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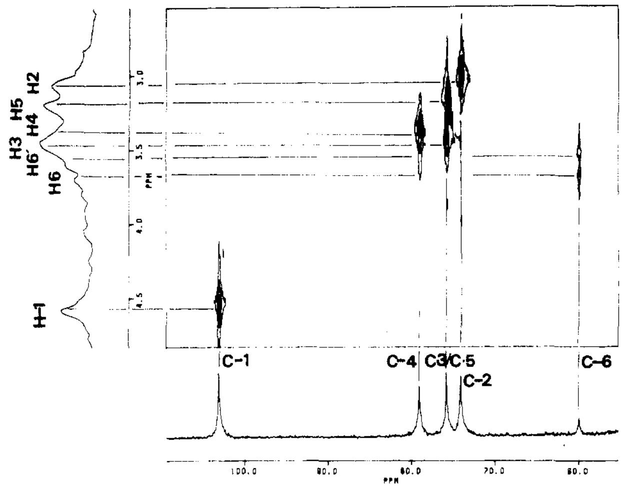

Figure 2. 2D heteronuclear ^{1}H–^{13}C correlated NMR spectrum of ^{13}C-enriched cellulose in *N,N*-dimethylacetamide-d_9–LiCl solution at 70 °C (contour plot). On the F_1 axis (vertical) is given the projection of the proton spectrum correlated to the carbon spectrum. On the F_2 axis (horizontal)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

References and Notes

(1) Gagnaire, D.; Mancier, D.; Vincendon, M. *J. Polym. Sci.* **1980**, *18*, 13.
(2) Bain, A. D.; Eaton, D. R.; Hux, R. A.; Tong, J. T. K. *Carbohydr. Res.* **1980**, *84*, 1.
(3) Gagnaire, D.; Saint-Germain, J.; Vincendon, M. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1983**, *No. 37*, 261.
(4) El-Kafrawy, A. *J. Appl. Polym. Sci.* **1983**, *27*, 2435.
(5) Saint-Germain, J.; Vincendon, M. *Org. Magn. Reson.* **1983**, *21*, 371.
(6) Lapierre, C.; Gaudillere, J. P.; Monties, B.; Guittet, E.; Rolando, C.; Lallemand, J. Y. *Holzforschung* **1983**, *37*, 217.
(7) Whistler, R. L. *Methods in Carbohydrate Chemistry*: Academic: New York, 1963: Vol. III.
(8) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
(9) Miyamoto, T.; Sato, Y.; Shibata, T.; Imagaki, H. *J. Polym. Sci.* **1984**, *22*, 2363.
(10) Kimura, K.; Shigemura, T.; Kubo, M.; Maru, Y. *Makromol. Chem.* **1985**, *186*, 61.
(11) Miyamoto, T.; Sato, Y.; Shibata, M.; Tanahashi, M.; Inagaki, H. *J. Polym. Sci.* **1985**, *23*, 1373.
(12) Maudsley, A. A.; Muller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463.
(13) Bodenhausen, G.; Freeman, R. *J. Magn. Reson.* **1977**, *28*, 471.
(14) Freeman, R.; Morris, G. *J. Chem. Soc., Chem. Commun.* **1978**, 684.
(15) Bobbit, T. F.; Nordin, J. H.; Gagnaire, D.; Vincendon, M. *Carbohydr. Res.* **1980**, *81*, 177.
(16) Bock, K.; Gagnaire, D.; Vignon, M.; Vincendon, M. *Carbohydr. Polym.* **1983**, *3*, 13.
(17) Rinaudo, M.; Vincendon, M. *Carbohydr. Polym.* **1982**, *2*, 135.
(18) Rinaudo, M.; Milas, M.; Lambert, F.; Vincendon, M. *Macromolecules* **1983**, *16*, 816.

