Carbon-13 Nuclear Magnetic Resonance Relaxation in Cross-Linked Polystyrene Gels

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ABSTRACT: Carbon-13 NMR spin–lattice relaxation times, line widths, nuclear Overhauser effects, and relative signal areas at 25.2 MHz in $CDCl_3$ at 30 °C have been measured for copolymers of styrene with 25 wt % (chloromethyl)styrenes cross-linked with 0–10% divinylbenzene. As cross-linking increases T_1 is almost invariant, line widths increase markedly, NOE ratios decrease significantly, the aliphatic signal area decreases markedly, and the aromatic signal area remains constant up to 6% cross-linker and decreases with 10% cross-linker. The results are discussed in terms of distributions of correlation times for polymer motions. A model is suggested for cross-linked polystyrene structure in which there are numerous linear polymer chains attached to the polymer network at only one end.

Dynamic NMR spectroscopy has been used to study molecular motion in a large number of polymers in solution and a smaller number of polymers as amorphous solids. Most solution experiments have used ^1H and ^{13}C nuclei. Amorphous solid studies have used mainly ^{13}C. Analysis of the relaxation times T_1 and T_2 and the nuclear Overhauser enhancement (NOE) of ^{13}C NMR spectra has enabled formulation of models in which broad distributions of correlation times are used to describe motions of high polymers in solution.[1-5] These data usually cannot be explained by a single correlation time model. Cross-polarization ^{13}C experiments on solids have been used to find rotating-frame correlation times ($\tau_{1\rho}$), cross-polarization relaxation times (τ_{CH}), and NOE's that also can be interpreted in terms of distributions of motional frequencies.[6,7]

Our interest in polymer motions centers on the cross-linked polystyrenes commonly used as supports for polymer-supported synthesis and catalysis, as the packings in gel permeation chromatography, and as the copolymer backbones for most ion-exchange resins. These cross-linked polystyrenes are usually employed in a solvent-swollen gel state. To learn about the motional behavior of the cross-linked polystyrenes we are currently using as supports for polymeric phase-transfer catalysts[8] and for organic syntheses, we have determined dynamic ^{13}C NMR parameters for styrene/(chloromethyl)styrene copolymers cross-linked with up to 10% divinylbenzene. Spectra of the least cross-linked gels have narrow lines resembling those of polymer solutions. Spectra of the more highly cross-linked gels have broad lines similar to spectra of amorphous solids which have been sharpened by dipolar decoupling and magic-angle spinning.

Previous ^{13}C NMR investigations of some polymers at temperatures well above T_g and as solvent-swollen gels have shown that high-resolution spectra may be obtained without use of cross polarization, magic-angle spinning, or dipolar decoupling. Gels of poly(vinyl chloride) in a poor solvent and a cross-linked ethylene/maleic anhydride copolymer give ^{13}C NMR spectra well enough resolved to reveal microstructure, but their ^1H NMR spectra have no high-resolution signals.[9] Hydrophilic gels of poly(*N*-vinylpyrrolidone) in D_2O have ^{13}C NMR spectra whose line widths depend upon water content.[10] Copolymers of *N*-vinylpyrrolidone and methyl methacrylate have sharp lines for the *N*-vinylpyrrolidone repeat units but no sharp PMMA peaks in D_2O and sharp lines for the PMMA repeat units but no sharp peaks for the PVP repeat units in $CDCl_3$.[10] Thus polymer gels show high-resolution ^{13}C NMR spectra in good solvents and only broad-line spectra in poor solvents. Fibrous proteins such as elastin and collagen have ^{13}C NMR spectra with high-resolution components when highly hydrated.[11] Cross polarization sharpens the broad-line components of the elastin and collagen spectra.[11] The only published ^{13}C NMR spectra of cross-linked polystyrenes show high-resolution in swelling solvents and have been used to estimate the degree of functionalization of resins for solid-phase peptide synthesis.[12] All of the experiments reported here have employed conventional PFT conditions at 25.2 MHz in $CDCl_3$, a good swelling solvent, to produce the highest resolution possible without use of solid-state techniques.

