Quantitative Solid State ^{13}C NMR Studies of Highly Cross-Linked Poly(divinylbenzene) Resins

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ABSTRACT: Three highly cross-linked poly(divinylbenzene) resins have been prepared from *p*-divinylbenzene and two grades of "divinylbenzene" from commercial sources using suspension polymerization methodology and employing toluene as a porogen. These materials along with XAD-2 and XAD-4 from the Rohm and Haas Co. have been examined by solid state ^{13}C nuclear magnetic resonance (NMR) techniques. In particular, quantitative single pulse excitation (SPE) experiments have been carried out to analyze the molecular structure of each resin in terms of *quantifying* the various types of carbon atom present. This has allowed the level of residual unreacted vinyl groups to be determined and hence the effective cross-link ratio of each resin. Whereas the monomer feed composition is known reasonably accurately for the in-house resins, no such information is available for XAD-2 and XAD-4. However, the SPE NMR spectra also allow the levels of ethylstyrene and divinylbenzene residues to be assessed as well, and so a full analysis of residual double bond content and cross-link ratio is also possible for the commercially sourced resins. In general real cross-link ratios are significantly lower than the feed ratio of divinylbenzene isomers. Thus ∼100% divinylbenzene yields ∼55% cross-linking, ∼80% divinylbenzene yields ∼40−45% cross-linking, and 50% divinylbenzene yields ∼30−35% cross-linking. There is therefore some uniformity in the percentage efficiency in the consumption of divinylbenzene in cross-links, with perhaps a marginal lowering of efficiency at very high absolute levels.

Introduction

High surface area polystyrene and polyacrylate-based resins without additional functionality have become increasingly important as sorbents both for liquid and gas phase streams. Recent environmental pressure has served only to accelerate and broaden their range of application. Certainly, in the case of styrene-based resins, the required high surface area is generated by using relatively high levels of cross-linker (typically >50 vol %) in the presence of a solvating porogen such as toluene.[1,2] A considerable amount of work has gone into characterizing the porous morphology of these materials and evolving an understanding of how the morphology evolves during resin synthesis. In this context Albright's contribution[1] has been remarkable. It has been known for many years that polymerization of vinyl groups is not complete in these materials, and indeed residual unsaturation can be exploited in terms of sites for facile chemical modification. Despite this, however, achieving adequate detailed molecular structural characterization of these resins has proved enormously difficult, primarily because of their highly cross-linked nature, but also because of the complex comonomer mixtures usually employed in the commercial synthesis of these species. In the case of styrene resins the cross-linker is "divinylbenzene". The latter is prepared industrially from diethylbenzene and the grade of the latter employed contains *meta*- and *para*-isomers and often smaller levels of other components as well. Consequently the "divinylbenzene" produced contains at least four components: *m*- and *p*-divinylbenzene (DVB) and *m*- and *p*-ethylstyrene (EtSt), arising from incomplete dehydrogenation of ethyl groups. Restricting the conversion to divinylbenzene seems to be deliberate since 100% divinylbenzene is rather unstable and readily gels on storage or in transport.

In principle solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy should provide a powerful method for molecular structural analysis of resins, and there have been some very constructive attempts in this direction.[3,4] However, the routine methodologies exploited in solid state ^{13}C NMR have been developed to provide optimum resolution and enhance the signal-to-noise ratio to improve sensitivity. For many applications this is admirable. Unfortunately the physics associated with the procedures used means that all the carbon atom types are not accounted for equally, so that the spectra obtained, for example, from normal cross polarization magic angle spinning (CP MAS) experiments, cannot be used to count carbon atoms in a highly quantitative manner. In recent years, however, this shortcoming has been recognized and the NMR fraternity have developed single pulse excitation (SPE) experiments[5] to overcome many of the problems associated with the more routine methodologies. In addition to offering opportunities in analyzing solid polymers, the SPE technique has been recognized and exploited by two of us in the quantitative molecular characterization of fossil fuels.[6,7] We have already reported on our use of these techniques in studying the structure of anion exchange resins and their precursors,[8] and hypercross-linked polystyrene resins with particular reference to the extent of diaryl methylene bridging.[9] We now report our results in studying conventional highly cross-linked polystyrene-type resins sorbents, where the primary aim has been to use SPE methodology to evaluate the real level of cross-linking, simultaneously quantifying the level of unreacted vinyl groups in these resins.

Experimental Section

Materials. *p*-Divinylbenzene was synthesised from terephthaldehyde using the Wittig reaction as previously reported.[10] Two grades of "divinylbenzene" were obtained from commercial sources. The first from BDH Chemicals Ltd. had a quoted composition as follows: ∼35 wt % *m*-divinylbenzene, 16 wt % *p*-divinylbenzene,

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31 wt % *m*-ethylstyrene, and ~15 wt % *p*-ethylstyrene. The second sample was from the Dow Chemical Co. and the composition was given as follows: ~57 wt % *m*-divinylbenzene, 24 wt % *p*-divinylbenzene, 11 wt % *m*-ethylstyrene, and 8 wt % *p*-ethylstyrene. No attempt was made to analyze these materials in-house.

Highly cross-linked resins HCR1−3 were synthesised in high yield (~95%) as previously reported[10] using a conventional free radical suspension polymerization methodology. Again details of this have been presented elsewhere.[11] HCR1 was prepared from *p*-divinylbenzene with no other comonomer component. An equal volume of toluene was used as a diluent/porogen. HCR2 was prepared similarly from "51% divinylbenzene" and HCR3 from "81% divinylbenzene". In each case no additional comonomer was used, and toluene was present in equal volume as a diluent/porogen. For the spin−lattice relaxation experiments other variants of HCR1−3 were produced in which the toluene:"divinylbenzene" ratio was adjusted to 0.5:1, 2:1, and 3:1.

HCR3 was brominated by treatment with excess bromine water at 20 °C for 24 h. The resultant resin was thoroughly washed with distilled water.