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

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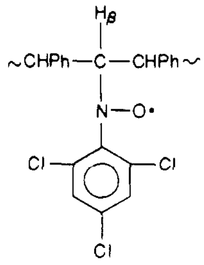
Introduction

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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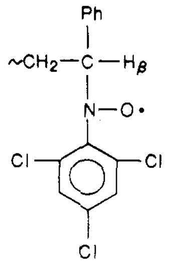
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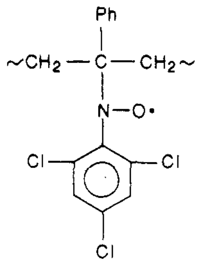
III

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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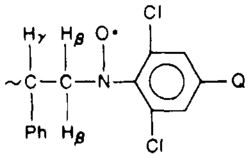


IV
TCNB, Q=Cl
DCNB, Q=H

Experimental Section

A PSt calibration standard (EGA product, $\bar{M}_n$ = 100 000, $\bar{M}_w/\bar{M}_n$ = 1.2) and 2,6-dichloronitrosobenzene (DCNB) were used for the experiments. DCNB (10^{-2} mol/L) was added to a 10% (by weight) benzene solution of PSt. Air was carefully removed from the samples by four freeze–thaw cycles in vacuo, and the tubes were sealed. The measurements were performed on a JEOL JES-FE 3X ESR spectrometer with a 100-kHz modulation frequency; the samples were tempered in the cavity of the spectrometer with ±1 °C accuracy. The ESR spectra were evaluated by computer simulation, and the theoretical spectra were obtained by a PDP 11 compatible Hungarian-made EMU 11 minicomputer (KFKI).

Results

Upon mild heating of the benzene solution of PSt and DCNB a signal consisting of nine hyperfine (hf) lines with superhyperfine (shf) structure was detected by ESR spectroscopy (Figure 1a). There are two ways to interpret this spectrum:

(i) The spectrum can be considered as a superposition of six-line and three-line (without additional shf structure) patterns, which can be assigned to radical I and/or II and radical III. The β-hydrogen coupling of the six-line signal is extremely large (about 1.8 mT). To our knowledge this is the case only when the radical is trapped by sterically hindered 2,4,6-tri-*tert*-butylnitrosobenzene and, because of steric reasons the β-hydrogen atom is twisted completely out of the CNO plane.[5] The large coupling should give a negative temperature coefficient, because with the increase of temperature the more effective inner rotation around the C–N bond results in a change of the average position of the β-hydrogen closer to the CNO plane.

(ii) The spectrum can be assumed to be a nine-line signal with alternating line width, which is assigned to radical IV. In this macro nitroxide radical the γ-carbon atom is a chiral center, because it is bonded to four sterically significantly different groups. Therefore the system has no mirror plane symmetry and the two β-hydrogens are not equivalent magnetically, which causes broadening of the central lines of the two β-hydrogen triplets (distorting the 1:2:1 intensity ratio for two equivalent β-hydrogens).[6] The hf coupling of the β-hydrogens is about 0.9 mT; this value can be detected in most of the cases when the radical is trapped by a not too bulky nitroso molecule. For this type of nitroxide radicals the β-hydrogen couplings usually have a weak temperature dependence.[7]

In order to decide between the two interpretations we investigated the temperature variations of the hf couplings of the nitroxide radicals formed. We observed that the hf coupling of the β-hydrogens increases slightly with temperature, while the widths of all nine hf lines decrease and the resolution of the shf structure is enhanced. The ESR spectra are shown in Figure 1, and the hf couplings are given in Figure 2. The temperature gradient of the β-hydrogen coupling (3.3×10^{-4} mT/°C) is twice that of the nitrogen coupling (1.6×10^{-4} mT/°C), which indicates that the gradient of the β-hydrogen coupling is not only a consequence of the increasing spin density on the nitrogen atom. On the basis of our results we can state that the ESR spectra detected can be assigned to radical IV, even though for the interpretation of shf structure an additional assumption should be made.

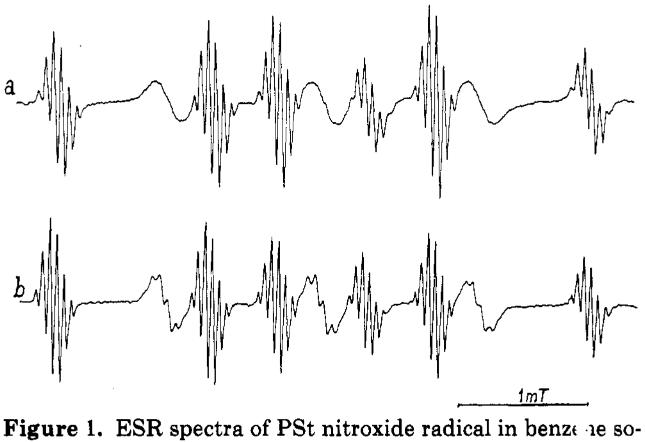


Figure 1. ESR spectra of PSt nitroxide radical in benzene solution at two different temperatures: (a) 26 °C; (b) 80 °C.

