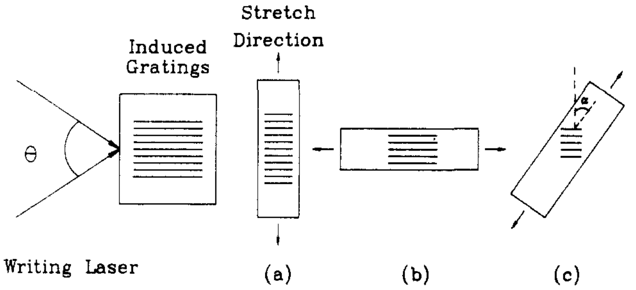

Figure 1. Orientation of the PC films with respect to the laser beams for the LIHGR measurement.

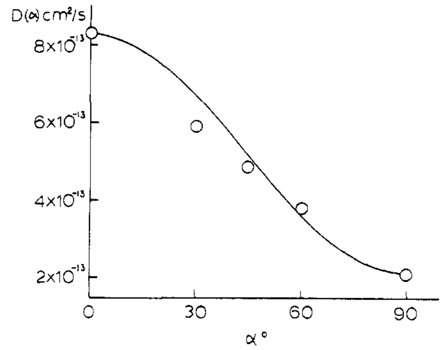

Figure 2. Effective diffusion coefficient, $D(\alpha)$, as a function of orientation angle α. The experimental data (○) are found to fit well to the equation $D(\alpha) = D_\parallel \cos^2 \alpha + D_\perp \sin^2 \alpha$ (curve).

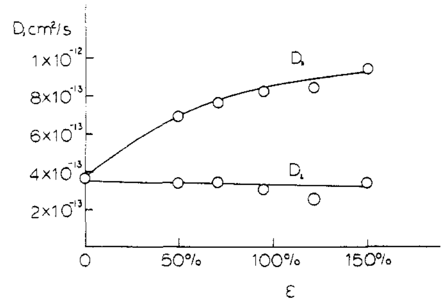

Figure 3. Diffusion coefficients $D_\parallel$ and $D_\perp$ plotted as a function of percent elongation.

causes the displacement vector to assume an angular dependence as **r** cos α + **r** sin α. Here **r** is the displacement vector of the diffusant. Comparisons of the measured with the calculated data are shown in Figure 2. The diffusion coefficient decreases by about a factor of 4 as α increases from 0 to 90°. Anisotropy in the diffusion coefficients increases as the drawing ratio is increased. Shown in Figure 3 are the diffusion coefficients $D_\parallel$ and $D_\perp$ plotted as a function of percent elongation. For the unstretched film $D_\perp = D_\parallel = 3.8 \times 10^{-13}$ cm^2/s, which is equal to the diffusion coefficient of CQ measured in a PC pellate at the same temperature.[4] Up to 150% elongation, $D_\perp$ appears to be independent of stretch, whereas $D_\parallel$ increases steadily with increasing stretch. At 150% elongation, $D_\parallel$ increases nearly 3 times the unstretched value.

Early studies of the orientation effect on the transport properties of dye molecules in semicrystalline polymer fibers have shown that the diffusion coefficient along the direction of stretch first increases and then decreases with a further increase of the stretch ratio.[5] The effect has been interpreted as due to an increase in microvoids and channels or cracks induced by the stretch, in addition to polymer relaxation.[6] In amorphous polymers such as PC, stretching causes orientation of the chains along the direction of stretch; the oriented chains are expected to create an open channel and ease the molecular transport provided that the average channel width is wider than the size of the diffusants. Hence we expect that upon stretching the film, an increase in the diffusion coefficient occurs in the direction of stretch. On the other hand, within the present stretch range, as shown by Brillouin scattering[7] the chain orientation is not affected in the transverse direction for polymers subject to uniaxial stress; thus, we do not expect a strong effect on $D_\perp$ by stretching the film. Stretch-induced crystallization may complicate the interpretation. However, the stress-induced crystallization in amorphous PC film is negligible.[8] Neutron-scattering studies have been used to investigate the chain deformation of PMMA below T_g.[9] It would be interesting to carry out similar studies in PC and find out whether affine deformation is maintained on the scale of the diffusion length. Work along this direction is being planned.