Rohm and Haas XAD-2 and XAD-4 were obtained from the Sigma Chemical Co.

All resins were exhaustively extracted with acetone in a Soxhlet and dried under vacuum at 40 °C for 24 h before being analyzed.

Instrumentation and Analysis. Fourier transform infrared spectra (FTIR) were recorded on a Mattson 5000 FT12 spectrometer. Typically 250 scans were collected for both the background and the sample. An automatic baseline routine was applied, and spectra were smoothed with a three-point "boxcar" function. The resolution was 4 cm^{-1} and the scanning range 4000−400 cm^{-1}. Samples were prepared as KBr disks, having previously been finely ground using a mortar and pestle. Assignments were made using a standard source.[12]

Nuclear magnetic resonance (NMR) spectra were recorded in a Bruker MSL 100 solid state NMR spectrometer operating at ~25.2 MHz for ^{13}C nuclei. The magic angle (MA) was set using KBr. Each ground sample (~200 mg) was packed into a 7 mm o.d. zirconia rotor and sealed with a Kel-F endcap. The samples were spun at ambient temperatures using a Bruker double bearing probehead. Proton decoupling fields were ~70 kHz. Samples were referenced using either the internal standard tetrakis(trimethylsilyl)silane (TKS) at 3.5 ppm or the external standard tetramethylsilane (TMS). An exponential line broadening weighting in the range 5−35 Hz was applied to each spectrum.

CP/MAS NMR experiments were carried out under the Hartmann−Hahn match condition which was set using adamantane. The ^{1}H 90° pulse length was ~3.5 μs giving a spin-lock and decoupling field strength of ~70 kHz. The experiments were generally carried out with a 1 ms contact time, and a recycle delay of 1.5 s. The acquisition time was typically 30 ms, and the spectral width was 30 kHz. Typically 2000−8000 points were zero-filled to 16 000. Generally 3000−4000 scans were recorded for each sample. Overnight accumulations (30 000+ scans) were carried out for samples of low sensitivity.

To allow the *quantitative* determination of the amounts of each carbon species in a spectrum the single pulse excitation (SPE) method was employed.[6,13] In this, a time delay of 5× ^{13}C spin−lattice relaxation times is inserted between pulses. Typically 800−3000 scans were recorded with a delay between each pulse of between 60 and 100 s. The ^{13}C 90° pulse length was 3.5 μs, and the ^{1}H decoupling field strength was as before. Typically acquisition times were between 0.1 and 0.2 s. To ensure quantitative measurements, tetrakis(trimethylsilyl)silane was used as internal standard for spin counting.[14] This acts as a reference to calibrate the spectra to an accuracy of ±0.3 ppm, but also since its methyl groups have a short ^{13}C T_1 relaxation time, it can be used for "spin counting" in SPE experiments to ensure that the recycle delay is not too short. For quantitative analysis, peak areas were determined by cutting and weighing,[6] and the estimated error was ± 1−2 mol% total carbon.

Nuclear Overhauser enhanced (NOE) solid state NMR spectra were also recorded to enhance the mobile parts of spectra which are often discriminated against using the cross-polarization technique. The approach of Findlay and Harris[15] was adopted.

Proton spin−lattice relaxation experiments were also carried out on a Bruker MSL100 solid state NMR spectrometer using the homonuclear wide line probehead operating at 100.13 MHz for ^{1}H nuclei. Samples were dried in 5 mm NMR tubes under vacuum at 1.33 × 10^{-4} Pa at 60 °C for 12 h to remove any traces of water. They were then loaded into a horizontal solenoid coil. For a relaxation experiment in the laboratory timeframe (T_1) the ^{1}H 90° pulse length was measured by looking for the null point (the 180° pulse) and then halving this value. The 90° pulse length was typically 3 μs and set using the signal from natural rubber. Spin−lattice relaxation times were determined by two methods with single point acquisition, namely, inversion recovery and saturation recovery. Since the initial point of free induction decay (FID) is proportional to the total intensity of the entire spectrum, it is possible to record only the first point of the FID and plot this as a function of time. Therefore, this technique allows a series of FIDS to be collected as a function of the delay, τ. Typically, 256 or 512 FIDS (single points) are collected with four or eight scans. The inversion recovery method was used when the sample had a long T_2 and/or a very fast relaxing component. The disadvantage of this technique is that since it is an equilibrium method, a delay of $5T_1$ is required between each scan. In the saturation recovery experiment the system starts in a nonequilibrium state with the magnetization in the *xy* plane. The relaxation back to the equilibrium state is monitored as a function time, τ. The advantage of this sequence is that it is not necessary to wait for a period of $5T_1$ between scans. The decay curve formed by this method was analyzed by a Simplex approximation followed by a Lavenberg−Marquardt approximation.[16] For relaxation experiments in the rotating time frame ($T_{1\rho}$), the single point acquisition method was used. The proton decoupling field strength was the same as that set up in the CP experiment (~70 kHz) in order to obtain comparable values for the relaxation when determined by this method and CP. The data were analyzed as before.

The errors quoted in Tables 1, 2, 3, 5, 7, and 8 have been estimated from the results; they are not deduced from a rigorous statistical calculation.