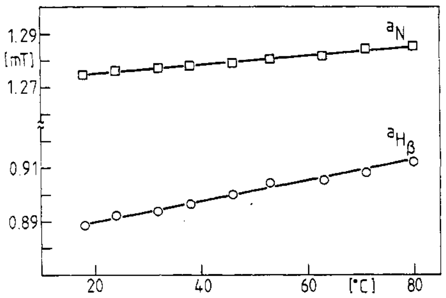


Figure 2. Temperature dependence of nitrogen and β-hydrogen hf couplings for PSt nitroxide radical.

A shf structure consisting of a symmetric 1:5:10:10:5:1 sextet corresponds to five equivalent protons. Since radical IV contains only one γ-hydrogen atom in addition to the three ring protons, the actual shf pattern should be a superposition of two radicals with similar structure. This is also supported by the asymmetries within the shf line groups. As radical IV has a chiral center, there are two stereoisomers and their ground conformations have different geometries (Figure 3). In one case the γ-hydrogen coupling is nearly zero, while in the other case the coupling of the γ-hydrogen is twice as large as the splitting measured on the equivalent ring protons. (For diortho-substituted rings, the couplings of the two meta protons and the para proton are nearly equal.[7]) In the first case the shf structure is given only by the ring protons, which yield a group of lines with a 1:3:3:1 intensity ratio, while in the second case the shf structure also depends on the γ-hydrogen; thus a 1:3:4:4:3:1 pattern is obtained. For both cases it was supposed that the corresponding couplings differ only slightly ($a_{H_\beta}' = a_{H_\beta}''$ and $a_N' = a_N''$) and the g values are equal; thus the sum of weighted intensities of shf structures with coinciding centers is

$$\begin{array}{r} 1:3:4:4:3:1 \\ +\quad 2:6:6:2 \\ \hline 1:5:10:10:5:1 \end{array}$$

Here the concentrations of the two chiral centers are taken to be equal. Our assumption was verified by computer simulation, where even the small asymmetries of shf patterns have been reconstructed (Figure 4).

An ESR spectroscopic curiosity is that two different ESR spectra can be assigned to the two ground conformations of radical IV with the chiral center. To our

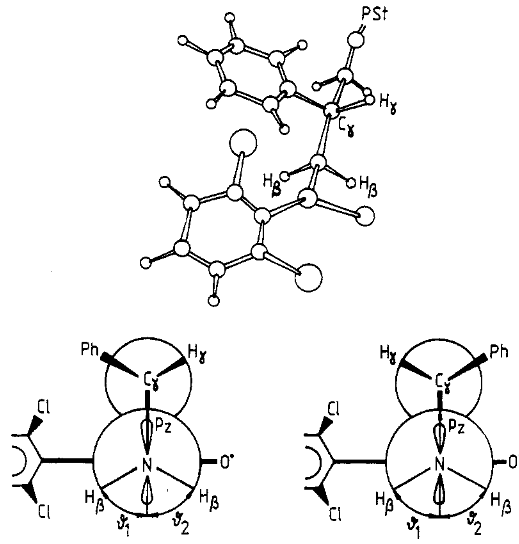


Figure 3. Molecular structure of the chiral PSt nitroxide radical. The two diagrams demonstrate the hypothetical stereoisomers of the two ground conformations.

