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Direct Polarization ^{13}C and ^{1}H Magic Angle Spinning NMR in the Characterization of Solvent-Swollen Gels

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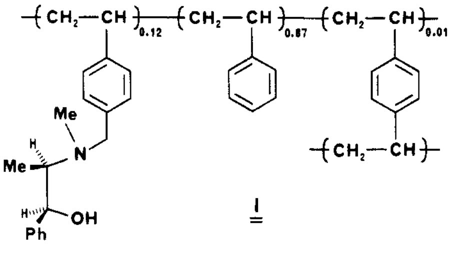
ABSTRACT: Direct polarization/magic angle spinning (DP/MAS) ^{13}C and ^{1}H NMR are shown to be well suited for the characterization of chemically modified cross-linked polymer gels. MAS is known to average out the residual motional anisotropies of the chain segments introduced by the cross-link points. At the same time, the ^{13}C direct polarization method exploits the rapid spin–lattice relaxation of the solvated chain segments to give good signal to noise for quaternary and protonated carbons alike.

Introduction

Functional groups on insoluble supports are as important as they are difficult to characterize. Our research work has frequently involved chemistry on solvent-swollen polystyrene beads,[1] which requires that reliable and facile NMR methods applicable to the gel state be available. Standard "solution-state" ^{1}H NMR[2,3] and especially ^{13}C NMR[4–6] have been used for swollen gels; the observed lines are, however, often broad due to the cross-link points, which restrict molecular motions of the chains.[7,8]

We have found high-field direct polarization/magic angle spinning (DP/MAS) ^{13}C and ^{1}H NMR to be well suited for the characterization of functionalized polystyrene beads swollen in deuteriochloroform. MAS averages out the residual motional anisotropy caused by the cross-link points, while the direct polarization method, in contrast to recently reported crosspolarization experiments,[9–11] takes advantage of the short spin–lattice relaxation times T_1 of the solvated chain segments.[2,12]

For example, Figure 1 shows ^{13}C NMR spectra of polymer I, which is a 1% cross-linked poly(styrene–divinylbenzene) resin in which 12% of the aromatic rings are functionalized with ephedrine moieties. This polymer was prepared by chemical modification of a corresponding chloromethylated resin in which 14% of the aromatic rings carried a chloromethyl group in their para position.[1] As can be seen in Figure 1b, the DP/MAS technique affords excellent signal to noise ratio and reliable representation of all carbon types, comparable to spectra taken[2,6] from soluble polymers.



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The corresponding ^{1}H MAS NMR spectrum (Figure 2, curve B) complements the ^{13}C data and demonstrates the chemical utility of this method using high magnetic fields.[8,12,13]

Experimental Section

A Doty Standard 7-mm VT-MAS probe was used with an IBM/Bruker AF-300 spectrometer operating at 75.47 MHz for ^{13}C NMR. Spectra were taken at room temperature in high-resolution mode, using the regular console power through the probe's ^{13}C observe and ^{1}H decouple coils. Shimming to 5-Hz resolution was done on the ^{1}H FID of a 20% $CHCl_3$ in $CDCl_3$ mixture spinning at 1000 Hz. Even better resolution should be achievable with ceramic or Kel-F spacers to restrict the sample volume.

Sapphire rotors with double O-ring sealed Macor end caps (both by Doty) were filled to 40% with the equilibrium-swollen gels under a slight excess of deuteriochloroform. At higher fill rates the combined hydrostatic and vapor pressures would slowly push out the end caps. Spinning rates were 2000 Hz for ^{13}C and 2350 Hz for ^{1}H spectra. No solvent leakage was detected when weighing a chloroform-filled rotor both before and after it was spun at 2000 Hz for 1 h.

The solution-state spectra were taken with a Bruker 5-mm dual tune high-resolution probe with 25-Hz spinning rate. Identical NMR acquisition parameters were used for both 5-mm solution-state and MAS spectra. The solvent resonance at 77.0 ppm and 0.05% tetramethylsilane were used as chemical shift references for ^{13}C and ^{1}H measurements, respectively. The data size was 16K, zerofilled to 32K. Pulse widths were 3 μs for ^{13}C spectra and 2 μs for ^{1}H spectra, corresponding to flip angles of less than 45°. Relaxation delays were 0.3 s (^{13}C) and 2 s (^{1}H). Exponential line broadening of 3 Hz was used for the ^{13}C spectra and none for the ^{1}H spectra. A total of 6150 scans were accumulated for all ^{13}C spectra, with broad-band proton decoupling (1 W).