Results and Discussion

Model In-House Resins HCR1−3. The ^{13}C CP/MAS NMR spectra of HCR1−3 are shown in Figure 1

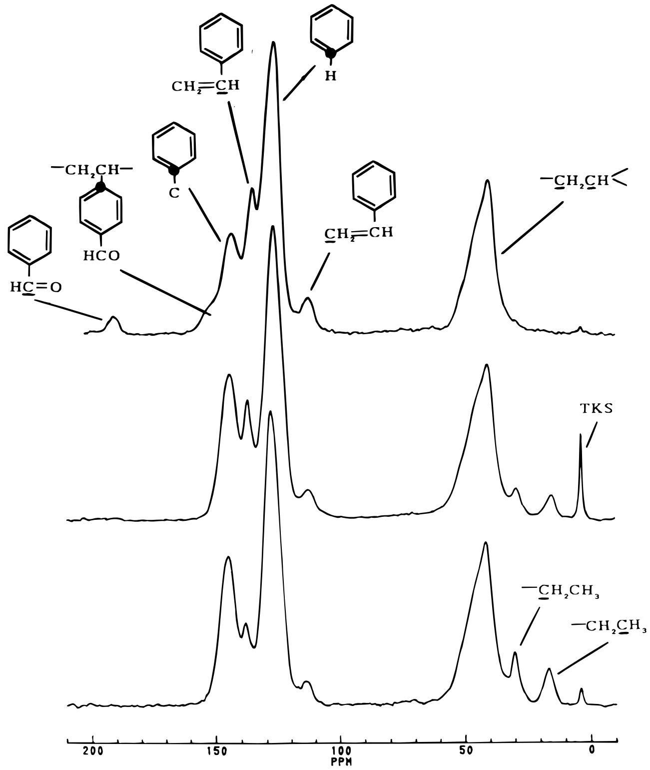

Figure 1. Solid-state (25.2 MHz) ^{13}C NMR CP spectra (top) HCR1, ns = 4000; (middle) HCR2, ns = 4000; (bottom) HCR3, ns = 4000. RD = 1.5 s, LB = 10 Hz (ns = number of scans; RD = recycle delay times; LB = exponential line broadening weighting).

along with the peak assignments. These are in agreement with data in the literature.[3,4] A key feature of the spectra is the presence of resonances due to the methine and methylene carbon atoms of unreacted vinyl groups at ~137.3 and 112.4 ppm respectively. The spectrum of HCR1 also shows the presence of a carbonyl group with a carbon resonance at ~190 pm. The divinylbenzene used in HCR1 was prepared from terephthaldehyde[10] via a Wittig reaction and contained a small level of *p*-vinylbenzaldehyde as a result of incomplete reaction. The clear shoulder at 150 ppm in the spectrum of HCR1 seems to have an intensity similar to that of the carbonyl peak, and most likely arises from the nonprotonated aromatic carbon atom *para* to the aldehyde group. Its position ~10 ppm downfield from resonances due to the normal quaternary carbon atoms attached to the aliphatic polymer chain is consistent with this assignment. The peak due to the nonprotonated carbon attached directly to the aldehyde group would be expected at 140 ppm under the main aromatic carbon resonances. The FTIR spectrum of HCR1 confirms the presence of an aromatic aldehyde with a band at 1703 cm^{-1}. Other important bands are at 1510 and 836 cm^{-1} demonstrating the *para*-substitution pattern of the aromatic rings.

The ^{13}C CP NMR spectra of HCR2 and -3 (Figure 1) show additional resonances in the aliphatic carbon region assigned to the methylene and methyl carbons (at ~29.7 and 14.5 ppm respectively) of the ethyl groups attached to the aromatic residues. These arise from the ethylstyrene component in the two grades of commercial "divinylbenzene" used to prepare these resins.

Comparison of Single Pulse Excitation (SPE) and Normal Crossed Polarization (CP) Experiments. In recent years there has been much debate on the reliability of "quantitative" CP NMR experiments[5,17] and in the case of fossil fuels, where the problems are accentuated by the presence of free radicals, two of us have developed more reliable procedures.[6,7] The same problems occur in polymers, but to a lesser degree, and this has been an underlying issue[18−21] in the quantitative analysis of solid polymers by ^{13}C NMR.

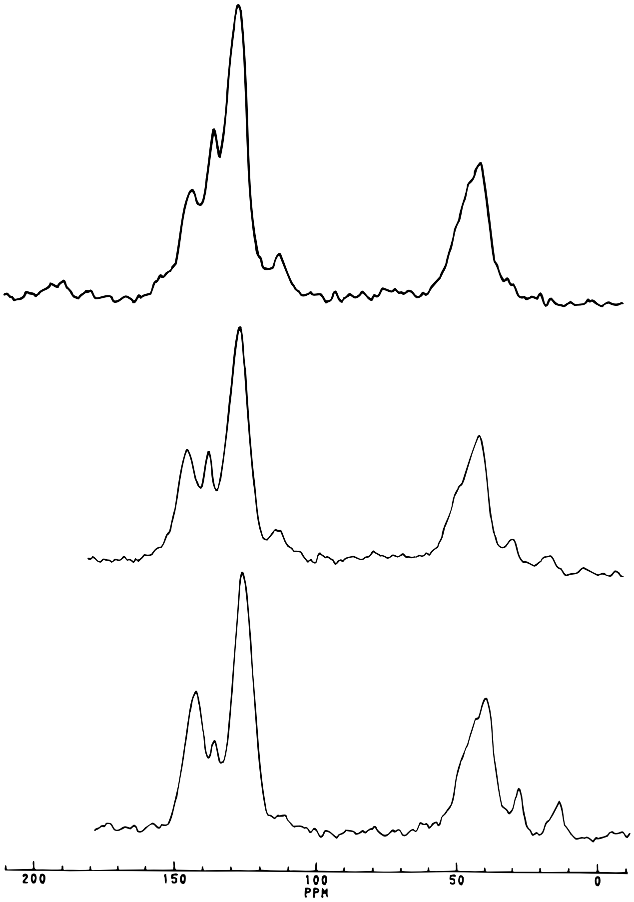

Figure 2. Solid-state (25.2 MHz) ^{13}C NMR SPE spectra (top) HCR1, ns = 800; (middle) HCR2, ns = 800; (bottom) HCR3, ns = 800. RD = 100 s; LB = 35 Hz.

