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Observation of Triad Stereosequences in a Polystyrene Derivative

Although the stereochemical structures of most vinyl polymers can be measured relatively easily by ^{1}H NMR and/or ^{13}C NMR spectroscopy,[1-3] this has not been the case with polystyrene or with many of its analogues.[4] The ortho-aromatic proton resonances of polystyrene contain stereosequence information but these are not adequately understood at present.[5-7] The methine proton resonance of polystyrene (e.g., Figure 1A, $\delta = 1.6$–2.3) occurs in two general areas, and recent studies on partially epimerized isotactic polystyrene samples have shown that the lower field methine proton resonance area is due to mm stereosequences.[8] Fine structure due to pentad or higher stereosequences is observed in the methine proton resonances of poly(β,β-dideuteriostyrene),[9,10] but it is not well defined and the (mr + rm)- and rr-methine proton resonances are not separated in the spectrum of this polymer, even when deuterium–proton decoupling is employed. The methylene[3,11] and quaternary aromatic carbon[3,12] resonances of polystyrene are sensitive to hexad and heptad stereosequence effects. The abundant information available in the ^{13}C NMR spectra of polystyrene cannot be extracted precisely, because the individual resonances cannot be resolved and because of the difficulty of making unequivocal assignments for the various resonances.

In contrast to polystyrene, the resonances of methine protons in poly(β,β-dideuterio-2-vinylpyridine)[13] and in poly(β,β-dideuterio-4-vinylpyridine)[14] are resolved into signals representing mm, (mr + rm), and rr triads when the polymers are dissolved in D_2SO_4 at 60 °C, although the methine proton resonance patterns of these polymers are similar to those of polystyrene when the polymers are dissolved in *o*-dichlorobenzene at 160 °C. This result suggested to us that the methine proton resonances might be resolved in the spectra of polystyrenes substituted with sufficiently electronegative groups, due either to a decreased "ring current" effect or to a change in the conformation of the polymer imposed by the electronegative groups. We therefore investigated the 300-MHz ^{1}H NMR spectra of various para-substituted polystyrenes (substituent: F, Br, Cl, NH_2, CH_3CO, CN) prepared by AIBN-initiated polymerization at 65 °C for evidence of enhanced separation of the methine proton resonances. In most cases the methine proton resonances of the polymers were very similar to those of polystyrene. However, in the case of poly(*p*-acetylstyrene) (Figure 1B), the resonances of methine protons centered in (mr + rm) and rr triads occurred about 0.3 ppm upfield from that of the corresponding resonances in polystyrene. This enabled the mm-resonance area to be completely resolved from the (mr + rm) and rr resonances, but, unfortunately, these latter resonances were shifted into the methylene proton resonance region. Cheng and Pearce[15] reported 220-MHz spectra of poly[*p*-(trifluoroacetyl)styrene] and poly[*p*-(difluoroacetyl)styrene] in nitrobenzene solution at 91 °C and a similar phenomenon is evident in these spectra.

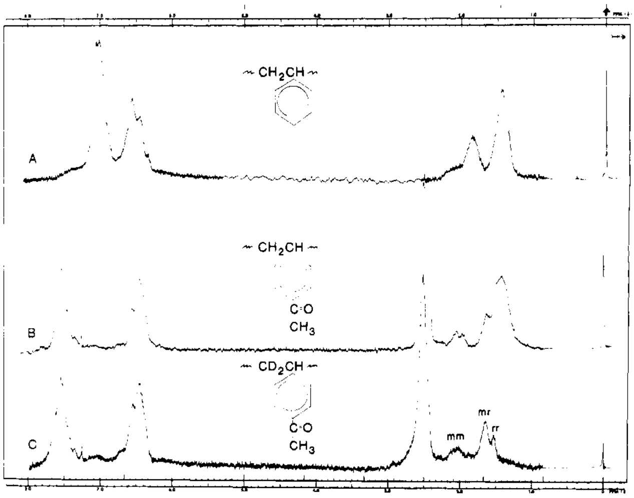

Figure 1. 300-MHz ^{1}H NMR spectra of (A) polystyrene, (B) acetylated polystyrene, and (C) acetylated poly(β,β-dideuteriostyrene) in $CDCl_3$ solution at room temperature.

To observe the (mr + rm)- and rr-methine proton resonances of poly(*p*-acetylstyrene) independently of methylene proton resonances, a sample of poly(β,β-dideuteriostyrene) prepared by AIBN-initiated polymerization at 65 °C was acetylated according to the procedure of Kenyon and Waugh.[16] The 300-MHz ^{1}H NMR spectrum of the product, poly(*p*-acetyl-β,β-dideuteriostyrene), is shown in Figure 1C. Resonances assignable to (mr + rm) and rr stereosequences are partially resolved in this spectrum and the mm-, (mr + rm)-, and rr-resonance areas are approximately in a 1:2:1 ratio, as would be expected for an essentially atactic polymer. The presence of a small amount of resonances due to residual methylene protons precludes an exact analysis from being made, but the mm area can be measured from spectrum 1B and it is 0.25 ± 0.02 of the total methine proton resonance area expected, indicating a σ value of $\sim$0.50 ± 02.

