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(15) Molecular weights are determined by size-exclusion chromatographs. They are reported as the molecular weight of equivalent elution volume polystyrene. This standard is not appropriate for these polymers, especially for copolymers with high contents in HMT and in fact explain the wrong measure for 50% HMT mol/mol monomer. Nevertheless these measurements allow us to evaluate the molecular weight variations with the different studied factors.

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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.

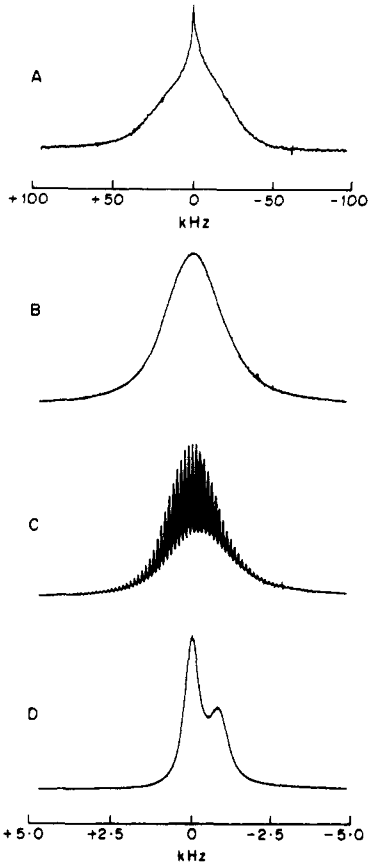

Figure 1. Static proton NMR spectra of hydrolyzed starch-*graft*-poly(acrylonitrile) gels (B–D): (A) Solid dry powder. The sharp line at the center is due to a very small amount of moisture picked up during the experiment by the completely dried sample. (B) Sample with 0.2% saturation. (C) Spin–echo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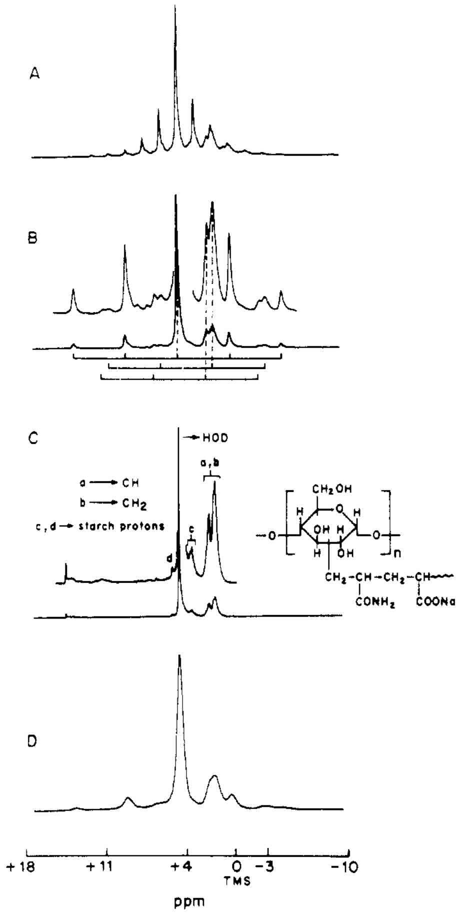

Figure 2. ^{1}H MASS spectra of hydrolyzed starch-*graft*-poly(acrylonitrile) gels: (A) 0.2% saturation, spinning at 450 Hz; (B) 0.2% saturation, spinning at 1.5 kHz; (C) 2% saturation, spinning at 3.1 kHz; (D) same as (B) but ~1° off-axis near the "magic angle". The expected positions of first- and second-order spinning side bands are marked by stick diagrams below the spectra.

poly(acrylonitrile) for this polymer were determined to be 48.0% and 120 000, respectively. All the gel samples for NMR measurements were prepared by adding required amounts of dry polymer to the known volume of D_2O (99.6% obtained from BARC, Bombay) for a given percentage saturation. The samples were allowed to homogenize for 3–4 days in sealed vials before transferring them to the MASS rotor.

In this superabsorbing polymer, even at very low concentration of water (0.2% saturation), the polymer proton spectrum at room temperature is quite narrow and exhibits a near super-Lorentzian line shape[14] due to extensive motional averaging of static proton dipolar interactions. This is shown in Figure 1B, where the residual line width is only 2.1 kHz and can be further narrowed by magic angle sample spinning (MASS) techniques.