Experimental Section

Suspension copolymers of styrene, (chloromethyl)styrene (Dow Chemical Co., 60/40 *m*/*p* isomers), divinylbenzene (Polysciences, 55% active), and ethylvinylbenzene were prepared by methods to be described elsewhere.[8] Each sample was washed thoroughly with water, dried under vacuum, Soxhlet extracted with chloroform, and dried under vacuum before use. The soluble polystyrene sample from Polysciences (MW = 20 000) was precipitated from toluene into methanol twice and dried under vacuum. Its viscosity-average molecular weight ($\bar{M}_v$) was determined to be 24 900 in chlorobenzene at 25.7 °C, using *K* and *a* values from the literature.[13]

Styrene-*co*-(chloromethyl)styrene was prepared by suspension polymerization, precipitated from toluene into methanol three times, and dried under vacuum. A series of solutions of the copolymer (0.150, 0.425, 0.782, 0.895, and 1.198 wt %) was prepared in chlorobenzene and the intrinsic viscosity $[\eta]$ was determined to be 1.1 at 25.7 °C from a plot of η_{sp}/c vs. c (in g/100 mL). Using *K* and *a* values for poly(α-methylstyrene-*co*-styrene) from the literature[14] as a model, we estimated the molecular weight $\bar{M}_v$ to be 49 600.

NMR samples of gel polymers were prepared by weighing dry polymer into a 12-mm tube and adding enough $CDCl_3$ to completely swell the polymer but leave no more than a 4-mm depth of solvent that contained no polymer beads at the bottom of the tube. Sample height was at least 30 mm, and the sample was centered in the receiver coil of the instrument. When poly(ethylene glycol) (Polysciences, MW = 1500) internal standard was used, it was weighed separately and dissolved in $CDCl_3$, and the solution was added to the dry polymer in the NMR tube. The more highly cross-linked polymers were prepared at least 12 h before use to attain complete swelling. NMR spectra were obtained at 25.2 MHz and ambient probe temperature (27–30 °C) with a Varian XL-100(15) spectrometer equipped with a Nicolet TT-100 PFT unit and quadrature phase detection. The ^2D resonance of the solvent was used for frequency lock. Sample spinning rates were 10–12 Hz. Spectra for line-width measurements contained 8K or 16K data points over a 6000- or 10 000-Hz frequency range with 4000–20 000 acquisitions. The 90° pulse width was 25 μs. Acquisition times ranged from 1.0 to 2.75 s with no delay between acquisitions. No line broadening was used. Line widths at half-height were measured on spectra expanded to a

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Table I

^{13}C T_1's, Line Widths, and NOE Ratios of Cross-Linked Polystyrenes at 25.2 MHz in $CDCl_3$ at 30 °C

sample[a]	wt % polymer in $CHCl_3$	T_1, ms					line width, Hz				NOE ratio[b]	
		o,m	p	methine	methylene	CH_2Cl	o,m	p	methine	CH_2Cl	arom	aliph
polystyrene	10	124	114	97	59		20	14	15		2.05	2.27
un-cross-linked	10	c	c	c	c	c	20.5	14	15	8	c	c
copolymer	19	c	c	c	c	c	21.5	15	15	8	2.13	2.20
	25	123	106	97	65	141	21	15	15.5	9	2.14	2.25
0.5% DVB	11	c	c	c	c	c	25.5	20	14	9	c	c
1.0% DVB	10	112	102	93	50	155	40	d	16	11.5	2.10	2.25
2.0% DVB	17	100	100	72	56	132	95	d	22.5	15.5	1.57	1.94
4.0% DVB	26	93		73	51	104	180		36	~15	1.58	1.85
6.0% DVB	30	113		78	72	110	~260		~65	~34	1.40	1.88
10.0% DVB	33	c	c	c	c	c	~470		d	d	1.55	1.92

[a] All copolymers contain 25% (chloromethyl)styrenes and the percent divinylbenzene indicated by weight. [b] Signal area fully ^{1}H decoupled divided by signal area gated decoupled. [c] Not determined. [d] Could not be measured.

500- or 1000-Hz frequency range. Spectrometer base line was used except for the CH_2Cl signal, for which a base line was drawn through the peak tops of the backbone methylene signals. Spectra of several polymers were repeated with fresh samples after several months, and from duplicate and triplicate results on these samples the line widths are reproducible to ±10% for cross-linked polymers and ±5% for soluble polymers.

