NMR Characterization of Cross-Linked Polystyrene Gels

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ABSTRACT: Direct polarization magic angle spinning (DP/MAS) NMR is ideally suited for the characterization of solvent-swollen cross-linked polystyrene gels. These gels exemplify a larger group of polymeric materials that undergo rapid but anisotropic reorientation on the molecular scale. The line broadening due to the residual dipolar coupling (^{1}H NMR) or chemical shift anisotropy (^{13}C NMR) in the swollen gel can be removed by moderate-rate magic angle spinning to give highly resolved ^{1}H and ^{13}C NMR spectra. Application of these methods permits full characterization of chemically modified polystyrene resins including well-resolved signals attributed to the cross-link junctions. The complementary nature of DP/MAS and CP/MAS NMR is discussed, as is the possible application of DP/MAS NMR to directly monitor cross-linking polymerization kinetics around the gel point.

Introduction

Solvent-swollen polymer gels continue to find new applications in areas as varied as slow-release drug reservoirs, matrices for photographic emulsions, and insoluble supports. Despite the generally acknowledged relationship between polymer network properties and materials performance, few methods suitable for the characterization of such polymers are currently available.[1] As the gel state is somewhat intermediate between the solid and liquid states, many classical characterization methods developed either for the solid state (e.g., CP/MAS) or for solutions (e.g., high-resolution NMR) prove to be of limited value, as they cannot fully cope with the peculiar characteristics of the gel state.

In a recent communication[2] we illustrated the efficiency of direct polarization magic angle spinning ^{1}H and ^{13}C NMR to provide high-resolution spectra of functionalized polystyrene gels swollen in chloroform. This paper aims to present a more thorough description of these methods and their application to some challenging problems of current interest.

Restricted Motion inside Polymer Gels

It appears useful to attempt a description of the gel state. Macroscopically, the gel point in a cross-linking copolymerization is defined as the point where the viscosity of the system increases rapidly to infinity, as measured, for example, by the failure of injected gas bubbles to rise to the surface. Microscopically however a distinction must be made between various types of interactions that cause gelation and the resulting different motional behaviors.

One type of polymer gel may be exemplified by certain carbohydrate polymers such as dextrans or cellulose derivatives swollen in water. In such systems the individual linear chains are interconnected by several weak hydrogen bonds or water bridges per unit. Due to this weak but continuous bonding between chains, mobility of the individual chains is severely restricted. While some carbohydrate polymers further contain a few percent of covalent cross-links, the chain mobility is actually determined by the weak but numerous hydrogen-bonding interactions.

In contrast to this type of gel are the nonpolar polymers cross-linked by only a few percent of covalent bonds. Prime examples of this group are poly(styrene-*co*-divinylbenzene) and poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate). Depending upon cross-link density, these polymers may absorb several times their own weight of suitable solvents such as chloroform, dichloromethane, or tetrahydrofuran.[3,4] In the resulting gels, interactions between solvent and polymer overcome the attraction between the polymer segments themselves. As a result the polymer network becomes solvated up to the point where its osmotic pressure or free energy of dilution is balanced by the networks strain and by its loss of entropy. This type of gel is characterized by highly solvated and mobile chain segments behaving similarly to linear soluble polymer segments except for their preferential orientation along the inter-cross-link vectors.

This intrinsic mobility of the individual chain segments has repercussions in terms of their characterization by NMR methods. In general, narrow NMR line shapes can be obtained only if the strong magnetic interactions between neighboring nuclei such as dipolar coupling or chemical shift anisotropy are averaged by a random motion that is faster than the frequency of these interactions.[5] In the case of soluble polymers this is readily achieved by normal Brownian motion in solution. Rigid polymers on the other hand would require magic angle spinning at the impossible rate of up to 250 kHz to eliminate the strong dipolar coupling. Natural-abundance ^{13}C nuclei show much weaker dipolar coupling between the dilute spins, and under high-power proton decoupling may be narrowed by magic angle spinning at a more accessible 5000 Hz. This forms the basis of the cross-polarization magic angle spinning (CP/MAS) experiment in solids.

The situation becomes more complicated for solid materials with rapid internal motions that partially average the strong dipolar coupling between spins.[5,6] Solvent-swollen polystyrene gels are a prime example of this type of materials. The fast local motion of the polymer chain segments located between the cross-links is only restricted with regards to their "end-over-end" reorientation. As a result, static ^{13}C NMR of solvent-swollen polymer gels show lines reminiscent of the soluble linear polymers with the exception of a superimposed chemical shift anisotropy broadening caused by the preferential alignment of the chains along the inter-cross-link vectors.[3,4,7-12] It was found that this signal broadening was directly related to the amount of cross-linker used.[3] ^{1}H NMR spectra of the same solvent-swollen polymer gels were described as

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broadened beyond use, due to the much larger residual dipolar coupling between the protons.