SPE experiments require five times the ^{13}C spin lattice relaxation time between each acquisition (30−100 s) and so are very time-consuming. Additionally, the signal-to-noise enhancement provided by CP experiments is lost. However, SPE experiments can be truly quantitative in terms of counting carbon atom types. Another important factor in quantifying solid state ^{13}C NMR spectra is the presence of spinning side bands. The latter are field dependent and this explains the choice of a low field instrument for the present work.

The solid state SPE ^{13}C NMR spectra for HCR1−3 are shown in Figure 2 and are qualitatively the same as the CP spectra (Figure 1). To be certain that all the carbon atoms were accounted for by SPE, the ^{13}C spin−lattice relaxation times were measured and the data are summarized in Table 1. With the recycle delay between acquisitions chosen to be five times the spin−lattice relaxation time of the longest carbon, all carbon atoms in the sample should be detected. Employing shorter delays would be expected to discriminate against carbon atoms with longer spin−lattice relaxation times. Some enhancement of the $-CH=$, $=CH_2$, $-CH_2-$, and CH_3- signals in the spectra of HCR2 is indeed seen with a shorter recycle delay (RD) (Figure 3). A further check

Table 1. ^{13}C NMR Spin−Lattice Relaxation Times (s) for Model Highly Cross-linked Resins HCR1−3

resin	QC[a]	$-CH=$[b]	ArH[a]	$=CH_2$[b]	aliphatic CH[c]	$-CH_2-$[d]	$-CH_3$[d]
HCR1	13.4	∼1.5	7.6	∼1.2	10.4		
HCR2	18.9	∼1.5	8.9	1.9	9.4	3.6	1.9
HCR3	15.4	∼1.5	9.7	1.8	11.9	4.6	2.1

[a] QC = quaternary aromatic carbon; ArH = protonated aromatic carbon; error ∼ ±4 s. [b] From unreacted vinyl groups; error ∼ ±0.5 s. [c] From polymer backbone; error ∼ ±4 s. [d] From ethyl groups arising from ethylstyrene comonomers; error ∼ ±0.5 s.

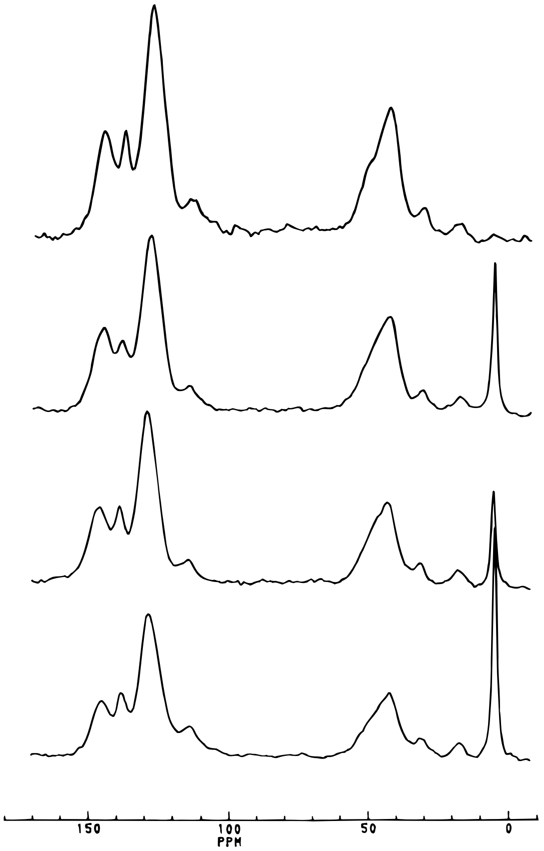

Figure 3. Solid-state (25.2 MHz) ^{13}C NMR SPE spectra of HCR2: (top) ns = 2314, RD = 15 s; (upper middle) ns = 1960, RD = 30 s; (lower middle) ns = 1428, RD = 60 s; (bottom) ns = 1000, RD = 100 s. LB = 35 Hz.

Table 2. Relative Peak Intensities[a] from the CP and SPE Spectra of Resins HCR3

experiment (recycle delay)	$ArH:CH_2=$	$ArH:CH_3-$	$Ar_{tot}:Al_{tot}$[b]
CP (1 ms)	18.9:1	11.7:1	1.42:1
CP (10 ms)	19.2:1	10.9:1	1.77:1
SPE (100 s)	24.7:1	9.3:1	1.48:1

[a] error ∼ ±5%. [b] Ar_{tot} = QC + ArH; Al_{tot} = unreacted vinyl + all aliphatic carbon atoms.

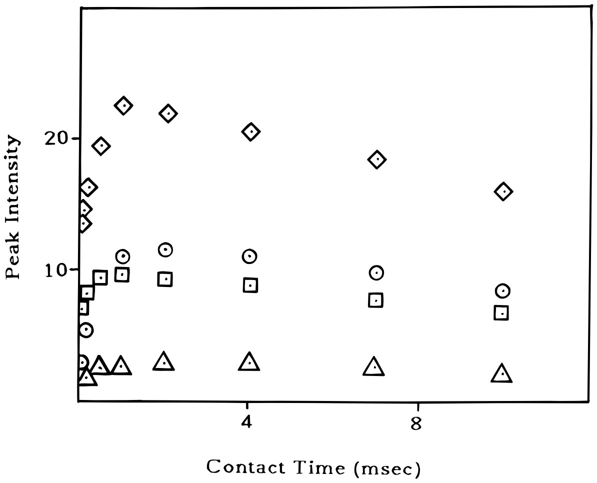

Figure 4. Intensity variation as a function of contact time in CP experiments on HCR2: (△) methyl carbons (15 ppm); (□) aliphatic carbon chain (41 ppm); (◇) protonated aromatic carbons (128 ppm); (○) quaternary aromatic carbons (145 ppm). Intensity units are arbitary.