Spin-lattice relaxation times T_1 were measured by the fast inversion recovery method with 4K or 8K data points in a 6000-Hz frequency range (8–12 spectra, 2400–6000 acquisitions per spectrum, 0.68- or 1.36-s acquisition time, 0–5-Hz line broadening, no delay after acquisition). Intervals τ between the 180 and 90° pulses ranged from 1 to 300 ms with usually 1 or 2 spectra at τ = 600–1000 ms. The three adjustable parameter method[15] was used to calculate T_1 from the intensities of peak maxima and minima. Occasionally when the signal-to-noise ratio was too low on backbone methylene signals, their intensities were determined from plotted spectra instead of by the Nicolet T1IR computer method, and the same three-parameter FIR program was used to calculate T_1. Estimated accuracy of the T_1 values is ±10% when $T_1 > 100$ ms, ±10 ms when $T_1 < 100$ ms, and ±30% for T_1's of backbone methylene carbons. Use of integrated aromatic and aliphatic signal areas instead of intensities at the peak maxima gave the same T_1's within experimental error.

NOE ratios and relative signal areas were measured by two methods. First, gated decoupled spectra were compared with fully decoupled spectra. The pulse sequence was (25-μs (90°) pulse–50-μs delay–1.02- or 1.36-s acquisition–10.14-s delay with decoupler off). Either 4K or 8K data points over a 6000- or 10 000-Hz frequency range centered 1500 Hz downfield from Me_4Si, 4000-7000 acquisitions, and 1–10-Hz line broadening were employed. Signal areas are averages of at least three electronic integrations. Spectra were rephased before each integration. Relative aromatic and aliphatic signal areas were checked by cut-and-weigh integration, but the latter results were less precise because of greater uncertainty in estimating base lines. The T_1 of poly(ethylene glycol), MW = 1500, in a 10% solution of polystyrene, MW = 20 000, in $CDCl_3$ was 0.98 s. Since the T_1's of solvent molecules decrease in the presence of gel polymer beads,[16] the T_1 of PEG never exceeded 1.0 s in these experiments, and each gated decoupled spectrum had a delay of $\geq 10T_1$ that allowed complete relaxation of poly(ethylene glycol). NOE ratios and relative signal areas are based on signals of the five protonated aromatic carbon atoms in samples with up to 2% cross-linker, and on signals of all six aromatic carbon atoms with ≥4% cross-linker in which the ipso carbon signal is not resolved from the other aromatic carbons. The T_1 of the ipso (nonprotonated) carbon atom of soluble polystyrene was 1.14 s; T_1 of the ipso carbon atom in cross-linked polymers was not measured. The errors in signal areas due to incomplete relaxation of the ipso carbon atom are insignificant compared with the other random errors in the measurements.

NOE ratios and relative signal areas also were determined from comparisons of fully coupled and fully decoupled spectra by using 4K or 8K data points, acquisition times of 0.68–1.36 s, a frequency range of 6000 or 10 000 Hz, 8000–20 000 acquisitions per spectrum, 2–5-Hz line broadening, and only a 0.14-s delay. The short delay and unknown T_1 of poly(ethylene glycol) in polymer gel samples prevented comparison of polystyrene signal areas to the internal standard.

The wt % $CHCl_3$ in swollen cross-linked polystyrenes was measured by weighing dry polymer into a fritted glass funnel, soaking it in $CHCl_3$ for 2–12 h, removing excess $CHCl_3$ by centrifugation for 5 min, and reweighing the swollen sample. Values reported are averages of 2 or 3 determinations.

Results

The ^{13}C NMR T_1, line width, and NOE ratio data for sytrene-*co*-(chloromethyl)styrene containing 25 wt % (chloromethyl)styrene and 0–10% divinylbenzene in $CDCl_3$ at 30 °C are in Table I. As cross-linking increases there is an apparent minimum in T_1 of the aromatic carbon atoms at 4% DVB, but the largest and smallest T_1 values in the series are almost within experimental error of one another. The aliphatic carbon T_1's and the chloromethyl carbon T_1's decrease slightly as the degree of cross-linking increases. Previous reports of polystyrene ^{13}C T_1's show a small solvent dependence with the longest T_1's in the least viscous solvents.[17-24] Our results for soluble polystyrene in $CDCl_3$ agree within 10% with earlier data obtained in low-viscosity solvents at 30–40 °C when spectrometer frequency differences are taken into account.