There are a number of materials in which much of the dipolar coupling in the ^1H NMR spectrum is removed by random but slow internal motions. In these systems, the ^1H NMR lines that are obtained cannot be narrowed further by spinning the sample at the magic angle.[6,13]

Doskocilová et al.[14-16] suggested that, in the case of solvent-swollen polystyrene gels, the residual proton line broadening caused by the cross-links is due not to a distribution of mobilities, as had been suggested earlier, but rather to a residual motional anisotropy along the inter-cross-link vector superimposed on the rapid segmental motion. As these inter-cross-link vectors remain essentially static on the NMR time scale, the residual solid-state behavior they cause may be eliminated by spinning at the magic angle at moderate rates of speed.[14] The principle that ^1H NMR lines of systems characterized by two widely different motional domains may be narrowed further by moderate magic angle spinning was elaborated in later work by Doskocilová and others on solvent-swollen polymer gels,[15-17] polymer melts,[18] and lipid bilayers and liquid crystals.[19] In essence, their work indicates that such systems should be understood as having largely solution-like mobility at the molecular level, superimposed with only a small solid-state contribution that can be eliminated by moderate magic angle spinning.

This interpretation is corroborated by the low signal-to-noise ratio found in cross-polarization magic angle spinning NMR of swollen polystyrene gels.[12,20] Most of the dipolar coupling required for efficient cross-polarization from proton to carbon in such gels is eliminated by the rapid segmental motion of the polymer network.[21]

In this paper we describe our application of Doskocilová's motional theory of polymer gels to the characterization of cross-linked polystyrene networks by MAS ^1H NMR, as well as our extension of this method to direct polarization MAS ^{13}C NMR. Further applications of these methods are discussed as well.

Experimental Section

NMR spectroscopy: A Doty Scientific Standard 7-mm VT-MAS probe was used on an IBM/Bruker AF-300 spectrometer operating at 75.47 MHz for ^{13}C NMR and at 300.13 MHz for ^1H NMR. The polymers were filled in the dry state into Doty 7-mm sapphire rotors and then swollen with deuteriochloroform. Standard Doty double O-ring-sealed Macor end caps were initially used to contain the swollen gels. No solvent was lost even after spinning at 2000 Hz for 1 h. To avoid pressure buildup during capping, an axial threaded hole was later machined into the Macor turbine end cap. During capping trapped air could escape through this hole, which was subsequently sealed with a small machined KEL-F screw that ended flush with the cap surface. These modified end caps allowed spinning speeds of up to 2600 Hz for completely filled rotors.

The use of standard Kel-F end caps limited the amount of gel sample that could be used to about 30% of the available rotor volume, in order to avoid excessive pressure build up during end-capping and subsequent cap expulsion at higher spinning speeds due to hydrostatic pressure.

^1H NMR spectra were taken through the decoupler channel. A chloroform-filled rotor spinning at 1000 Hz was used to FID-shim the probe to 5-Hz resolution in ^1H line width and to better than 2-Hz resolution in ^{13}C NMR. Even better resolutions were achieved in some experiments using two short Kel-F spacers to center the sample volume within the rotor. Both ^1H and ^{13}C DP/MAS NMR spectra were taken at room temperature by using the regular console transmitters. Low-power broadband proton decoupling was used for ^{13}C NMR. Spinning rates were 220–2600 Hz for ^1H NMR and 1800 Hz for ^{13}C NMR spectra. The deuteriochloroform ^{13}C resonance at 77 ppm and the ^1H resonance of 0.05% tetramethylsilane (added to some samples, not including those containing Si) were used as chemical shift references. All chemical shifts are reported in ppm relative to tetramethylsilane. The data size of all spectra was 16K, zero-filled to 32K. Pulse widths were 3 μs (55°) for ^{13}C and 2 μs (30°) for ^1H spectra. Relaxation relays were 0.3 s for ^{13}C and 2 s for ^1H spectra. Exponential line-broadenings of 3 (^{13}C) and 1 Hz (^1H) were used. Typically, 3000–6150 scans were accumulated for ^{13}C spectra, and 32–128 scans for ^1H spectra.

For comparison purposes, solution-state (static) spectra were obtained with a Bruker 5-mm dual-tune high-resolution probe, with 25-Hz spinning about the z axis. Identical acquisition and processing parameters were used for both DP/MAS and static spectra.