We have shown in this work that the LIHGR technique can be used to study the anisotropic translational diffusion behavior of probing molecules in the oriented polymer film, when other measuring techniques are difficult for the study. In the polycarbonate film the diffusion coefficient of camphorquinone along the direction of stretch increases with stretch ratio, whereas the diffusion coefficient perpendicular to the direction of stretch remains nearly independent of stretch. The effect is interpreted as due to the orientation of the polymer chains. The LIHGR technique is anticipated to be applicable in the diffusion measurements for a variety of polymer films.

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Registry No. Camphorquinone, 465-29-2.

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Homo- and Copolymerization of Unprotected 2-(Hydroxymethyl)thiirane Initiated by Quaternary Ammonium Salts of Dithiocarboxylic Acids

Functionalization of polymers is an important purpose and copolymerization is one of the outstanding methods to reach it. Many functionalized polythiiranes have been synthesized.[1-6] Polythiiranes themselves are mainly obtained by the ring-opening polymerization of thiiranes.[7] We have previously described a new type of initiator for anionic thiiranes polymerization, namely, the crystallized, stable, quaternary ammonium salts of carbo(di)thioic

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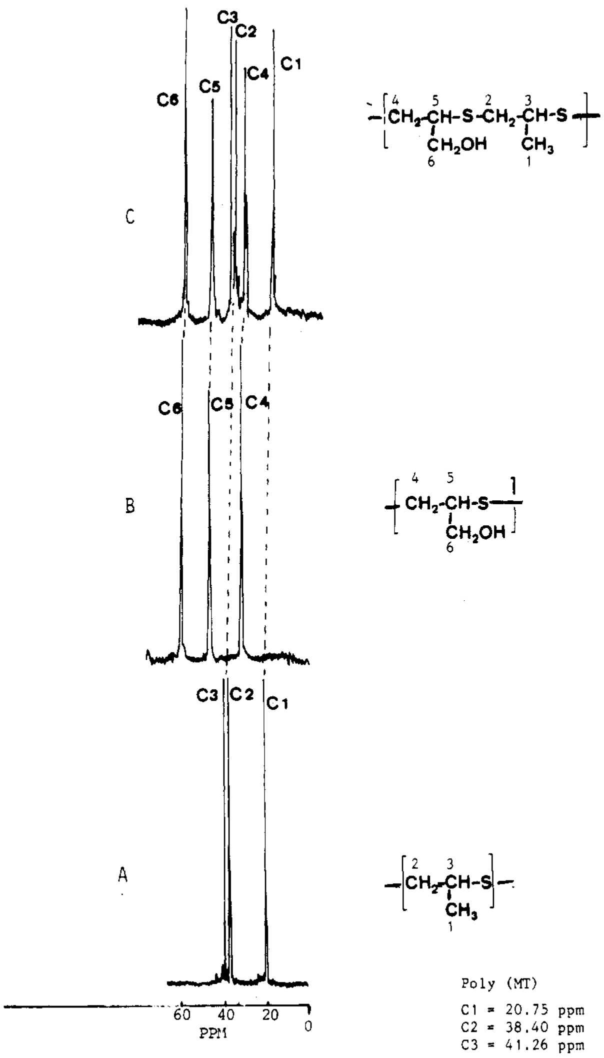

Figure 1. ^{13}C NMR spectra (Varian FT 80A at 20.1 MHz) in pyridine-d_5: (A) poly(MT); (B) poly(HMT); (C) copolymer (45% HMT/55% MT).

acids.[8] High molecular weight polythiiranes are readily obtained with use of these catalysts.[9]