Table 3. Polarization Transfer Times, T_{CH}, for Carbon Atoms in Resin HCR2

carbon type	T_{CH} (μs)[a]
ArH	60
QC	350
aliphatic carbon backbone	50
CH_3CH_2-	240

[a] error ∼ ±20%.

was also introduced by use of tetrakis(trimethylsilyl)silane (TKS) as an internal standard to measure the total amount of carbon observed in the resins. For HCR1−3 this was ∼100, 94, and 98% respectively. Typical relative peak intensities using CP and SPE experiments are shown in Table 2 for resin HCR3. At longer contact times the CP values for $Ar:CH_2=$ and $ArH:CH_3$ start to approach those of the SPE experiment, but these rotationally mobile groups are still underestimated. With extended contact, polarization transfer is more complete and proton spin−lattice relaxation in the rotating frame is dominant. This results in less distorted relative peak intensities. The values of Ar_{tot}:Al_{tot} for the CP (1 ms) and SPE (100 s) are very similar and in reasonable agreement with the data reported by Ford *et al.*[3,4] of 1.34:1 and 1.59:1 for resins XAD-2 and XAD-4 respectively.

Different carbon atom types undergo polarization transfer at different rates, $(T_{CH})^{-1}$. This can be probed by varying the contact time in CP experiments. Figure 4 shows the results for resin HCR2. T_{CH} values can be calculated from the initial slopes and these data are shown in Table 3. The rate of polarization transfer, $(T_{CH})^{-1}$ is dependent upon the distance between carbon and hydrogen atoms and on local motion. Carbon atoms, which are far from protons or are very mobile, will take a longer time to cross polarize. This then makes it difficult to determine relative peak intensities accurately as the values will change for each chosen contact time in an experiment as seen in Figure 4. Thus carbon atoms with the closest associated protons, i.e. protonated aromatic carbons (ArH) and the aliphatic carbons of the polymer backbone, have very short T_{CH} values. The carbon atoms with more distant protons, such as the nonprotonated aromatic carbons (QC), and the more mobile carbons, such as the methyl carbon atoms, have much longer T_{CH} times.[13,22] On these grounds therefore the latter groups will be adversely discriminated against intensitywise in CP experiments.

Overall therefore these studies confirm that the SPE experiments provide much more reliable quantitative data in terms of relative abundance of carbon atom types.

Quantitative Analysis of SPE ^{13}C NMR Spectra of Resins HCR1−3. Examining firstly the protonated aromatic carbon (ArH) and the methyl carbon signals for resins HCR2 and 3 (*note*: HCR1 contains no ethylstyryl residues) (Table 4), it is clear that there is good agreement with the theoretical values based upon the

Table 4. Ratio of Protonated Aromatic Carbon Atoms to Methyl Carbon Atoms from ^{13}C SPE NMR Spectra

	ArH:CH_3	
resin	exptl	calcd[a]
HCR2	23.5:1	20.0:1
HCR3	9.3:1	8.9:1
XAD-2	8.2:1	N/A
XAD-4	19.3:1	N/A

[a] Assuming comonomers (DVB and EtSt) incorporated as in monomer mixture.

composition of monomer phase employed in the syntheses. For HCR2, the “divinylbenzene” employed was ~35% *m*-DVB, ~16% *p*-DVB, ~31% *m*-ethylstyrene, and ~15% *p*-ethylstyrene, and for HCR3 the “divinylbenzene” composition was ~57% *m*-DVB, ~24% *p*-DVB, ~11% *m*-ethylstyrene, and ~8% *p*-ethylstyrene. The theoretical data in Table 4 were calculated assuming that these comonomer mixtures were incorporated unchanged into the resins, and this seems to be confirmed by the SPE NMR data.

Comparing the peak areas of the protonated aromatic carbon (ArH) signal and the methylene carbon signal (from residual unreacted vinyl groups) in the SPE spectra (Figure 2) of HCR1−3 yields the data in Table 5. Likewise summing the aromatic and aliphatic carbon signals yields the Ar_{tot}:Al_{tot} data. HCR1 is prepared from ~100% *p*-divinylbenzene, and assuming a divinylbenzene isomer content of 81% and 51%, respectively, for HCR2 and -3 theoretical ArH:CH_2= ratios can be calculated assuming *no* cross-linking. Comparing the theoretical ratios and the real ratios hence allows the percent of unreacted divinylbenzene to be computed, and hence the percent reacted in each resin. Finally, from the latter and percent divinylbenzene isomers in the original feed, the percent of all aromatic groups cross-linked, i.e. the effective cross-link ratio, can be calculated.

Techniques other than NMR, notably IR[23−26] and Raman[26−28] spectroscopy have previously been used in an attempt to quantify the level of unreacted vinyl group in poly(styrene-divinylbenzene) resins. However, these techniques rely on the use of model compounds for calibration which can lead to systematic errors. Conventional chemical analyzes have also been employed.[4,28] In principle, for example, exhaustive bromination[28] of residual double bonds followed by elemental bromine microanalysis should be a useful methodology. In practice even these approaches are not without their problems. The ^{13}C CP NMR spectrum of brominated HCR3 is shown in Figure 5 (top). This appears to indicate complete removal of residual vinyl groups with essentially total absence of the CH_2= resonance of ~112 ppm. However, examination of the corresponding SPE spectrum (Figure 5, bottom) indeed shows that while the CH_2= resonance is reduced considerably, a measurable signal remains. It seems therefore that residual double bonds deep in the highly cross-linked and entangled microgel particles in these resins are extremely inaccessible and hence resistant to chemical modification. Elemental bromine analysis would therefore be expected to underestimate the residual double bond content and hence overestimate the effective cross-link ratio.