Preparation of bis(vinylbenzyl)dimethylsilane (mixture of meta and para isomers): The in situ Grignard coupling technique to dichlorodimethylsilane was adapted for work at 0 °C from the procedure by Coughlin and Salomon.[22] Magnesium turnings (0.61 g, 25 mmol) were covered with 25 mL of dry tetrahydrofuran under nitrogen. A 10% solution of 3.36 g (22 mmol) of chloromethylstyrene (67:33 meta–para; Dow Chemical) in 20 mL of dry tetrahydrofuran was added at room temperature. After the Grignard reaction had started, the mixture was cooled in an ice bath, and dimethyldichlorosilane (1.29 g, 8.5 mmol) was added, followed by the rest of the chloromethylstyrene over 1 h. The mixture was stirred for another hour at 0 °C, and the solvent evaporated below 0 °C on a Büchi rotavapor equipped with a dry ice condenser. The oily residue was taken up in 100 mL of pentane–ice water, and the phases were separated. The pentane phase was washed three times with 20 mL of ice water and once with 20 mL of saturated sodium chloride and then dried over magnesium sulfate. The solvent was evaporated below 0 °C, and the crude product purified on a silica column, eluting with 10:1 hexane:ethyl acetate. The oily product was stored in the freezer (1.7 g, 69%). ^1H and ^{29}Si NMR indicated a mixture of 11% di-para, 47% di-meta, and 42% para–meta products, in close agreement with the product distribution expected from the chloromethylstyrene mixture used.

^1H NMR: 7.3–6.9 (m, 4 H, aromatic); 6.79–6.65 (dd, 2 H, vinyl CH); 5.80, 5.71 (dd, 4 H, vinyl CH_2, trans, meta); 5.79, 5.68 (dd, 4 H, vinyl CH_2, trans, para); 5.28, 5.23 (dd, 4 H), vinyl CH_2, cis, meta); 5.23, 5.18 (dd, 4 H, vinyl CH_2, cis, para); 2.15 (s, 4 H, methylene); 0.013, 0.003, −0.008 (s, 6 H, methyl, meta–meta, meta–para, para–para). ^{13}C NMR: δ 140.00, 139.98, 139.67, 139.66, 133.61 (aromatic quaternary); 137.47, 137.12, 136.74 (vinyl CH_2); 128.35, 128.30; 127.76, 127.75; 126.15, 126.11, 122.1 (aromatic CH); 113.38 (vinyl CH, meta); 112.13 (vinyl CH, para); 25.09 (methylene); −3.8 (methyl). ^{29}Si NMR (relaxation delay 5 s; pulse width 63°; 77 scans; gated decoupling): δ 2.02 (s, para–para); 1.99 (s, meta–para); 1.97 (s, meta–meta).

Preparation of bis(4-vinylbenzyl)dimethylsilane: The procedure described above was used, starting from pure *p*-chloromethylstyrene. ^1H NMR: δ 7.34, 7.33, 7.02, 6.99 (dd, 4 H, aromatic); 6.78–6.69 (dd, 2 H, vinyl CH); 5.77–5.71 (dd, 2 H, vinyl CH_2, trans); 5.23–5.20 (dd, 2 H, vinyl CH_2, cis); 2.156 (s, 4 H, methylene); 0.01 (s, 6 H, methyl). ^{13}C NMR: δ 139.67, 133.72 (aromatic quaternary); 136.61 (vinyl CH_2); 128.31 126.18 (CH, aromatic); 112.13 (vinyl CH); 25.13 (methylene); −3.80 (methyl).

Preparation of poly[styrene-*co*-bis(3-vinylbenzyl)dimethylsilane]: Distilled styrene (4.94 g, 47.5 mmol), bis(vinylbenzyl)dimethylsilane (0.733 g, 2.5 mmol), and azobisisobutyronitrile (0.082 g, 0.5 mmol) in 6 mL of toluene were degassed and heated to 65 °C under nitrogen. After 48 h 50 mL of toluene was added, and the obtained gel was ground and washed repeatedly with toluene, dichloromethane, and methanol. Drying under vacuum at 40 °C for several hours gave 5.7 g (99%) of the cross-linked polymer in the form of a white powder.

Preparation of poly[styrene-*co*-bis(4-vinylbenzyl)dimethylsilane]: The polymerization was carried out as described above. The characterization of these copolymers is described below. Other 1 and 2% divinylbenzene-cross-linked polystyrene resins were obtained from Bio-Rad Laboratories.

