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 (δ = $\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

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

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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Table I
Specific Resistivity (ρ) and Activation Energy of Electrical Conductivity (E_a) for Polycation-TCNQ Complex Salts with Various Degrees of Methylation

degree of methylation, %	ρ,[a] Ω cm	E_a, eV
45	204	0.058
60	90	0.031
78	36	0.018
100	21.8	0.016

[a] The values of ρ were measured at 25 °C.

thermal activation energies. The reason for the low activation energies is difficult to explain and further investigations are in progress. It seems that the low E_a values are related to higher polarizability of the sulfur atom as compared with the nitrogen atom. This effect of high polarizability of cation may be important in reduction of Coulombic repulsions, thus leading to low E_a values.

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