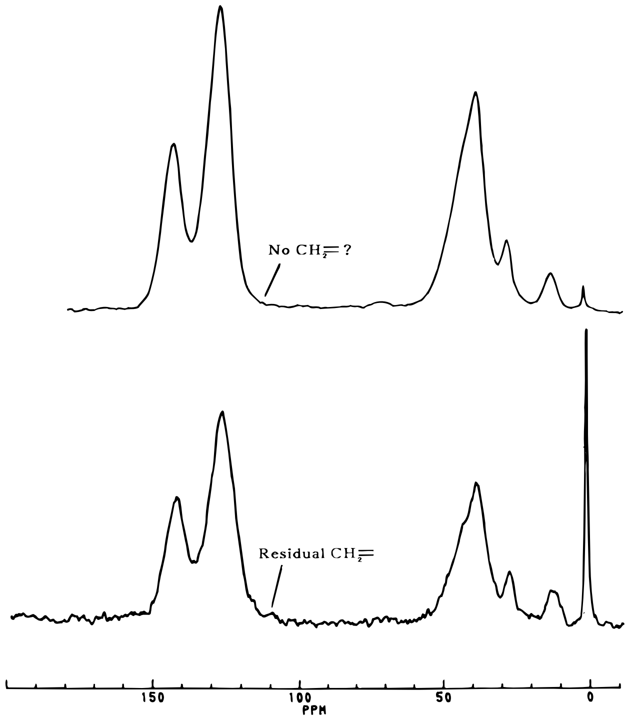

Figure 5. Solid-state (25.2 MHz) ^{13}C NMR spectra of brominated HCR3: (top) CP experiment, ns = 4000, RD = 1.5 s, LB = 15 Hz; (bottom) SPE experiment, ns = 2723, RD = 60 s, LB = 15 Hz.

The present NMR analysis (Table 5) shows that employing ~100% divinylbenzene with toluene as a porogen (1:1 v/v monomer/porogen) yields a resin with ~56% aromatic groups cross-linked; likewise, an ~80% divinylbenzene mixture yields ~45% aromatic cross-links and ~50% divinylbenzene yields ~37% aromatic cross-links. Perhaps not surprisingly therefore the efficiency of cross-linking diminishes significantly at very high levels of divinylbenzene. What is perhaps surprising are the low absolute values of cross-linking (relative to the divinylbenzene feed) i.e. the high absolute values of residual vinyl groups. While this may indeed be a surprise, the ^{13}C SPE spectra (Figure 2) are unequivocal, and even simple visual observation is sufficient to indicate a significant level of residual vinyl groups in each resin.

Table 5. Ratios of Protonated Aromatic Carbon Atoms to Unreacted Vinyl Methylene Carbon Atoms from ^{13}C SPE NMR Spectra and Calculated Levels of Unreacted Vinyl Groups and Effective Cross-Link Ratios

	ArH:CH_2=		DVB feed			
resin	exptl	theoretical[a]	unreacted (%)[b]	reacted (%)	effective[c] cross-link ratio (%)	exptl Ar_{tot}:Al_{tot}[f]
HCR1	9.0:1	4.0:1	44	56	56	1.5:1
HCR2	11.0:1	4.9:1[d]	45	55	45[d]	1.3:1
HCR3	24.7:1	7.8:1[e]	32	68	35[e]	1.5:1
XAD-2	16.6:1	7.8:1[g]	47	53	27[g]	1.7:1
XAD-4	10.4:1	5.1:1[h]	49	51	40[h]	1.4:1

[a] Calculated assuming comonomers incorporated as in feed but second vinyl group of DVB not reacted at all, i.e. no cross-linking. [b] Ratio (%) of column 3 to column 2; error ± 10%. [c] % of all aromatic residues cross-linked. [d] Based on ~81% DVB isomers in feed. [e] Based on ~51% DVB isomers in feed. [f] Ar_{tot} = ArH+QC; Al_{tot} = vinyl + aliphatic carbon; theoretical value = 1.5. [g] Based on 51% DVB in feed, calculated from ArH:CH_3 (see text). [h] Based on 79% DVB in feed, calculated from ArH:CH_3 (see text).

Table 6. N_2 Sorption BET Surface Area Data for Resins HCR1−3, XAD-2, and XAD-4[29]

resin	DVB (%)	porogen/monomer (v/v)	surface area ($m^2\ g^{-1}$)
HCR1	100	toluene 1/1	370
HCR2	51	toluene 1/1	680
HCR3	81	toluene 1/1	610
XAD-2	*a,b*	*a*	315
XAD-4	*a,b*	*a*	490

[a] Not disclosed by manufacturer. [b] See calculated data, this work, Table 5.

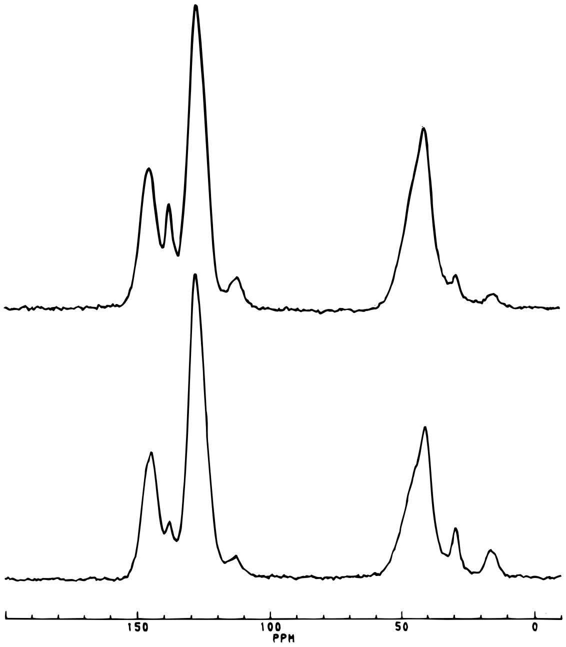

Figure 6. Solid-state (25.2 MHz) ^{13}C NMR CP spectra: (top) XAD-4, ns = 4000; (bottom) XAD-2, ns = 4000. RD = 1.5 s; LB = 10 Hz.