Results and Discussion

The changes in the ^1H NMR spectra of 2% DVB-cross-linked polystyrene beads (Bio-beads SX-2) swollen in deu-

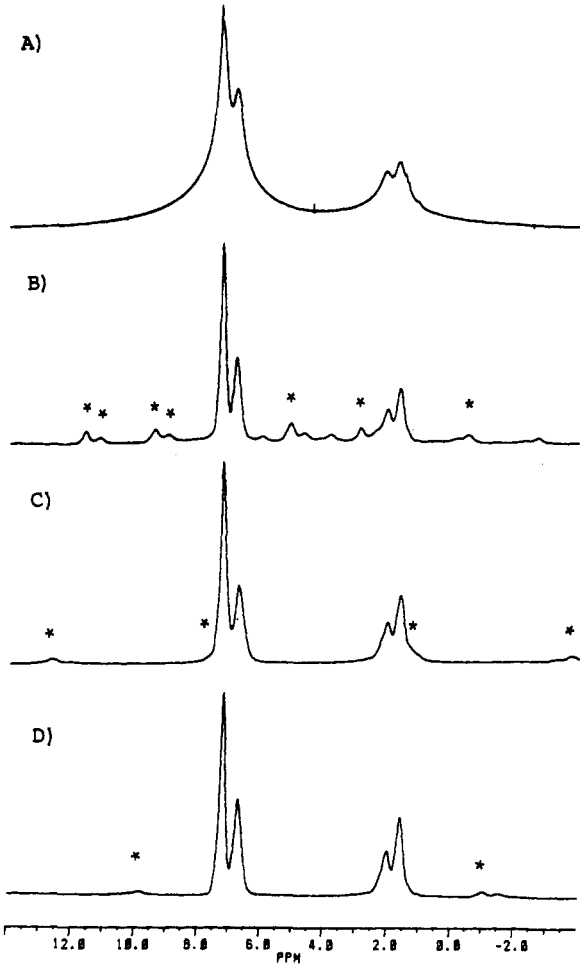


Figure 1. ^{1}H MAS spectra of 2% DVB-cross-linked polystyrene beads swollen in deuteriochloroform. (A) Static spectrum in 5-mm high-resolution probe, (B) MAS spectrum at 650-Hz spinning rate, (C) 1520-Hz MAS spectrum, (D) 2500-Hz MAS spectrum. First- and second-order spinning sidebands are indicated with a star.

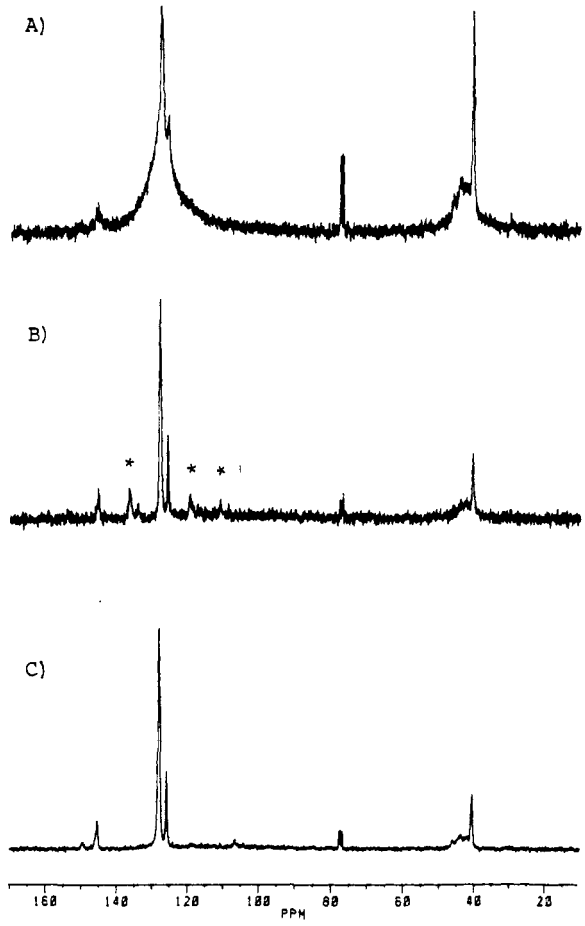


Figure 2. ^{13}C NMR spectra of 2% DVB-cross-linked polystyrene beads swollen in deuteriochloroform. (A) Static spectrum in 5-mm high-resolution probe, (B) DP/MAS spectrum at 800-Hz MAS. Spinning sidebands are marked with a star. (c) DP/MAS spectrum at 1800-Hz MAS.

teriochloroform upon magic angle spinning are illustrated in Figure 1. Whereas in the static spectrum 1a the lines are broadened by the residual dipolar coupling, slow (650 Hz) magic angle spinning (1b) suffices to collapse the dipolar powder pattern to a set of sharp central signals surrounded by spinning sidebands at multiplets of the spinning frequency. Using a MAS spinning rate of ca. 1520 Hz eliminates most of the sidebands (1c), while MAS spinning at 2500 Hz provides a 10 ppm wide window free of spinning sidebands (1d).

