single experiment allows the assignment of one type of nucleus (^{13}C) starting from the known assignments of the others (^{1}H) or conversely. Only scalar-coupled correlated nuclei ($^1J_{C\text{-}H}$) are observed in 2D heterocorrelated spectra.

There is an inherent problem in ^{13}C NMR spectroscopy with respect to signal sensitivity for macromolecular solutions of low concentration. Since a 2 wt % cellulose solution in DMA–LiCl solvent gives the maximum viscosity allowed for NMR, such a solution would not permit the observation of a 2D heteronuclear ^{13}C–^{1}H spectrum, as a long time accumulation is needed. To overcome this problem and increase sensitivity, we used ^{13}C-enriched cellulose sample, uniformly labeled (5%) on each carbon atom. It was obtained by extraction from a wood sample grown in an enriched $^{13}CO_2$ atmosphere.[6]

Figure 2 shows the contour plot of the 2D heteronuclear ^{13}C–^{1}H correlated spectrum of ^{13}C-enriched cellulose in a DMA–LiCl solution. On the F_2 axis (horizontal) we can see the projection of the ^{13}C spectrum correlated with proton nuclei. The F_1 vertical

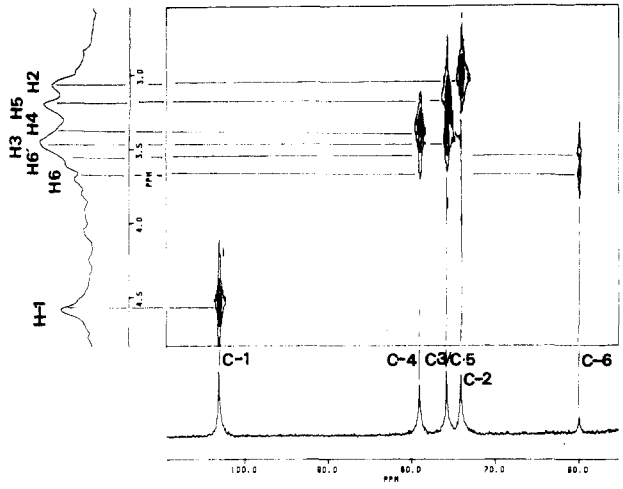

Figure 2. 2D heteronuclear ^1H–^{13}C correlated NMR spectrum of ^{13}C-enriched cellulose in *N,N*-dimethylacetamide-d_9–LiCl solution at 70 °C (contour plot). On the F_1 axis (vertical) is given the projection of the proton spectrum correlated to the carbon spectrum. On the F_2 axis (horizontal) is given the projection of the carbon spectrum correlated to the proton spectrum.

axis shows the projection of the proton spectrum correlated with carbon nuclei.

This 2D NMR spectrum reveals in one experiment all the correlations between ^{13}C and scalar-coupled ^1H nuclei. With the ^{13}C spectrum as a basis, the two well-known C-1 and C-4 low-field resonances—the two carbon atoms being involved in the $\beta(1\rightarrow4)$ interunit bond—confirmed the position of the H-1 and H-4 signals. The C-6 resonance, the only methylene carbon atom of the D-glucopyranosyl unit, yields two contour signals and thus allows the assignment of the two H-6 signals which were not visible in the COSY spectrum. Then from the known resonance of the COSY spectrum the C-2, C-3, and C-5 resonances can be assigned via their correlations with the corresponding protons.

It is shown here that cellulose, one of the most difficult natural polymers to dissolve, can be studied by classical 2D correlated NMR techniques. The latter yield important results concerning assignment which are not possible by other NMR techniques, owing to the high solution viscosity and consequently the lack of resolution of the spectra.

2D heteronuclear ^{13}C–^1H NMR is a time-consuming technique for macromolecular solutions and therefore the use of uniformly ^{13}C-enriched samples is justified.

The total assignment of both ^{13}C and ^1H spectra for cellulose makes it possible to use NMR to study macromolecular conformations in solution, as well as that of the existing hydrogen bonds, or to study the dissolution mechanism of natural hydroxylated polymers. Work is in progress for more complicated polysaccharides, for which the constitutive blocks are as follows: (i) two D-glucopyranosyl units (i.e., nigeran),[15,16] (ii) three D-glucopyranosyl units (i.e., scleroglucan),[17] and (iii) five sugar units (i.e., xanthan).[18]

Registry No. Cellulose, 9004-34-6.

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ESR Study of Polystyrene Chain Scission Induced by 2,6-Dichloronitrosobenzene: Observation of Chiral Nitroxide Radical Pair

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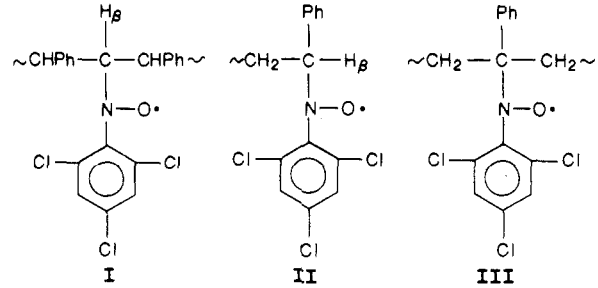
Introduction

Recently, Watanabe et al. observed that polymer main-chain scission is induced by chloro-substituted nitroso compounds.[1-3] These compounds interact with the macromolecules, resulting in hydrogen abstraction.[4] Watanabe et al. studied in detail the main-chain scission induced by 2,4,6-trichloronitrosobenzene (TCNB) in a benzene solution of polystyrene (PSt).[1,2] The main-chain scission was established from the decrease of molecular weight, and the polymer radicals formed were identified from ESR spectra. The experimental ESR spectra were assumed to be a superposition of signals originating from the radicals



in accordance with a theoretical reaction mechanism (see Scheme I in ref 1). The spectroscopic parameters of these radicals were listed in Table I in ref 1. In the case of main-chain scission, however, besides radical II the presence of a radical with two β-hydrogens can also be expected. The aim of the present work is to demonstrate the formation of radical IV in the process of main-chain scission of PSt induced by chloro-substituted nitroso compounds.

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