The line widths in ^{13}C NMR spectra of styrene-*co*-(chloromethyl)styrene are the same as those of polystyrene over a 10–25% range of concentration, even though the viscosity of the 25% solution is much greater than that of the 10% solution. The line widths in spectra of soluble polymers are due at least in part to unresolved stereochemical heterogeneity of the aliphatic methine and the aromatic carbons. Partial resolution to the hexad level for the ipso (nonprotonated) aromatic carbon atoms and to the pentad level for the backbone methylene carbon atoms has been observed in atactic polystyrene.[25,26] Our spectra in these regions resemble those of atactic polystyrene. Cross-linking increases the breadth of the aromatic region of the spectra dramatically as the ortho, meta, and para carbon resonances merge into a single broad band that even overlaps with the ipso carbon resonance at ≥4% cross-linking. Aliphatic carbon signals also become broader as cross-linking increases until with 10% cross-linker no distinct peaks for the backbone methine and chloromethyl carbon atoms can be seen. The aliphatic band appears to broaden less than the aromatic band as cross-linking increases, but the aliphatic signal area decreases markedly as cross-linking increases.

The NOE ratios in Table I for the soluble polymers agree with literature values at 30–40 °C for atactic polystyrene and for ring-methyl derivatives of polystyrene to ±0.1.[19-24] The NOE ratios decrease as cross-linking increases, and the decrease is greater for the aromatic signals

Table II
Aromatic and Aliphatic ^{13}C Signal Areas in Cross-Linked Polystyrenes

sample[a]	gated decoupled spectra[b] arom/ PEG	aliph/ PEG	aliph/ arom	fully coupled spectra[b] aliph/arom
polystyrene	0.98	0.87	0.89	0.89
un-cross-linked copolymer				
10% soln	*c*	*c*	0.87	*c*
19% soln	*c*	*c*	0.84	*c*
25% soln	*c*	*c*	0.87	0.91
0.5% DVB	0.96	0.84	0.88	0.84
1.0% DVB	1.12	0.86	0.77	0.77
2.0% DVB	1.06	0.76	0.72	0.60
4.0% DVB	0.93	0.50	0.54	0.58
6.0% DVB	1.04	0.45	0.43[d]	*f*
10.0% DVB	0.48	0.20	0.42[e]	*f*

[a] See Table I, footnote *a*. [b] Signal areas per carbon atom. PEG is poly(ethylene glycol), MW = 1500, used as internal standard. [c] Not determined. [d] 0.51 in a separate determination with shorter delay between acquisitions. [e] 0.56 in a separate determination with shorter delay between acquisitions. [f] Could not be measured.

than for the aliphatic signals.

Peak areas per carbon atom for the aliphatic and aromatic resonances in gated decoupled spectra are compared with the peak area per carbon atom of a poly(ethylene glycol) internal standard in Table II. Some of the gated decoupled spectra are shown in Figure 1. The aromatic/PEG area ratio is effectively 1.0 for samples with up to 6% cross-linking, but the aliphatic/PEG and aliphatic/aromatic area ratios decrease as cross-linking increases to 6%. Both aromatic and aliphatic peak areas are reduced at 10% cross-linking. The results were confirmed for some samples by comparisons of peak areas in fully coupled spectra. Agreement between the gated decoupled and fully coupled aliphatic/aromatic area ratios is remarkably good.

Discussion

Data in Table I demonstrate that the changes in T_1, line width, and NOE with increased cross-linking are due to the cross-linking itself and not just to increased concentration of polymer in the gel. The 10–25% solutions of polystyrene and polystyrene-*co*-(chloromethyl)styrene have the same concentrations in $CDCl_3$ as the 0.5–4% cross-linked gels, but only the gel relaxation data vary with concentration.

T_1, line width, and NOE data for soluble polystyrenes cannot be explained by a single rotational correlation time (τ_c) for motion of backbone carbon atoms or by two correlation times for aromatic carbon atoms due to polymer backbone motion and to libration of the aromatic rings.[1-5] Neither can the cross-linked polystyrene ^{13}C relaxation data be explained by a single τ_c. All of our data require a distribution of correlation times for dipolar relaxation of the ^{13}C nuclei. Several methods are available for calculation of distributions of correlation times in soluble polymers,[1-5] but we choose not to apply them and to discuss our results only qualitatively because none of the measurements truly represent the entire sample. We elaborate on this point later.