This paper describes the synthesis of homopolymers of unprotected 2-(hydroxymethyl)thiirane (HMT) in the presence of benzyltrimethylammonium dithiobenzoate in dimethylformamide solution, this solvent allowing the solubility of all reagents and polymers. No HMT polymer seems to have been previously described but some have been claimed in an old patent.[10] Copolymers of HMT with 2-methylthiirane were also prepared without hydroxyl group protection. HMT polymerizations and copolymerizations were conducted under conventional conditions.[8,9] Both monomers were obtained according to known methods: HMT from 3-mercaptopropane-1,2-diol[11] and methylthiirane (MT) from propylene oxide.[12]

HMT homopolymers obtained in nearly quantitative yields are soluble only in highly polar hydrogen-bonding solvents such as dimethyl sulfoxide and dimethylformamide but insoluble in water, as well as THF, acetone, and chlorinated solvents. Their ^{1}H NMR (90 MHz) spectra in DMSO-d_6 are in accordance with the postulated structure: 2.80–3.10 ppm (m, 3 H, SCH$_2$ and SCH), 3.60 ppm (large s, 2 H, CH$_2$O), 4.50 ppm (s, 1 H, OH). Their ^{13}C NMR spectra seem to be consistent with "head-to-tail" linkages as in poly(MT).[8] Assignments of the different peaks to carbon atoms, as referred to numbers in the Figure 1B, were made from "off-resonance spectra" and comparison with equivalent carbons: the carbon atom C$_4$, corresponding to the main-chain methylene group, shows a single peak at 33.11 ppm; the methine carbone C$_5$ is located at 48.94 ppm; and the carbon C$_6$ bearing the hydroxyl group in the side chain is located at 61.78 ppm. Anionic polymerization of HMT is likely under these conditions and the ring opening probably occurs at the CH$_2$–S bond, but there is no evidence currently for this opening. Molecular weight determination of homopolymers was not directly possible in relation to their low solubility. Therefore we have transformed the hydroxyl groups into acetoxyl ones by means of acetyl chloride in DMF. The modification was nearly quantitative (^{1}H NMR). The modified polymer, poly(AcOMT), was then soluble in THF and we succeeded in determining the molecular weight by GPC (Table I). Under the same conditions, modification of a 12% HMT copolymer has proceeded without degradation (Table I).

Table I
Molecular Weights of Modified (Co)polymers[15]

	M_n	M_w/M_n
poly(HMT)	3150[a]	
poly(AcOMT)	4600	1.8
copoly(HMT/MT)	13900	1.9
copoly(AcOMT/MT)	28900	1.8

[a] Calculated from the value of the acetylated polymer, assuming no chain scission has occurred in the acetylation process as in the copolymer.

Poly(methylthiirane-*co*-(hydroxymethyl)thiiranes) are amorphous, colorless materials. Yields are generally high (>75%), often quantitative before purification. These copolymers are soluble in THF and chlorinated solvents, except for those with a HMT content larger than 60%. Their ^{1}H NMR spectra (90 MHz) show nearly identical signals as those of the homopolymers: in DMSO-d_6 the following signals are observed: 1.25 ppm (d, CH$_3$), 2.50–3.20 ppm (m, CH$_2$ and CH of the chain), 3.60 ppm (large s, CH$_2$O), 4.90 ppm (s, OH). The ^{13}C NMR spectra exhibit the same signals as both MT and HMT homopolymers and also additional peaks. Copolymers of different compositions have shown the same additional peaks with variable intensities according to the comonomer amounts. Assignments of the different peaks to the carbon atoms, as referred to number in the Figure 1C, were made from off-resonance spectra and identification with the homopolymer spectra. The chemical shifts for the different carbon atoms are (main peaks) 20.91 ppm for the methyl carbon C$_1$, 34.43 ppm for the methylene carbon C$_4$ of the HMT unit, 43.19 ppm for the methylene carbon C$_2$ of the MT unit, 46.10 ppm for the methine carbone C$_3$ of the MT unit, 55.00 ppm for the methine carbone C$_5$ of the HMT unit, and 68.43 ppm for the methylene carbon C$_6$ bearing the hydroxyl group. Since both monomers seem to give head-to-tail linkages, we have thought that these supplementary peaks (expanded spectrum Figure 2) correspond to sequences of different distribution. The presence of several signals for each carbon atom may prove the existence of statistical copolymers, but more investigations will be carried out to assign each signal exactly.