The corresponding development of the ^{13}C MAS NMR spectra at different MAS spinning rates is shown in Figure 2. Moderate (800 Hz) magic angle spinning collapses the chemical shift anisotropy broadening to a set of spinning sidebands (2b) that trace out the powder pattern seen in the static spectrum (2a). Spinning rates near 1800 Hz reduce the intensity of the spinning sidebands below noise level (2c).

To verify the dipolar nature of the ^{1}H NMR line broadening in these gels, a hole-burning experiment was performed on 2% divinylbenzene-cross-linked polystyrene beads swollen in deuteriochloroform. Continuous-wave homodecoupling at different positions in the static ^{1}H NMR spectrum and with different power levels led only to an overall reduction in signal intensity throughout the whole spectrum. This again indicates homogeneous dipolar broadening of the static ^{1}H NMR signals rather then heterogeneous broadening by chemical shift dispersion. As well, continuous-wave decoupling of the aromatic proton region caused only a very minor narrowing of the static aromatic ^{13}C NMR lines, resulting from the removal of the carbon–proton J coupling. The broad super-Lorentzian line shapes seen in the static ^{13}C NMR spectra of these gels can thus be attributed to chemical shift anisotropy rather than to dipolar broadening. This finding is in interesting contrast with the results obtained on the ^{13}C static NMR line width of poly(sodium acrylate) swollen in water. Line-width variation with magnetic field strength and successful ^{13}C NMR hole-burning experiments in that case showed the ^{13}C lines in this system to be broadened inhomogeneously by chemical shift dispersion rather than by homogeneous chemical shift anisotropy effects.[23]

In the present work the MAS spectra of polystyrene gels closely resemble spectra obtained from the corresponding soluble linear polymers. Again this confirms the intrinsic mobility of the solvated polymer chain segments in the lightly cross-linked network. The first application of these methods obviously lies in the characterization of chemically modified polymer gels. Figure 3 shows the ^{1}H and ^{13}C magic angle spinning NMR spectra of 50% chloromethylated, 1% DVB-cross-linked, polystyrene beads swollen in deuteriochloroform. Integration of the ^{1}H NMR chloromethylene signal at 4.38 ppm gives a chloromethylation level in close agreement with that determined by other methods.

As well, this chloromethyl signal has a characteristic chemical shift and thus serves as a useful probe for the degree of conversion in a subsequent substitution reaction.

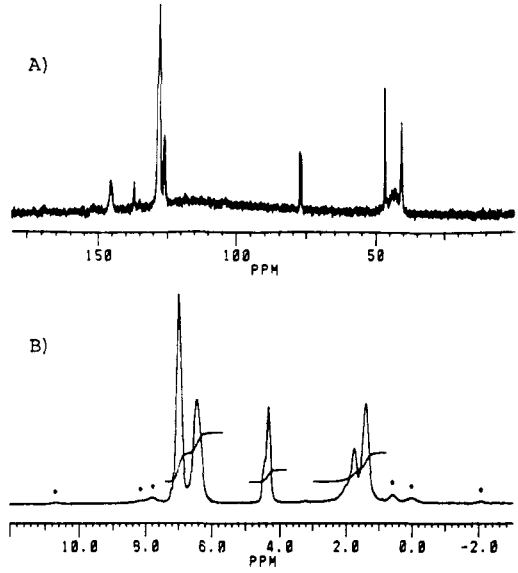


Figure 3. DP/MAS spectra of 50% chloromethylated 1% DVB-cross-linked polystyrene beads swollen in deuteriochloroform. (A) ^{13}C DP/MAS spectrum at 2200 Hz MAS. (B) ^{1}H MAS spectrum at 2300 Hz MAS. The signals marked with a star are spinning sidebands.