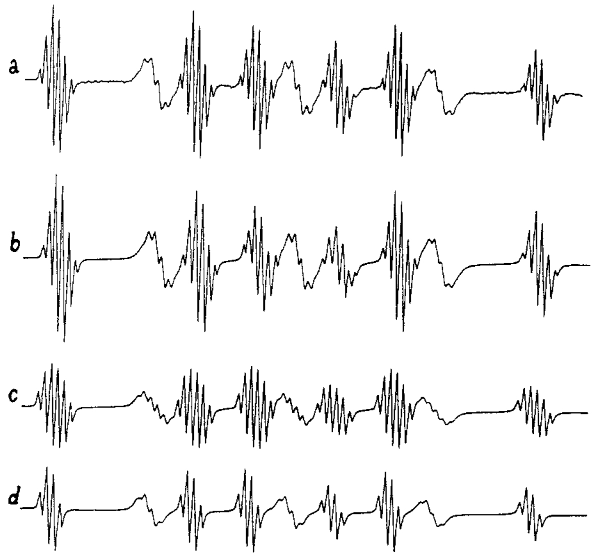


Figure 4. Experimental spectrum of the PSt nitroxide chiral radical pair at 80 °C (a) and its simulated version (b). The theoretical spectrum (b) consists of two components (c and d) which are superposed with equal weights. The best fitting spectrum parameters are as follows: (c) $g = 2.0066$, $a_N = 1.290$ mT, $a_{H_\beta} = 0.925$ mT, $a_{H_{m,p}} = 0.058$ mT, $a_{H_\gamma} = 0.120$ mT; (d) $g = 2.0066$, $a_N = 1.300$ mT, $a_{H_\beta} = 0.915$ mT, $a_{H_{m,p}} = 0.060$ mT, $a_{H_\gamma} = 0.005$ mT.

knowledge, no such radicals have been described in the literature.

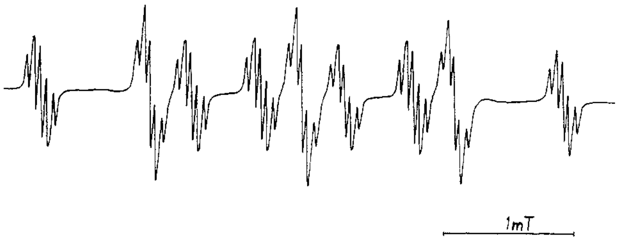
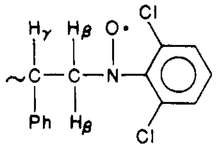


Figure 5. ESR spectrum of styrene nitroxide radical in benzene solution at 20 °C. Spectral parameters: $g = 2.0067$; $a_N = 1.253$ mT, $a_{H_\beta} = 0.904$ mT; $a_{H_{m,p}} \simeq a_{H_\gamma} = 0.060$ mT.

Indirect evidence was also obtained for the identification of the PSt radical adduct with structure IV. Reaction of styrene with chloro-substituted nitrosobenzene yields a nitroxide radical containing two β-hydrogens[8]



V

The corresponding ESR spectrum consists of nine hf lines with slight line-width alternation. In the case of DCNB each hf line splits into a symmetric five-line shf structure with an approximate 1:4:6:4:1 intensity ratio, which can be assigned to three ring protons and to the γ-hydrogen atom having nearly equal coupling constants (Figure 5). It is noteworthy that the coupling of the γ-hydrogen of radical V is equal to the mean value of the γ-hydrogen couplings assumed for the two-ground-conformation model of the chiral centers of radical IV.

The identification of radical IV in the system investigated is a completion and support of the findings of Watanabe et al.[1] about the degradation of PSt.

Acknowledgment. We express our thanks to Drs. L. Jõkay and M. Gyor for their technical cooperation and discussions.

Registry No. PSt, 9003-53-6; DCNB, 601-88-7.

References and Notes

(1) Watanabe, O.; Tabata, M.; Sohma, J. *Macromolecules* **1984**, *17*, 1139.
(2) Watanabe, O.; Tabata, M.; Sohma, J.; Lund, A. *Polym. Degrad. Stab.* **1984**, *7*, 13.
(3) Tabata, M.; Watanabe, O.; Sohma, J. *Polym. Degrad. Stab.* **1981**, *3*, 443.
(4) Rockenbauer, A.; Sümegi, L.; Mőger, G.; Simon, P.; Azori, M.; Gyor, M. *Tetrahedron Lett.* **1978**, *50*, 5057.
(5) Rockenbauer, A.; Gyor, M.; Jõkay, L.; Tüdos, F. *Adv. Mol. Relax. Int. Proc.* **1979**, *15*, 311.
(6) Gilbert, B. C.; Trenwith, M. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1834.
(7) Rockenbauer, A.; Gyor, M.; Jõkay, L.; Tüdos, F. *Adv. Mol. Relax. Int. Proc.* **1980**, *18*, 231.
(8) Mulvey, D.; Waters, W. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1059.