The copolymers composition must be determined exactly. With high contents of HMT, ^{1}H NMR spectral intensities study is a suitable method for this purpose. But its accuracy is poor and inadequate for the smaller HMT contents. For such an occurrence we have modified the hydroxyl groups with 1-naphthyl isocyanate according to ref 13 in rigorously anhydrous conditions and titrated the naphthyl carbamate content in modified copolymers by UV spectroscopy. The molar extinction coefficient of

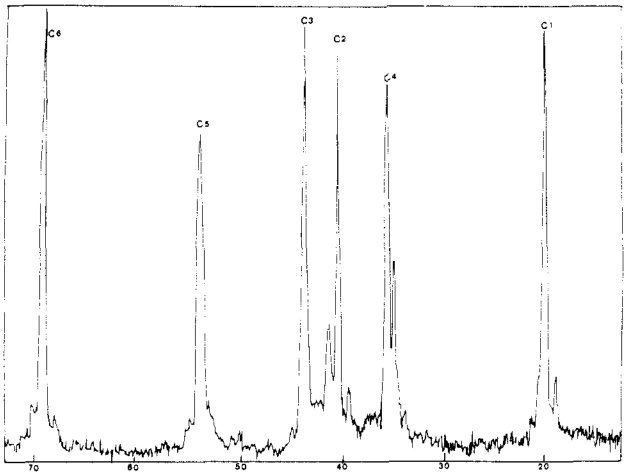

Figure 2. Expanded spectrum of Figure 1C.

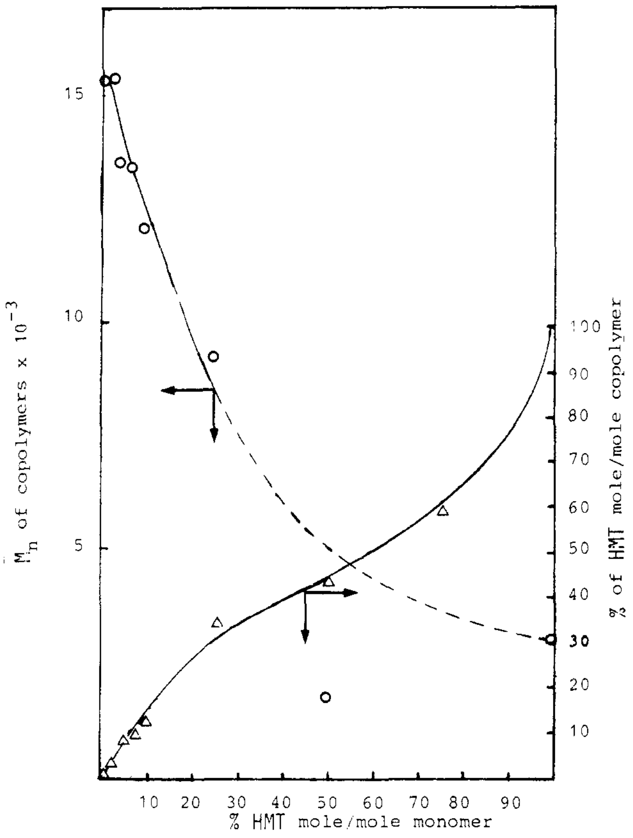

Figure 3. Effect of the monomer composition on the copolymerization. Monomer, 12.5 mol/L; initiator, 1% mol/mol monomer; $T = 20$ °C. (○) M_n of copolymers;[15] $1.6 < M_w/M_n < 1.9$, except for 50% $M_w/M_n = 3.5$. (△) Copolymer composition.