We show in Figure 2 the corresponding ^{1}H MASS spectrum of the polymer gel where the 2.1-kHz line broadening of the static sample has been removed by MASS to give a very high resolution proton NMR spectrum. With the MASS spectral resolution it is possible to resolve the chemical shifts from the different chemical functional groups in the polymer. It may be noticed that on MASS the static spectrum (Figure 1B) breaks into a number of center bands as well as intense side bands, the envelope of which maps the static proton line shape. The side-band pattern is especially pronounced at slow spinning speeds (Figure 2A). By comparison of MASS spectra taken at different spinning speeds, the center bands were identified. The assignments are shown for the different protons in the polymer (see Figure 2C).

The success of MASS to yield high-resolution proton spectrum in our gel system can be traced to the fact that the proton–proton spin interactions can become inhomogeneous in character[15] and can therefore be further narrowed by MASS at moderately available spinning speeds (2–4 kHz). Inhomogeneous spin–spin interactions can be refocused in a spin–echo experiment [e.g., CPMG: $(\pi/2)_x$–τ–$(\pi)_y$–τ–echo] pulse sequence.[16] Here the successive application of π pulses will refocus the proton magnetization repeatedly until the spin–echo has decayed to zero by spin–spin relaxation time (T_2). The Fourier transform of such an echo train gives rise to a spectrum in which the powder pattern of the anisotropic spin interaction is split into a number of peaks separated by the reciprocal of the pulse spacing in the sequence.[17,18] Figure 1C is a FT spin–echo spectrum of the 0.2% saturated gel that shows the above effect. The inhomogeneous nature of the proton line broadening in our polymeric gel is demonstrated in this spectrum by the presence of many narrow peaks which, in a way, map the static proton line shape of Figure 1B. In this superabsorbing polymeric gel, the solvent polymer interactions are such as to induce molecular motions of the polymer segments, which are likely to be nearly isotropic in nature. Such motions would decouple ^{1}H–^{1}H spin–spin interactions to a greater extent and render the proton line shape inhomogeneous in character. We also carried out a cross-polarization[19] experiment. Inhibition of proton spin diffusion was also evident from our observation that no cross-polarization ^{13}C spectra could be obtained in this superabsorbing polymer gel. It may be noted that the maximum external averaging by mechanical rotation of the sample can be accomplished only at the magic angle[20] (spinning axis at 54.7° with respect to B_0). This is demonstrated in Figure 2D where a slight missetting of the "magic angle" leads to loss of resolution of polymer signals and to the broadening of the spinning side bands.

We also find that in these superabsorbing gels, the observed spectral breadths of static proton spectra and the final resolution obtainable by mechanical spinning at the magic angle depends strongly on the polymer to solvent (water in this case) concentration. As an example, we show in Figure 1D the static proton spectrum of a gel with 1% saturation. Here we see the improved separation of the spectral bands corresponding to residual HOD and aliphatic protons. Similarly, the ^{1}H MASS spectrum shows improved chemical shift resolution with the increase in percentage saturation, an example of which is shown in Figure 2C for a gel with 2.0% saturation. It appears that at a very low concentration of water there is a homogeneous broadening as well, in which case it is likely that it will be necessary to combine MASS with homonuclear multipulse techniques[21] for optimum line narrowing. However, addition of more water to the polymer causes an extensive increase in polymer chain mobility and results in increased resolution to be obtained in the final MASS spectrum. A detailed study on the dynamics by this superabsorbing polymer is under way and will be reported later.

All the experiments were carried out on a Bruker MSL-300 FT-NMR spectrometer at ambient probe temperature (21 °C) with a MASS probe, which gave negligible proton background signal. The pulse sequences used and the MASS speeds employed are indicated in the legends of the figures.

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Copolymerization of *N*-Phenylmaleimide and Propylene Oxide Initiated with Organozinc Compounds

Copolymerization of cyclic monomer with vinyl monomer has been of considerable interest but difficult because the polymerization reactivity and mechanism of such monomers are generally quite different from each other. Only a few reports have been available including those of the copolymerization via zwitterion,[1,2] though new types of polymers might be produced by copolymerization of these two extremely different types of monomer and new fields of application should be expected.