As cross-linking increases, T_1's of backbone and aromatic ^{13}C nuclei change little, line widths increase greatly, and NOE ratios decrease significantly. Cross-linking causes low-frequency motions in the polymer that affect T_2 and NOE processes but have little effect on T_1. The small decreases in T_1 of the CH_2Cl group as cross-linking increases indicate that those T_1 values are on the motional narrowing side of the minimum value of T_1, attained at $\tau_c \sim 5 \times 10^{-9}$ s in a 25.2-MHz ^{13}C experiment. The internal rotational motion of the CH_2Cl group makes its T_1 longer than that of any other protonated carbon atom in the polymer in all samples.

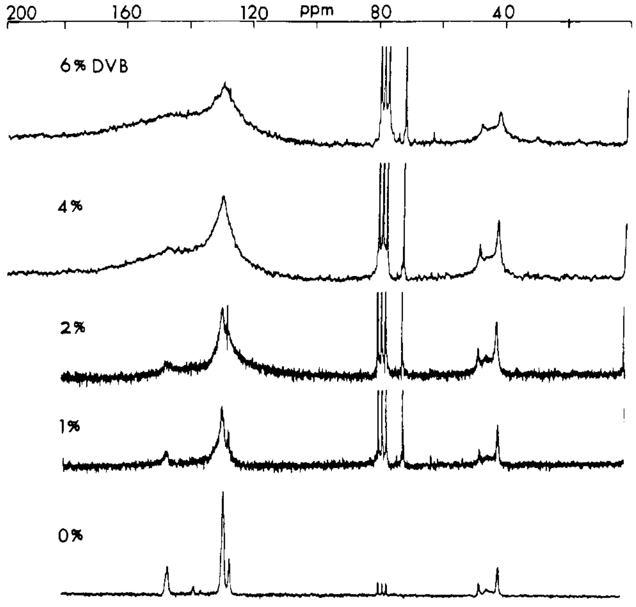

Figure 1. Gated decoupled ^{13}C NMR spectra of polystyrenes containing 25 wt % (chloromethyl)styrenes and 0–6% divinylbenzene. Spectra of cross-linked samples were taken with a 10-s delay between acquisitions and contain poly(ethylene glycol) as internal standard. The $CDCl_3$ and PEG peaks have been truncated. The spectrum of soluble polymer was taken with a 1.0-s delay between acquisitions, and the sample contains no PEG. Peak assignments are as follows: aromatic C_1, 145.3 ppm; aromatic $C_{2,3,5,6}$, 127.9 ppm; aromatic C_4, 125.8 ppm; CH_2Cl, 46.4 ppm; backbone methylene, 40–47 ppm; backbone methine, 40.4 ppm.

It may be instructive to compare the line widths in a ^{13}C NMR spectrum of solid polystyrene obtained with dipolar decoupling and magic-angle spinning[28] to line widths in the spectrum of a cross-linked polystyrene gel. In the former (Figure 5 of ref 28) the aromatic and aliphatic line widths are about 300 and 900 Hz, while in the most nearly comparable spectrum in our work, that of the 6% cross-linked polymer in Figure 1, the aromatic line width is 240 Hz with an additional broad shoulder on its low-field side, but the methine and CH_2Cl signals in the aliphatic region are still till clearly seen and only 65- and 28-Hz wide. If we assume that the line widths in the spectrum of solid polystyrene are due strictly to T_2 processes (all dipolar couplings and chemical shift anisotropies have been removed), then comparison with spectra of cross-linked gels indicates that cross-linking limits the aromatic ring motions that affect aromatic ^{13}C T_2's more than it limits backbone motions responsible for T_2's of all ^{13}C nuclei. That assumption seems unreasonable. A better explanation for the relative differences in line widths between the spectra of solid polystyrene and of polystyrene gels is that magic-angle spinning failed to remove all of the dipolar broadening in the aliphatic region of the spectrum of the solid. The signal area comparisons discussed next support the latter explanation.