As a control experiment, to determine whether the stereochemical structure of polystyrene is altered by the acetylation conditions, a sample of partially epimerized isotactic polystyrene[11] known to have an mm content of 0.70 was acetylated according to the procedure of Kenyon and Waugh.[16] The mm content of the resulting polymer was 0.72, based on the intensity of the lowest field methine proton resonance area, indicating that the polymer configuration does not change under the acetylation conditions employed and that the resonance assignments provided in Figure 1C are probably valid. It is possible, as a reviewer has pointed out, that the mr + rm + rr pattern may not be separated clearly into triad resonances, but that it may be the result of overlapped pentad resonances. Extensive

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studies on acetylated samples of partially epimerized isotactic poly(β,β-dideuteriostyrene) will be necessary to clarify this point.

It should be noted that the acetylation reaction occurs essentially quantitatively, judged by the relative intensities of the ortho- and meta-aromatic proton (δ = 6–8) and CH_3CO proton ($\delta = \sim 2.55$) resonances of the acetylated polymers.

The ortho-proton resonance of polystyrene (δ = 6.3–6.8) consists of a three-peak pattern when observed with a 300-MHz spectrometer (Figure 1A). A similar pattern is well resolved in the spectrum of poly(2-vinylthiophene) and has been interpreted in terms of pentad stereosequences.[17] It is interesting that this pattern seems to be reversed in the case of the *p*-acetyl derivative of polystyrene. Since many of the resonances of acetylated polystyrene occur upfield from those of polystyrene, it does not seem that our results can be explained in terms of a decreased "ring current" effect. It seems reasonable to believe that dipole–induced dipole interactions between carbonyl groups and neighboring aromatic rings are responsible for the effects observed, since they can influence the energies of various conformations available to the polymer and can thereby influence NMR shieldings. It would seem worthwhile to investigate this phenomenon further.

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Synthesis and Electrical Conductivity of TCNQ Complex Salts with Polycations Containing Sulfur Atoms in the Main Chain

7,7,8,8-Tetracyanoquinodimethane (TCNQ) salts with polycations are known to be organic semiconductors.[1] Their electrical properties are dependent both on the structure of the polymer ionene component and on the composition of the complex salts. Most attention has been focused on the influence of the chemical structure of the ionene on the electrical properties of simple and complex salts of TCNQ. In this communication we describe the electrical properties of some TCNQ complex salts with ionenes containing tricoordinated sulfur atoms in the backbone.

The polymer used to synthesize the polycation was obtained by phase-transfer-catalyzed polycondensation of 1,4-dibromobutane with 1,6-hexanedithiol, according to the method described by Imai et al.[2] (eq 1). The high purity

$$Br(CH_2)_4Br + HS(CH_2)_6SH \xrightarrow[\text{aq KOH}]{\text{cat}} \underset{\text{I}}{-[(CH_2)_4S(CH_2)_6S]_n-}$$

of the polymer was proved by elemental analysis and IR spectroscopy. Anal. Calcd for $(C_{10}H_{20}S_2)_n$: C, 58.77; H, 9.86; S, 31.37. Found: C, 58.29; H, 9.82; S, 31.22. The absence of an absorption band at 2500 cm^{-1}, which is characteristic of SH stretching vibrations, indicates that the polymer is free of 1,6-hexanedithiol. The intrinsic viscosity of the product in chloroform solution at 25 °C was $[\eta] = 0.175$ dL/g.

Methylation of the sulfur atoms in polymer I was carried out in solution with methyl iodide. The degree of methylation was determined by titration of the formed iodide anions by Mohr's method.[3] It was found that in a chloroform/dioxane mixture (1:1 by volume) the degree of substitution was lower than 50%, whereas in chloroform/nitromethane (1:1) higher degrees of substitution, up to 100%, were obtained. The products were isolated by vacuum evaporation of the solvent and any excess methyl iodide and dried at 40 °C under reduced pressure. Polymers with degrees of methylation of 45, 60, 78, and 100% were used to prepare complexes of TCNQ salts.

The TCNQ complex salts were prepared by the two-stage method reported by Rembaum et al.[4] The calculated ratios of the absorption intensities at 395 and 842 nm for the TCNQ complex salts were in the range 2.2–2.4, consistent with a $M^{2+}(TCNQ^{-\cdot})_2TCNQ_2^0$ structure for the complex, where M^{2+} denotes the repeated unit of the polycation chain. The electrical properties of the TCNQ complex salts prepared as 1-mm-thick pellets with deposited gold electrodes were measured in a nitrogen atmosphere. The resistivities were determined from current–voltage characteristic curves over the temperature range −130 to +60 °C. Activation energy of electrical conductivity was calculated by

$$R = R_0 \exp(E_a/kT)$$

where R_0 is the constant value (Ω), k is the Boltzmann constant (eV/K), and T is the absolute temperature (K). The specific resistivities (ρ) and activation energies (E_a) are presented in Table I. It can be seen from the data in Table I that the specific resistivity and activation energy decrease with increasing degree of methylation. In comparison with electrical properties of TCNQ complex salts with polycations containing quaternary nitrogen atoms in the polymethylene chain,[5,6] the above-discussed complex salts are characteristic of the much lower resistivities and

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