In a previous paper, it was reported that *N*-phenylmaleimide (*N*-PMI) gave the appreciable yields of poly(*N*-PMI) initiated with organozinc complex of $[Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6]$ (**3** in Table I).[3] This organozinc complex which is synthesized from diethylzinc and methanol has also been known as a polymerization catalyst for epoxides and studied in detail.[4-6]

In Table I the activity of various organozinc initiators on the homopolymerization of *N*-PMI and of propylene oxide (PO) is qualitatively summarized. This table suggests that *N*-PMI and PO may be copolymerized by the initiation system of **3** since the zinc complex gives both homopolymers of *N*-PMI and of PO.

As a preliminary work, the present paper describes the results of copolymerization of *N*-PMI and PO with organozinc compounds.

Table I
Orgnozinc Compounds as Initiators for Homopolymerizations of *N*-PMI and PO

orgnozinc compd	activity for homo-polymerization[a] *N*-PMI	activity for homo-polymerization[a] PO	ref
$(C_2H_5)_2Zn$ (**1**)	△	×	3, 7
$(C_2H_5ZnOCH_3)_4$ (**2**)	△	×	3, 8, 9
$[Zn(OCH_3)_2(C_2H_5ZnOCH_3)_6]$ (**3**)	○	○	3-6
$(Zn(OCH_3)_2)_n$ (**4**)	△	⊙	3, 9, 10

[a] (⊙) excellently active; (○) fairly active; (△) a little active; (×) inactive.

Table II
Copolymerization of *N*-PMI with PO Initiated with Organozinc Compounds[a]

initiator	polymer yield,[b] g CH_3OH sol.	polymer yield,[b] g CH_3OH insol.
1	0	0.12 (3.1)
2	0	0
3	1.28 (33)	0.73 (19)
4	0.45 (11)	0

[a] Initiator, 0.1 mmol; *N*-PMI, 3 mmol (0.5 g); PO, 59 mmol (3.4 g); in THF; total volume 10 mL; at 80 °C; 24 h. [b] The values in parentheses are yields of polymer in percent calculated from the following equation: yield (%) = [(polymer obtained, g)/(total amount of monomers fed, g)] × 100.

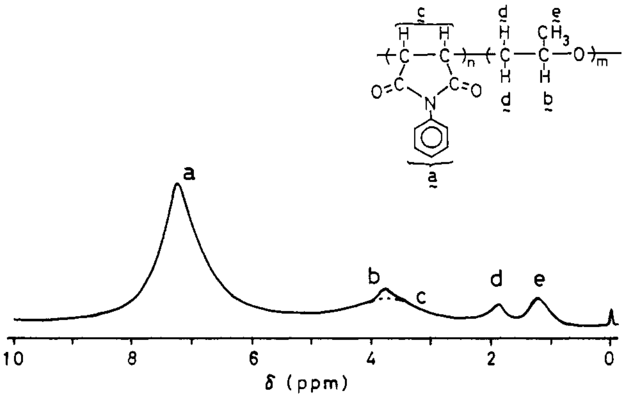

Figure 1. ^{1}H NMR spectrum of the methanol-insoluble polymer obtained by the copolymerization of *N*-PMI and PO with **3**.

Polymerizations were carried out with purified *N*-PMI and PO in sealed glass ampules under purified nitrogen atmosphere.[11] The reaction was terminated with hydrochloric acid/methanol and the reaction mixture was poured into methanol. The precipitate (methanol-insoluble part) was filtered off and dried under vacuum at 110 °C. The methanol-soluble polymer was collected by evaporation of methanol (precipitant) and extraction with benzene, followed by freeze-drying of the benzene solution.

Results of copolymerization of *N*-PMI (3 mmol) and PO (59 mmol) with organozinc compounds are summarized in Table II. Only **3** gives an appreciable yield of copolymer from *N*-PMI and PO as methanol-insoluble polymer.

Figure 1 shows ^{1}H NMR[12] of the methanol-insoluble polymer obtained by the copolymerization with **3** in Table II. Absorptions at 1.2 (e), 1.8 (d) and 3.8 ppm (b) are assignable to methyl, methylene and methine groups of PO units in the polymer, respectively. A peak at 7.2 ppm (a) and broad one from 3.0 to 5.3 ppm (c: shown by dotted line with the overlapping signal of methine groups of PO units) are assigned, respectively, to phenyl and methine

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