The most remarkable effect of cross-linking on ^{13}C NMR spectra of polystyrene gels is the decrease in signal area of the aliphatic resonances relative to both the internal standard and the aromatic signal area. The same effect occurs in gated decoupled spectra that have a pulse repetition time of 11.5 s and in completely coupled spectra that have a pulse repetition time of 0.75 or 1.5 s. Therefore the signal area losses cannot be due to large increases in T_1 of part of the aliphatic carbon atoms. T_1 increases with correlation time when $\tau_c > 10^{-8}$ s. Previous investigations of fibrous proteins[11] and of hydrophilic polymer gels[10] also found decreased intensity or absence of some signals in ^{13}C NMR spectra. The most likely explanation for the disparity in signal areas is that cross-linking limits motion of some of the backbone carbon nuclei so that they are dipolar coupled, and the resulting broad signals are not distinguishable from base line in our spectra. Effectively the aliphatic/PEG and aromatic/PEG signal area ratios indicate the fractions of aliphatic and aromatic carbon atoms that undergo isotropic reorientation at a frequency $>10^6$ s^{-1}. Low-frequency motions ($<10^6$ s^{-1}) are present in the backbones of all of the cross-linked polymers. The aromatic carbons maintain isotropic reorientation up to a 6% level of cross-linking but lose signal area with 10% cross-linking. The aromatic carbons can maintain isotropic reorientation at higher cross-linking than can the aliphatic carbons because they have an oscillatory motion about the sp^2–sp^3 single bond available to them that the aliphatic carbon atoms lack. This motion is effective in relaxing $C_{2,3,5,6}$ of the aromatic ring but not C_1 and C_4. Proof for its effect in T_1 processes can be seen in the T_1 data in Table I and in ^{13}C T_1 data on polystyrene in the literature,[17–20,22–24] in which $C_{2,3,5,6}$ consistently have about a 10% longer value of T_1 than does C_4. Studies of T_1 in ^{1}H NMR of cross-linked *cis*-1,4-polybutadiene and other cross-linked polymers have shown that T_1 is determined by high-frequency motion and is not affected much by changes in cross-link density.[27]

The loss of theoretical signal areas with increased cross-linking calls attention to other difficulties in interpretation of NMR relaxation data on polymers. A fundamental problem is that the carbon atoms giving rise to a particular spectral band are structurally heterogeneous. The heterogeneity can be due to differences in primary stereochemical sequences and in the many local conformations available to the polymer chains. In the cross-linked polystyrenes there is far greater heterogeneity than in homopolymers because seven different monomers (styrene, *m*-(chloromethyl)styrene, *p*-(chloromethyl)styrene, *m*-divinylbenzene, *p*-divinylbenzene, *m*-ethylstyrene, and *p*-ethylstyrene) are incorporated into the network, and branches in the network may restrict motional freedom of atoms several bonds away from the branch points. The T_1 values in Table I and most other polymer ^{13}C T_1 values in the literature are based on peak intensities at the maxima of broad spectral bands. These intensities are due to weighted averages of all of the different carbon nuclei giving an NMR signal at the frequency of the band maximum. Those carbon nuclei having the narrowest natural line width contribute most to the intensity at the maximum, and those having the greatest line width contribute least. Dipolar coupled carbon nuclei do not contribute at all. All polymer T_1 values measured by peak intensities necessarily weigh most heavily the fastest relaxing carbon atoms. We calculated some T_1's by using integrated signal areas instead of intensities at peak maxima, but the results did not change. T_1 is insensitive to low-frequency motions and is insensitive to rotational correlation times in the experiments of Table I.

Measurements of T_2 suffer from similar difficulties. If the spectral bands are broad, the contribution from field inhomogeneities, T_2*, to the observed line width is small. The ^{13}C nuclei causing the signal are structurally heterogeneous. Sometimes individual lines can be resolved for different stereochemical sequences, as in the aromatic C_1 and backbone methylene signals of polystyrene, but when the dispersion of chemical shifts is not great enough to allow resolution, as in the backbone methine signal of polystyrene, one cannot tell how much of the line width at half-height is due to natural T_2 and how much is due to structural heterogeneity. Another problem with the use of line widths to measure T_2 is that they also tend to weigh more heavily the carbon atoms having the narrower natural line widths. Carbon nuclei that have longer rotational correlation times give wider bands that contribute less to intensity between the frequencies where intensity is half of its maximum value ($I = I_{\max}/2$).

If T_2 was measured by a multipulse method, such as the Carr–Purcell method or one of its improved versions, and peak intensities were used for the T_2 calculation, the results would be biased in favor of the fastest relaxing nuclei just as the T_1 values obtained from peak intensities are in principle. One could use integrated signal areas instead of peak intensities to calculate T_1 and T_2 values more representative of the average carbon nuclei in the heterogeneous sample, but even relaxation data calculated from integrated signal areas would not be true averages if some of the nuclei were dipolar coupled and not counted in the integrals. NOE measurements, which normally employ integrated signal areas rather than peak intensities, also weigh the faster relaxing nuclei more heavily if dipolar coupling causes some of the nuclei not to be counted in the integrals. We conclude there is no way to measure relaxation times of heterogeneous polymers, in which some signal is lost by dipolar coupling, that does not bias the measurement in favor of the faster relaxing nuclei.