Quantitative Analysis of Commercially Available Resins, XAD-2 and XAD-4. Resins XAD-2 and XAD-4 manufactured by the Rohm and Haas company are well known and widely exploited nonfunctional "poly(styrene−divinylbenzene)" resin sorbents. They have been designed specifically with a macroporous morphology[1,2] in which there is only limited aggregation of the microgel particles, resulting in a rather large surface area as measured by N_2 sorption BET. Our own data for XAD-2 and XAD-4 are shown in Table 6. In synthesising HCR2 and HCR3 we chose levels of divinylbenzene, and toluene as a porogen, in order to generate resins similar to XAD-2 and XAD-4 at least in terms of their surface areas. HCR1 was prepared from ~100% *p*-divinylbenzene as a structurally unambiguous model. Surface area data for HCR1-3 are also shown in Table 6. Superficially, at least therefore the in-house resins are similar to the commercial resins.

The CP and SPE ^{13}C NMR spectra of XAD-2 and XAD-4 are shown in Figures 6 and 7 respectively. Even before attempting a detailed analysis of these the clear visual similarity between the spectrum of XAD-2 and that of HCR3, and between that of XAD-4 and that of HCR2 is apparent and all the assignments correspond to those shown in Figure 1 for the HCR series. Although from time to time authors have speculated about the comonomer compositions of XAD-2 and XAD-4,[25,28,30] there appears to be no definitive information in the open literature, and in any event, we chose an *ab initio* method to disregard earlier calculations and speculations.

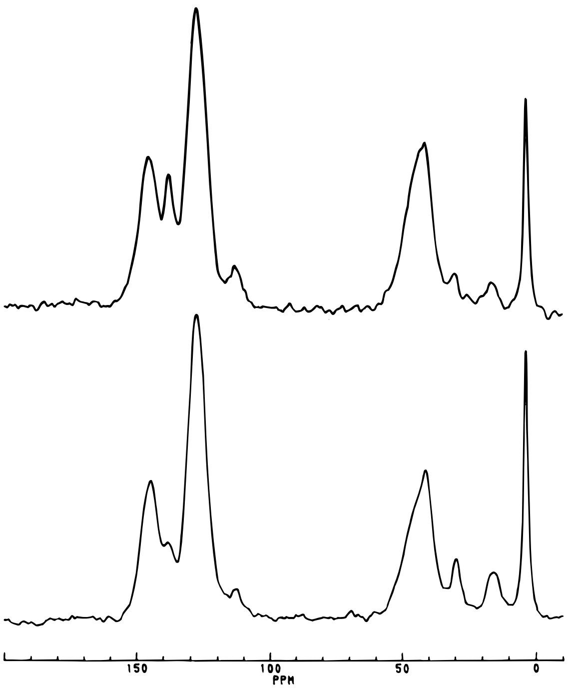

Figure 7. Solid-state (25 MHz) ^{13}C NMR SPE spectra: (top) XAD-4, ns = 1237; (bottom) XAD-2, ns = 2277. RD = 60 s; LB = 35 Hz.

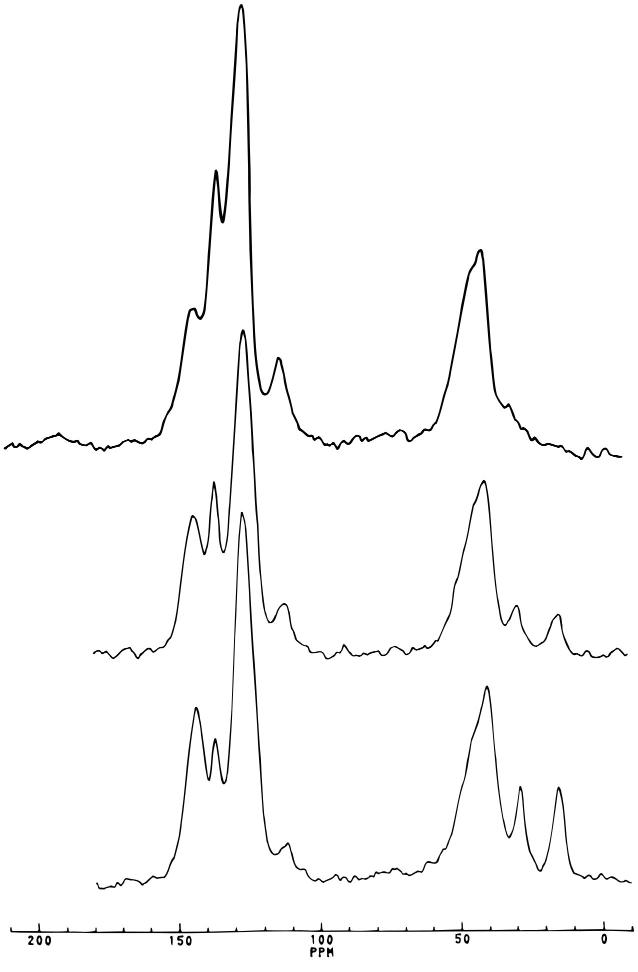

Figure 8. Solid-state (25 MHz) ^{13}C NOE NMR Spectra: (top) HCR1, ns = 800; (middle) HCR2, ns = 800; (bottom) HCR3, ns = 800. RD = 100 s; LB = 35 Hz.

Our own spectroscopic evidence suggests firstly that there is no styrene component in the comonomer feeds. Analysis of the SPE ^{13}C NMR spectra of XAD-2 and

Table 7. NOE Factors for Carbon Atoms in Resins HCR1−3

carbon type	chem shift (ppm)	NOE (η)[a]		
		HCR1	HCR2	HCR3
QC attached to backbone	144.6	0.2	0.3	0.3
$-CH=$	137.3	0.6	0.6	0.6
ArH	127.2	0.5	0.4	0.4
$=CH_2$	112.4	0.7	0.7	1.0
backbone CH/CH_2	40.9	0.4	0.4	0.4
$-\mathit{C}H_2CH_3$	29.7		0.9	0.8
$-CH_2\mathit{C}H_3$	14.5		1.2	1.4

[a] Error ∼ ±5%.