2-(methylthio)ethyl N-1-naphthylcarbamate $\epsilon = 7460$ at 293 nm was used for a naphthyl carbamate unit in the copolymers. In order to test the accuracy of our hydroxyl group determination we have compared ^{1}H NMR and UV measurements: both methods were in agreement in the limits of experimental methods. The evolution of copolymer composition is described in Figure 3 as a function of monomer composition.

The molecular weight of the copolymers depends on several factors: concentration of the HMT in the monomer mixture (Figure 3); concentration of initiator (Figure 4); reaction temperature (Table II).

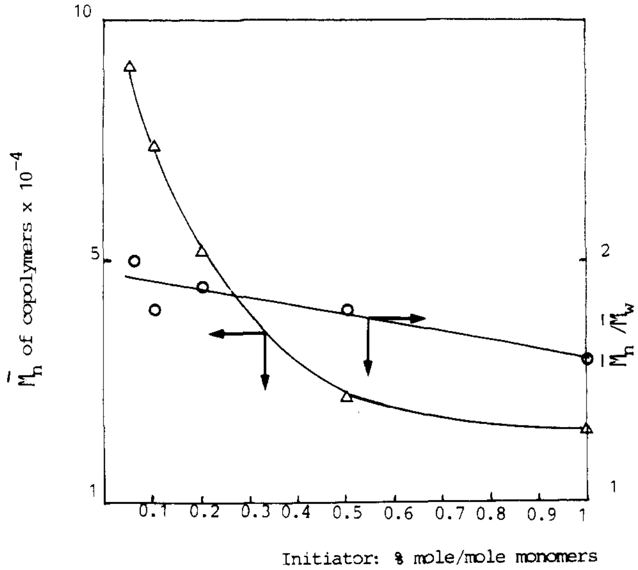

Figure 4. Effect of the initiatior amount on the copolymerization. Monomer, 12.5 mol/L; $T = 20$ °C; HMT in monomer, 2%; HMT in copolymer, 3–4% (UV determination). (△) M_n of copolymers; (○) M_w/M_n.

Table II
Effect of the Copolymerization Temperature on the Copolymer Molecular Weights[a]

T, °C	yield, %	M_n	M_w/M_n
20	55	90 300	2.0
0	70	126 100	1.8
−20	75	120 500	2.1

[a] Monomer concentration, 12.5 mol/L; HMT, 2% mol/mol monomer; initiator, 0.05% mol/mol monomer.

These results indicate the highest molecular weights are obtained at low temperatures and by using the lowest ratios of initiatior to monomer and of HMT to MT; thus, it seems likely that chain transfer to hydroxyl group acts as a limiting factor for molecular weight as was previously observed in MT polymerization.[14]

The syntheses of these new (co)polymers confirms the properties of dithiobenzoic acid ammonium salts as anionic initiators of thiiranes polymerization. The reactivity of the (co)polymers with acetyl chloride or naphthyl isocyanate emphasizes the numerous possibilities for further modifications of these new materials. Investigations are now in progress to determine more accurately the influence of free hydroxyl groups on the polymerization mechanism and the (co)polymer structure. We are also developing the use of (di)thiobenzoic ammonium salts in the polymerization of other functionalized thiiranes.

Registry No. Poly(HMT) (homopolymer), 119529-46-3; poly(HMT) (SRU), 119618-79-0; (HMT)(MT) (copolymer), 119529-47-4; benzytrimethylammonium dithiobenzoate, 86878-59-3.

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High-Resolution Solid-State Proton MASS NMR of Superabsorbing Polymeric Gels†

There is growing use of superabsorbing polymers in view of their potential applications in the fields of agriculture, macromolecular separations, medical care, etc. These materials hold anywhere from 100 to 1000 g of water per gram of dry polymer. In our laboratory we have been actively involved in the synthesis and characterization of a variety of such polymers. A study of the literature in the area of science of superabsorption indicates that whereas aspects of thermodynamics,[1,2] kinetics of absorption,[3,4] and phase transitions[5] have been extensively studied, there is practically no study reported on the structural and dynamical characterization of this class of superabsorbing polymers through solid-state NMR techniques. This was the main motivation for undertaking this work.