Results and Discussion

In Figures 1B and 2B we show ^{13}C and ^{1}H DP/MAS NMR spectra of 12% ephedrine-functionalized polymer I. For comparison purposes the corresponding 5-mm solution state spectra of the gel are shown directly above as Figures 1A and 2A. While in the ^{13}C solution-state spectrum (Figure 1A) the superlorentzian backbone signals dominate the aromatic region, MAS line narrowing (Figure 1B) reveals a wealth of smaller aromatic signals. At the same time, the direct polarization technique ensures reliable representation of quaternary and mobile pendant carbons.

The ephedrine phenyl signals can be seen at 142.5 ppm (quaternary) and at 126.1 and 126.9 ppm (*o*- and *p*-CH). The high motional freedom of the pendant ephedrine phenyl makes their signals quite sharp compared to the

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Table I
Chemical Shifts[a] of Polymer-Bound (1*R*,2*S*)-Ephedrine

	C^q	$CH_{o,m,p}$	O-*CH*	N-CH_2	N-*CH*	N-CH_3	CH-CH_3	O*H*
$\delta(^{13}C)$, ppm	142.5	126.9 126.1	73.3	63.7	59.0	38.5	10.0	n/a
$\delta(^1H)$, ppm	n/a	7.28	4.84	3.41	2.84	2.15	0.95	1.84

[a] The proton backbone signals have been assigned earlier.[2,15]

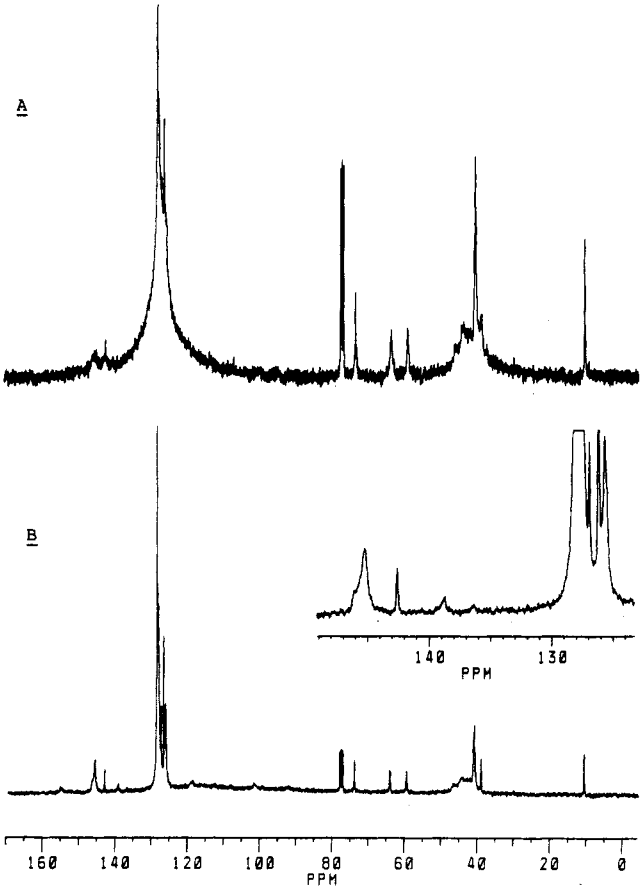

Figure 1. ^{13}C spectra of polymer I: (A) 5-mm solution-state spectrum; (B) direct polarization/magic angle spinning spectrum.