XAD-4 shows that the Ar_{tot}:Al_{tot} ratios (Table 5) are close to 1.5:1, the theoretical value for a resin composed only of divinylbenzene and ethylstyrene residues. Linear polystyrene yields a value of 3.0:1. The FTIR spectra are also very diagnostic. There is a complete absence of bands at 1028 and 760 cm^{-1} characteristic of monosubstituted phenyl groups, and hence styryl residues.[23] This is in accord with earlier Raman spectroscopic studies of XAD-2[28] and designed copolymers of ethylstyrene/divinylbenzene and styrene/divinylbenzene.[27] The SPE NMR spectra also allow evaluation of the ArH:CH_3 ratios (Table 4) and the superficial similarity between XAD-2 and HCR3 and that between XAD-4 and HCR2 are confirmed quantitatively in these data. Assuming an absence of styryl residues allows calculation of the levels of divinylbenzene and ethylstyrene residues in these resins. For XAD-2 the ethylstyrene content is ∼49% and the divinylbenzene content ∼51%. For XAD-4 the corresponding figures are ∼21% and 79% respectively. Assuming these data reflect the composition of the feed, there is a remarkable similarity with the composition of the two grades of "divinylbenzene" routinely available commercially. Indeed, as mentioned earlier, our syntheses of HCR2 and HCR3 are based upon these two grades of commercially sourced "divinylbenzene".

Assuming these comonomer feed compositions for XAD-2 and XAD-4 it is now possible to revisit their SPE NMR spectra and perform the same analysis as earlier to determine the residual levels of vinyl groups in these resins and their effective cross-link ratios. The resultant data are shown in Table 5. As for HCR1−3, despite the relatively high levels of divinylbenzene isomers used in the comonomer mixtures their consumption is rather inefficient, and the effective cross-link ratios are far lower than might have been anticipated. Again, therefore very significant levels of vinyl groups must remain buried within the cross-linked microgel regions of these resins. The structural similarity between XAD-2 and HCR3, and between XAD-4 and HCR2 is also confirmed, bearing in mind the experimental limitations of the analyzes and the totally different source of these materials and their precursors. With care therefore it seems that application of SPE experiments offers an extremely powerful tool for evaluating the molecular structural composition of resins of this type.

Nuclear Overhauser Enhancement (NOE) and Relaxation Measurements. In principle NOE data and relaxation experiments may provide additional information on cross-linking in resins. Absolute NOE values were measured by comparing the relative intensities of peaks obtained from 100 s recycle delay SPE experiments (Figure 2) with those from NOE experiments with a 60 s pulse saturation train of the same number of scans (Figure 8). The results are shown in Table 7. Within a given resin there are obvious differences which can be rationalized in terms of local motions within the polymer structure. The most mobile carbons are those in the methyl groups in the ethylstyrene residues. These show the highest degree of enhancement. Likewise the associated methylene group in the ethyl functions is relatively mobile. Although conjugated with the aromatic ring the vinyl group also is rather mobile reflected in the enhancements for both the methylene and methine carbons, and particularly the former. The protonated aromatic carbon atoms are more mobile than their nonprotonated counterparts, and the latter, like the backbone methine and methylene carbons, are rather rigid. It was thought that the level of cross-linking might influence some of these motions and therefore be reflected in the NOE factors. However, this proves not to be so. The differences between the data for the various resins are small, and no systematic trends are evident. NOE factors are influenced by motions in the MHz frequency range as reported before,[31] and perhaps on reflection changes in cross-link density would not therefore be expected to be influential.

In contrast spin−lattice relaxation in the rotating frame (^1H $T_{1\rho}$) is sensitive to KHz motions within polymer molecules and may therefore be more indicative of cross-linking than spin−lattice relaxation in the laboratory frame (^1H T_1). Relevant relaxation times are summarized in Table 8. In the case of the ^1H T_1 measurements, in addition to the resins HCR1−3 previously examined, a more extensive matrix of materials was looked at in which the toluene porogen:monomer v/v ratio used in resin synthesis was adjusted from the normal 1:1 value. Clearly there are no large variations in the ^1H T_1 data and certainly no trends with level of cross-linker nor with the porogen:monomer ratio. In the case of ^1H $T_{1\rho}$, there are significant differences even accounting for the likely experimental error. Unfortunately the trend in ^1H $T_{1\rho}$ does not correlate exactly with the effective cross-link ratio of these three resins (Table 5) although HCR1, which is significantly more cross-linked than both HCR2 and 3 and contains only *para*-aromatic linkages, does display a significantly lower relaxation time (rotating frame) than the other two. To some extent therefore motions in the KHz frequency range and the level of cross-linking do seem to be interrelated although a strict correlation may be disturbed by different levels of the very mobile ethyl groups in HCR1−3.

Table 8. Spin−Lattice Relaxation Times[a] for HCR1−3 Resins

ratio (v/v) toluene porogen: monomer in resin[c]	HCR1		HCR2		HCR3	
	^1H T_1 (s)	^1H $T_{1\rho}$ (ms)	^1H T_1 (s)	^1H $T_{1\rho}$ (ms)	^1H T_1 (s)	^1H $T_{1\rho}$ (ms)
0.5:1	0.36	*b*	0.54	*b*	0.63	*b*
1:1[c]	0.40	17	0.45	62	0.56	43
2:1	0.37	*b*	0.36	*b*	0.49	*b*
3:1	0.41	*b*	0.50	*b*	*b*	*b*

[a] Error ±10% throughout. [b] Not recorded. [c] 1:1 v/v corresponds to HCR1−3 used in all other studies.

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