Even though it is not possible to obtain representative values of T_1, T_2, and NOE in the cross-linked polystyrene gels, the results still enable a qualitative description of the distributions of motions. The signal areas smaller than those from theory indicate clearly that a fraction of the ^{13}C nuclei are dipolar coupled and have motions that are anisotropic over time periods of $\sim 10^{-6}$ s. The fraction of such nuclei in the polymer backbone increases as cross-linking increases. The loss of signal area is significant in the aromatic band only with 10% cross-linking. In the spectrum of the 10% cross-linked sample 80% of the aliphatic signal and 58% of the aromatic signal are so broadened that they cannot be distinguished from base line. Increasing line widths and decreasing NOE ratios also indicate that the distributions of correlation times shift to longer values as the degree of cross-linking increases.

Finally, the nearly invariant T_1 values for aromatic and backbone carbon atoms suggest a model for cross-linked polystyrene structure in which there are significant numbers of polystyrene chains dangling from the branch points in the cross-linked gel network. The number of carbon–carbon bond lengths over which the three-point conformational jump occurs in the model of Jones and Stockmayer[4] is 17. This suggests that a dangling chain of nine to ten styrene repeat units should give the same T_1 values as a high molecular weight linear polystyrene. In the most highly cross-linked sample whose T_1 was measured, the 6% divinylbenzene sample, the median distance between cross-links in each chain is about nine repeat units. There must be a sizable fraction of polymer chains with more than nine repeat units between cross-links, and those are the structural units that give ^{13}C NMR signals with only scalar decoupling.

The method used for synthesis of the copolymers should produce structures in which there are long chain segments with no cross-link. Free radical copolymer reactivity ratios for styrene (M_1) and *m*-divinylbenzene (M_2) are $r_1 =$

0.5–0.9 and r_2 = 0.6–1.1, and those for styrene and *p*-divinylbenzene are r_1 = 0.2–0.7 and r_2 = 1.0–1.2 for incorporation of the first double bond of the divinylbenzene.[29] The divinylbenzene is consumed more rapidly than the styrene, so when polymerization is carried to complete conversion, substantial amounts of long polystyrene chains are formed during the the latter stages. These long chains can account for the near invariance of T_1 over a range of 0–6% cross-linking. The (chloromethyl)styrenes used in our syntheses do not alter the conclusions because sytrene (M_1) and (chloromethyl)styrenes form nearly ideal copolymers, r_1 = 0.72, r_2 = 1.08.[33]

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Molecular Dynamics in Solid Polycarbonate by Proton Magnetic Resonance

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ABSTRACT: The proton magnetic resonance line shape is measured for the solid polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene over a temperature range of −120 to +120 °C by pulse Fourier transform techniques. A detailed second moment analysis, including separation of the intramonomer and interchain contributions, reveals the dynamical details of the polymer behavior below the glass transition. Clear evidence is present for phenylene rotation as the only significant intramolecular motion in the bulk phase. A phenomenological treatment for motional narrowing in solid-state NMR is applied to the data and is indicative of the existence of two overall dynamical processes, one predominant at low temperatures (below −40 °C) and the other at somewhat higher temperatures. The molecular nature and cooperativity of these two thermally activated processes are discussed in relation to their contribution to NMR relaxation. These findings are in overall agreement with and yield insight into previous dynamic mechanical studies on similar systems.

Introduction

The use of proton magnetic resonance (^{1}H NMR) techniques on bulk polymers can yield insight into both structure and molecular dynamics.[1-4] This information can be used to complement direct observation of mechanical properties and in some cases provides a probe at the molecular level for the origin of specific mechanical characteristics. Molecular reorientations occurring at a rate comparable to the ^{1}H NMR line width ($\sim 10^4$ Hz) will cause line narrowing in accordance with the reorientation geometry. The ^{1}H NMR absorption line shape for a solid is dominated by the nuclear dipole–dipole interaction between neighbor and near-neighbor magnetic nuclei. Complete analysis of the absorption line shape in a complex system like a bulk polymer is not feasible, but the problem can be obviated by the measurement and analysis of the second moment of the absorption line shape.[5,6]

In this investigation the ^{1}H NMR second moment is measured for the polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (chloral) shown in Figure 1. The