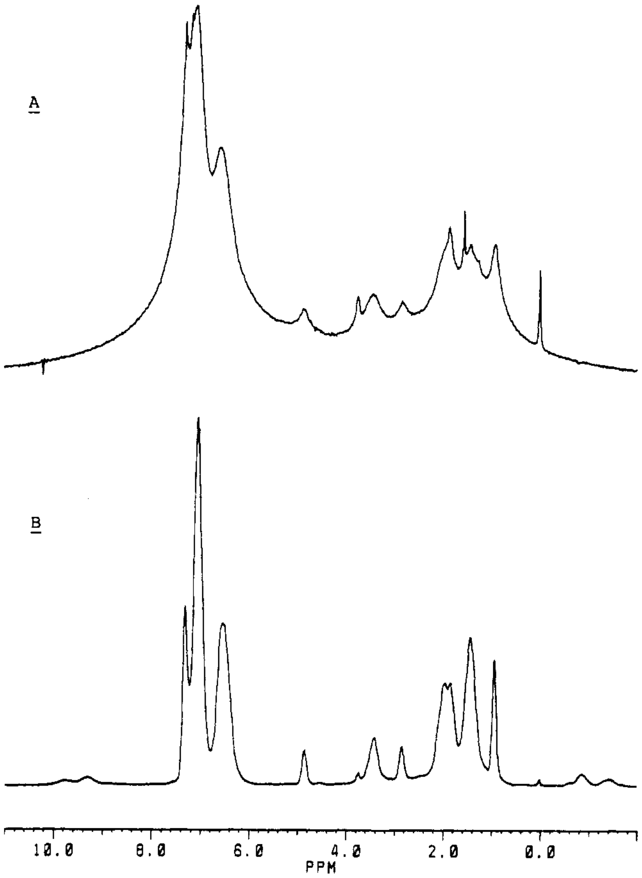

Figure 2. ^1H spectra of polymer I: (A) 5-mm solution-state spectrum; (B) magic angle spinning spectrum.

less mobile and atactically broadened backbone signals.[3]

There are three broad signals corresponding to the backbone quaternary carbons. The signal at 145.2 ppm represents both unsubstituted and para-substituted styrene groups. The signals at 138.6 and 136.3 ppm correspond to the quaternary carbons bearing ephedrine and unreacted chloromethyl groups,[6,7] respectively. These three carbons reside on similar backbone units and should thus have similar spin–lattice relaxation times, T_1, and nuclear Overhauser enhancements (nOe). Accordingly, their relative intensities should directly reflect the degree of functionalization with ephedrine. In fact, comparing the integrated area of the peak at 138.6 ppm with the area of the peak at 145.2 ppm gives an ephedrine functionalization of 11.5 ± 1%, in good agreement with the value of 12 ± 1% found by nitrogen analysis.

In addition, MAS narrows the lines corresponding to the five aliphatic ephedrine signals by a factor of 2. For example, even the *N*-methyl peak at 38.7 ppm is now base-line-resolved (Figure 1B; see Table I for complete assignments).

As assigned earlier,[7] the polystyrene backbone gives ^{13}C signals at 145.2 ppm (quaternary), 127.9 ppm (*o*-CH + *m*-CH), 125.6 ppm (*p*-CH), 46–40 ppm (CH_2), and 40.43 ppm (CH). The divinylbenzene cross-link did not give rise to an observable signal. This is not surprising, considering that Periyasamy and Ford were unable to resolve the cross-link signal in polystyrene gels prepared with 1% of α,α' ^{13}C-labeled DVB, using both high-resolution and CP/MAS NMR.[10] The small, broad peaks at 154, 101, and 118 ppm (Figure 1B) are all first-order spinning sidebands of the peaks from the protonated and the quaternary aromatic carbons, respectively. The base-line hump between 160 and 80 ppm is the Kel-F background from the MAS stator, which can be subtracted easily.

The ^1H MAS NMR spectrum (Figure 2B) demonstrates again the resolution gained by removing residual static anisotropies of motion.[12,13] The base-line-resolved signals now allow spectral assignments and useful integration, compared to the solution-state spectrum (Figure 2A; see Table I for assignments). The small signals at +9 and −1 ppm are first-order spinning sidebands of the aliphatic and aromatic peaks, respectively.

The same amount of sample was used in both solution-state and MAS NMR measurements. The improved signal to noise observed in the MAS spectrum (Figure 1B) is largely due to the sharper lines.

Since DP/MAS only requires a MAS NMR probe but not the auxiliary power amplifiers needed for CP/MAS, it should be seen as a rather routine NMR technique, both from experimental and instrumental standpoints. A complete experiment, including sample preparation, probe change, and acquisition of both ^1H and ^{13}C DP/MAS spectra, can be done in 1–2 h.

Conclusion

Direct polarization/magic angle spinning (DP/MAS) NMR is shown to give quantitative high-resolution ^{13}C spectra of the linear chain segments of cross-linked functionalized polystyrene gels. Together with ^{1}H MAS NMR this allows for extensive characterization and quantification of the chemistry which is carried out on these insoluble supports.

The question remains whether the less mobile divinylbenzene (DVB) cross-links and their nearest neighbors contribute to the observed NMR spectra. Work is currently in progress in out laboratory to study cross-link visibility and mobility, using multinuclear DP/MAS and CP/MAS in conjunction with model cross-link groups.

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Registry No. (Styrene)(divinylbenzene) (copolymer), 9003-70-7; ephedrine, 299-42-3.

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