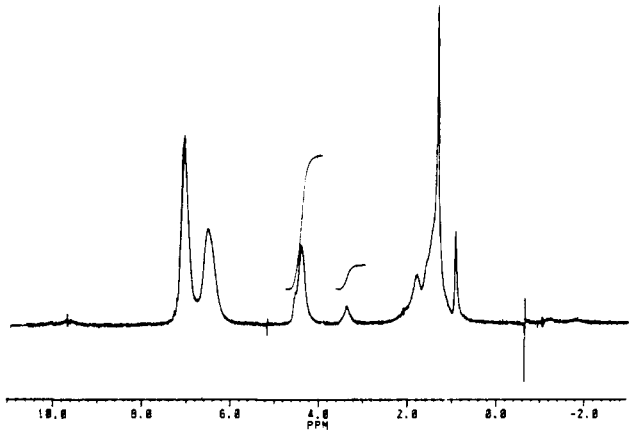


Figure 4. ^{1}H MAS NMR spectrum of 50% chloromethylated 1% DVB-cross-linked polystyrene gel in which 18% of the chlorine atoms have been replaced with *n*-decyl ether groups. MAS speed 2400 Hz.

Consider, for example, replacement of the chloride by a long-chain alcohol such as decanol. This reaction may be complicated by the partial collapse of the polymer matrix upon introduction of the long alkyl chain. ^{1}H MAS NMR permits the determination of an accurate degree of conversion as illustrated in Figure 4, showing the corresponding spectrum of 50% chloromethylated, 1% divinylbenzene-cross-linked, polystyrene beads reacted with sodium decoxide in tetrahydrofuran and swollen in deuteriochloroform. From integration of the ether methylene signal at 3.4 ppm, it may be determined that only 18% of the chloromethyl groups have been converted to decyl ether moieties. This type of information is extremely useful in determining the extent of functionalization of resins with reagents containing poorly solvating groups such as long-chain alkyls that may cause partial collapse of the swollen polystyrene matrix.

Other polymer systems that would be amenable to facile DP/MAS NMR characterization include functionalized and reactive polymer gels[24-26] and interpenetrating polymer networks.[27]

Copolymerization Kinetics. Beyond the improved characterization of modified polymer gels, direct polarization magic angle spinning NMR appears uniquely suited to monitor the cross-linking kinetics of a styrene–divinylbenzene system or of a methyl methacrylate–ethylene glycol dimethacrylate system in situ. High-resolution NMR has repeatedly been used to determine the copolymerization kinetics of such systems but was largely restricted to the reaction period prior to the gel point due to the line broadening that appears as gelation occurs.[28-30] These gels with low cross-linking densities are substantially different from those formed by curing of divinyl or trivinyl derivatives alone, where the conversion may be followed by either the high-resolution NMR signal of the remaining unreacted monomer[31] or through the CP/MAS signal of the obtained rigid polymer network.[32] In solvent-swollen, lightly cross-linked gels such as those described above, gelation introduces a gradually increasing NMR line-broadening, leading to substantial signal overlap[33] and even loss of integrated signal at higher cross-link densities. Sophisticated scaling models are in fact being designed to predict the gelation point from the copolymerization kinetics measured in the pregel state.[34,35] Direct polarization magic angle spinning NMR could allow quantitative observation of monomers, cross-linker, and polymer from the sol state, through the gel point, and into the post gelation period. This would provide kinetic data for the period around the gel point, a period during which both the kinetics and the mechanism of the copolymerization process are considered to undergo dramatic changes.

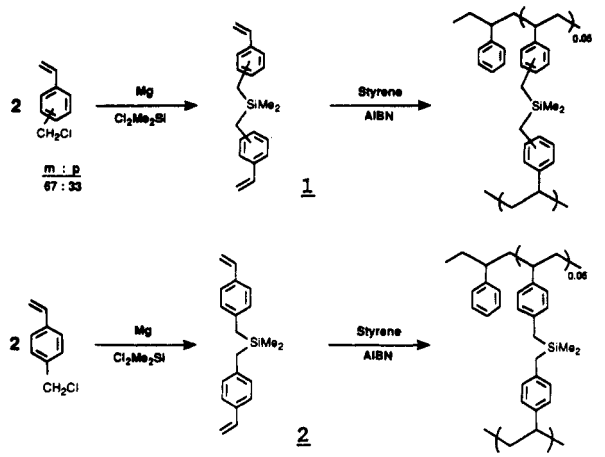
Copolymerization of styrene and divinylbenzene could therefore be studied by using a mixture of monomer, cross-linker and radical initiator in a liquid-tight rotor as used for the solvent swollen gels. The polymerization can then be followed directly at any desired temperature using ^{1}H or ^{13}C MAS NMR. If desired, the system may be diluted with the appropriate amounts of deuteriotoluene to reach the final swelling ratio.