Polymeric solids are hard to characterize by proton magnetic resonance owing to the inherently large spectral line broadening, which arises from static dipole–dipole interactions among the abundant proton spins.[6,7] As an example, we show in Figure 1A the static proton spectrum of dry hydrolyzed starch-*graft*-poly(acrylonitrile), a superabsorbing polymer syntheszied in our laboratory. The proton spectrum is a featureless broad line with a line width of approximately 28 kHz. This severe line broadening is so large that it obscures fine spectral features such as the proton chemical shifts and coupling constants and renders the study of polymeric solids difficult.

Macromolecular mobility can cause a motional averaging of static proton dipolar interactions and reduce the observed proton spectral line width.[6,8,9] The extent of proton line narrowing, however, depends on the exact nature of the polymer mobility. Unless the polymer motions are isotropic, or nearly so, the dipolar couplings cannot be averaged to zero, and therefore, fine resolution of polymer structure cannot be revealed. In fact, the spectrum of Figure 1A already exhibits some motional averaging at room temperature due to restricted polymer mobility. Here the observed line width is nearly half compared to a rigid lattice line width for a prefectly rigid polymer.

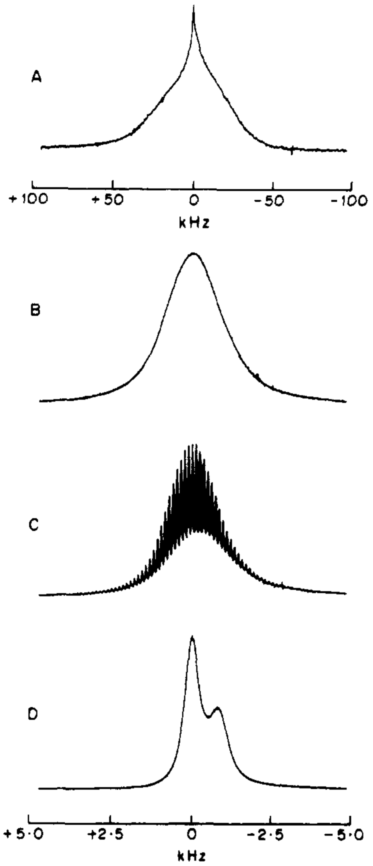

Figure 1. Static proton NMR spectra of hydrolyzed starch-*graft*-poly(acrylonitrile) gels (B–D): (A) Solid dry powder. The sharp line at the center is due to a very small amount of moisture picked up during the experiment by the completely dried sample. (B) Sample with 0.2% saturation. (C) Spin–echo spectrum of (B) with a 4-ms delay between the π pulses (see text). (D) Sample with 1.0% saturation.

It is well-known that the addition of solvent or plasticizer to a polymer enhances the polymer mobility.[10–12] The details of the chain dynamics depend on the specific nature and extent of polymer–solvent interactions and this in essence determines the observed residual proton spectral line width. In cross-linked polymers, the degree of cross-linking determines the equilibrium swelling capacity of the polymer in suitable solvents. The extent of chain mobility depends upon the degree of cross-linking and the type of the solvent used. This has been shown to cause proton line narrowing in polystyrene–divinylbenzene.[13]

We report herein the observation of high-resolution solid-state proton NMR spectra from superabsorbing polymeric gels. We believe this is the first such reported observation on this class of polymers. We are specifically concerned about hydrolyzed starch-*graft*-poly(acrylonitrile), a superabsorbing polymer, which was synthesized by graft copolymerization of acrylonitrile onto gelatinized starch. This graft copolymer was subsequently alkali hydrolyzed and isolated in the form of dry powder. It has the equilibrium water absorption capacity of 160 g per gram of dry polymer. This equilibrium water absorption capacity corresponds to 100% saturation in water. The percentage grafting and the molecular weight of the grafted

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