Direct Observation of Cross-Links. In most applications of covalently cross-linked polymer gels the chemistry of the cross-links themselves receives very little attention. Due to the small amount of cross-links present in the network (0.1 to ca. 10%), their contribution to the chemical and mechanical performance of the network is often held to be almost negligible. On the other hand one may argue that the cross-link is in fact the most important component of three-dimensional polymer networks and that its structure and mobility warrant very much attention. Several recent papers have addressed these questions for different polymeric gels.[20,36,37]

One of the problems associated with cross-link characterization is the ability to detect and measure small amounts of cross-links in the presence of a large excess of linear polymer backbone. In the case of 1% cross-linked polystyrene gels, even 99% ^{13}C enrichment of the methine carbon in *p*-divinylbenzene was not sufficient to observe a signal from the cross-link.[20] Direct observation of the cross-links in bulk poly(propylene oxide) networks by ^{31}P NMR was achieved through use of a cross-link incorporating thiophosphate.[36]

Our approach to cross-link visualization involved the use of polystyrene-containing dimethylsilane-labeled cross-links. In these cross-links the methyl signals should appear around 0 ppm, thus potentially free from overlap with the large aliphatic backbone signal. Scheme I shows the preparation of the dimethylsilane cross-linkers **1** and **2** by in situ Grignard reaction from chloromethylstyrenes and dichlorodimethylsilane. Copolymerization of these cross-linkers with styrene was performed in toluene solution (50% v:v). Figure 5 shows the ^{1}H NMR spectra of the

Scheme I



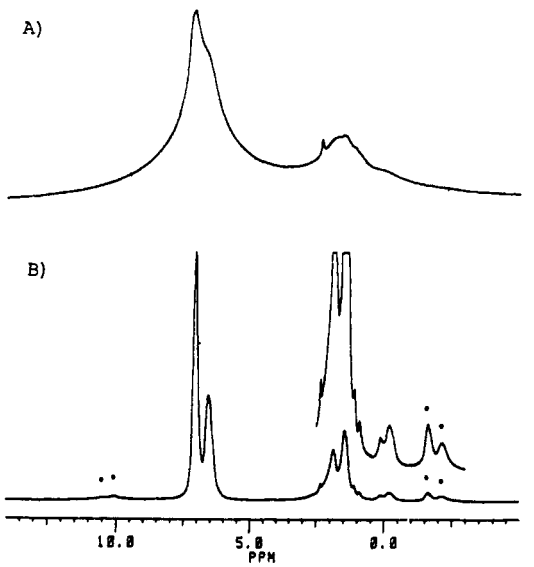


Figure 5. ^{1}H NMR spectra of polystyrene cross-linked with 5% of dimethylsilane cross-linker 1 and swollen in deuteriochloroform. (A) Static spectrum, (B) 2500-Hz MAS spectrum. The signals marked with a star are the first-order spinning side bands.

polystyrene gel containing 5% cross-linker 1. The static spectrum (5a) shows only the very broad dipolar coupling envelope with its broad wings characteristic of the super-Lorentzian line shape seen in these gels. In contrast, the ^{1}H magic angle spinning NMR spectrum (5b) gives a high-resolution spectrum with resolved signals around 0 ppm attributed to the silyl methyls of the cross-links. It must be noted here that no residual vinyl signals are seen for the cross-linked polymers prepared with 1 and 2. The signals attributed to the Si–CH_3 groups at the cross-link points show some fine structure in the form of a shoulder near 0.15 ppm. This feature could simply be due to the fact that a mixture of *m*- and *p*-chloromethylstyrene was used to prepare the cross-linker. To shed more light on this point, the pure para form of bis(4-vinylbenzyl)dimethylsilane **2** was prepared from *p*-chloromethylstyrene by using the reaction sequence shown in Scheme I. The ^{1}H magic angle spinning spectrum of the corresponding polystyrene cross-linked with 5% **2** is shown in Figure 6. The signal from the dimethylsilyl groups at the cross-links still has a small shoulder near 0.15 ppm as seen in Figure 5b. Since pure para cross-linker had been used for this polymer, the most likely explanation for the observed fine structure is a partial cyclization or back-biting either within the cross-linkers themselves to form the corresponding cyclophanes or through inclusion of a few styrene

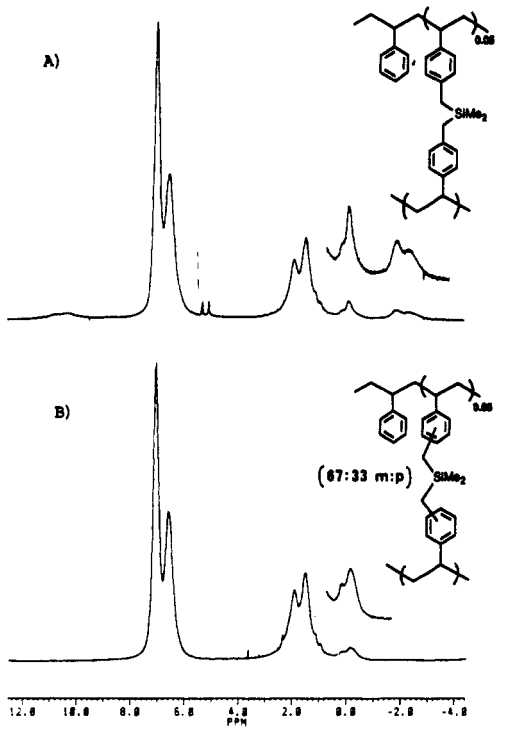


Figure 6. Comparison of deuteriochloroform-swollen polystyrene gels containing different cross-linkers. ^{1}H MAS NMR spectra of polystyrene gels incorporating 5% of dimethylsilane cross-linker **2** (A) and 5% of cross-linker **1** (B). The signals marked with a star are the first-order spinning sidebands.

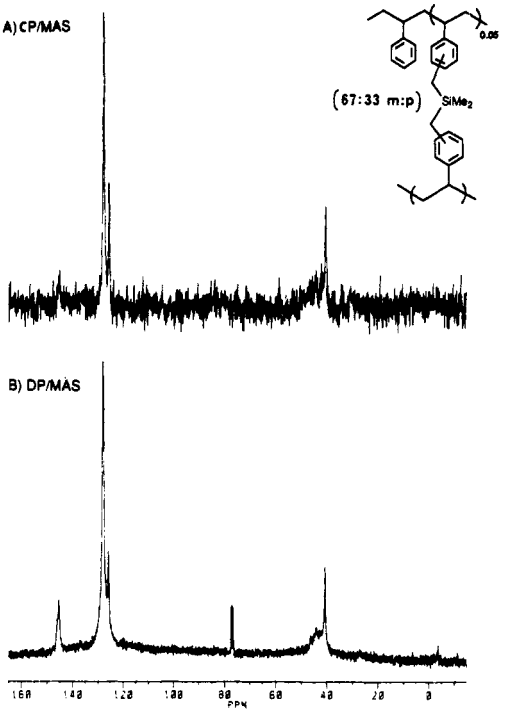


Figure 7. Comparison of ^{13}C CP/MAS NMR (A) with ^{13}C DP/MAS NMR (B) of polystyrene cross-linked with 5% **1** and swollen in deuteriochloroform. For each spectrum 3000 scans were acquired.

units. Information of this nature could help to determine cross-link morphologies and distributions in inhomogeneously cross-linked copolymers.[33]

To further illustrate the potential of ^{13}C DP/MAS NMR in characterization of cross-linked systems and to compare its use with cross-polarization MAS NMR, Figure 7 shows the CP/MAS and DP/MAS ^{13}C NMR spectra of poly-

styrene containing 5% 1 swollen in deuteriochloroform. The same number of scans was used in both acquisitions, requiring 3 h for the CP/MAS spectrum and 20 min for the DP/MAS spectrum. While the CP/MAS spectrum (Figure 7A) gives a well-resolved spectrum similar to the one observed by Ford et al.,[12] again the signal-to-noise is very low and the intensities are distorted due to insufficient and unequal dipolar coupling between protons and carbon nuclei. The DP/MAS spectrum (Figure 7b), on the other hand, trades some resolution for a much improved signal-to-noise that even allows observation of the dimethylsilyl carbons of the cross-links at −3.8 ppm.

Conclusions

With the current push to develop new polymeric materials, the development of methods suitable for their characterization becomes more and more important. Direct polarization magic angle spinning NMR should take its place between high-resolution NMR of solutions and cross-polarization magic angle spinning NMR of solids as it is particularly well suited to the restricted motions found in many polymeric materials including solvent-swollen polymer gels, liquid-crystalline polymers, and many polymer melts where the "chain-in-the-tube" model applies. In this paper we have demonstrated the efficiency of ^{13}C and ^{1}H DP/MASNMR to provide insight into the chemical structure of the backbone and of the cross-link itself. In addition suggestions for the further application of DP/MAS NMR to obtain cross-linking polymerization kinetic data are given.

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Registry No. 1 (copolymer), 131236-83-4; 2 (copolymer), 131236-84-5; Me_2SiCl_2, 75-78-5; $ClCH_2C_6H_4CH{=}CH_2$, 30030-25-2; $ClCH_2C_6H_4$-*p*-$CH{=}CH_2$, 1592-20-7; bis(vinylbenzyl)dimethylsilane, 121390-31-6; bis(4-vinylbenzyl)dimethylsilane, 131236-77-6; Bio-beads SX-2, 67712-67-8.