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Analysis of Cross-Linking of Poly[(chloromethyl)styrene] by High-Resolution ^{13}C NMR Spectroscopy

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ABSTRACT: Poly[(chloromethyl)styrene] cross-linked by treatment with stannic chloride, poly[styrene-*co*-(chloromethyl)styrene] cross-linked with divinylbenzene (DVB), and chloromethylated 1% DVB-cross-linked polystyrenes have been analyzed by high-resolution ^{13}C NMR spectroscopy at 25 and 75 MHz. The *m*- and *p*-chloromethyl isomer contents of ≤0.5% DVB-cross-linked poly[(chloromethyl)styrene] can be determined from spectral peak areas. The line widths in ^{13}C spectra of the ≤0.5% DVB-cross-linked polymers and of analogous soluble polymers are determined almost entirely by chemical shift dispersions. More extensive cross-linking either with DVB or by intrapolymer Friedel–Crafts alkylation gives polymers whose ^{13}C spectral peaks are broadened and reduced in area by dipolar coupling. Carbon atoms in cross-linked repeat units are not detected in scalar-decoupled ^{13}C spectra.

Cross-linked polystyrenes are widely used as supports for ion-exchange resins, size exclusion and ion chromatography packings, peptides in solid-phase syntheses, transition-metal and phase-transfer catalysts, and synthetic reagents. Chloromethyl-substituted polystyrenes are key intermediates in many of these resin preparations. The methods of polymerization and chloromethylation of the polymers can have great effects on their ultimate performance, yet usually little attention is paid to how these methods affect the properties of the cross-linked polymer. In addition to the customarily reported % DVB cross-linking of suspension-polymerized polystyrene beads, factors that affect polymerization kinetics, such as temperature, structure and amount of initiator, presence of residual inhibitors, and inert diluents in the organic phase, may affect the properties of the product. Diluent in the organic phase may lead to macroporous polymers or to polymers that become cross-linked in swollen condition but collapse upon drying.[1-3]

Chloromethyl groups have been introduced most often by Friedel–Crafts alkylation with chloromethyl methyl ether, a carcinogen. Chloromethylation of alkylbenzenes gives predominately the para isomer.[4] The Friedel–Crafts conditions also lead to cross-linking of polystyrene by intrapolymer alkylation, first recognized by the formation of insoluble gels during chloromethylation of soluble polystyrene and by decreased swelling of polystyrene resins after chloromethylation.[5-7] Chloromethylation of polystyrene beads often proceeds by a shell diffusive mechanism in which functionalization starts on the bead surface and proceeds to the center as the alkylating agent and Lewis acid diffuse into the bead.[8] Alternatively chloromethyl groups can be introduced by copolymerization of styrene with (chloromethyl)styrene and DVB.[9,10] (Chloromethyl)styrene is available as a mixture of meta and para isomers[10] (M_1), which copolymerizes nearly randomly ($r_1 = 1.08$, $r_2 = 0.72$)[9,10] with styrene (M_2). The chloromethyl repeat units in polymers so formed lead to branching of the copolymers but not to detectable cross-linking.[11]

This paper reports a high-resolution ^{13}C NMR investigation of the structures of cross-linked chloromethyl-functionalized polystyrenes. The aims are to analyze directly the isomer distribution of the chloromethyl groups and to analyze both DVB and Friedel–Crafts (FC) cross-linking from chemical shifts, peak areas, and line widths. Previously we reported differences in ^{13}C NMR line widths between (chloromethyl)styrene copolymers and chloromethylated polystyrenes[12] and dependence of line widths and detectable peak areas on % DVB cross-linking.[13]

Experimental Section

The cross-linked copolymers of (chloromethyl)styrene (Dow Chemical Co. vinylbenzyl chloride, reported to be a 60/40 meta/para mixture[10]) were prepared as before.[14] The homopolymers of *p*-(chloromethyl)styrene and *p*-(bromomethyl)styrene were provided by Dr. A. S. Gozdz (Textile Research Institute, Princeton, NJ).[15] The chloromethylated, 1% DVB-cross-linked polystyrenes were 200/400 mesh and were provided by Lab Systems, Inc., San Mateo, CA. Although the method of chloromethylation was not disclosed, the samples were all prepared from the same batch of 1% DVB-cross-linked polystyrene.

Friedel–Crafts cross-linked polymers 1–5 were prepared as follows. To each of five 25-mL round-bottom flasks containing 1.0 g of 100/200-mesh 0.5% DVB-cross-linked poly[(chloromethyl)styrene] in 15 mL of chloroform under nitrogen was added dropwise 0.17 mL of stannic chloride (1.45 mmol). The mixtures were shaken at room temperature for times of 1, 3, 9, 21, and 49 h. Each reaction mixture was filtered and washed with 1/1 chloroform/methanol six times, 3/1 dioxane/water six times, 2/1 dioxane/10% HCl six times, 3/1 dioxane/water six times, water five times, acetone five times, and methanol five times. The recovered polymer beads (800–980 mg) were dried at 65 °C under vacuum.

All NMR spectra were determined with $CDCl_3$ (99.8 atom % D containing 1% Me_4Si, Aldrich Chemical Co.) solutions or $CDCl_3$-swollen beads prepared as described before.[13] A vortex plug (Wilmad) was placed over the swollen beads to retard solvent evaporation. ^{13}C NMR spectra at 75.43 MHz of polymers in 16- or 5-mm tubes were run on a Varian XL-300 spectrometer with broad-band ^1H decoupling at 24 °C. For peak area measurements the decoupler was gated off during the 5-s preparation time to suppress the nuclear Overhauser effect (NOE). Areas were measured by electronic integration with an estimated error of ±10%. Normal acquisition conditions were 16-kHz spectral width, 16K data points, 0.5-s acquisition time, 38- or 18-μs (90°) pulse width for 16- and 5-mm sample tubes, respectively, 3.5-Hz line broadening, and a proton decoupling field strength (γH_2) of 2400 Hz. ^{13}C NMR spectra at 25.2 MHz of samples in 12-mm tubes were run on a Varian XL-100(15) instrument equipped with a Nicolet TT-100 PFT accessory with broad-band ^1H decoupling at 30 °C. Normal acquisition conditions were 6-kHz spectral width, 8K data points, 1.36-s acquisition time, 14-μs (90°) pulse width, no delay between acquisition and the next pulse, and 3-Hz line broadening. Line widths at half-height were measured on expanded spectra and corrected for the artificial line broadening. Random errors in line widths are estimated to be ±5%. Use of either higher or lower decoupling power in the 75.43-MHz spectra did not change the line widths outside of experimental error.

Swelling ratios were measured by volume in flat-bottomed 16-mm NMR tubes as $CDCl_3$-swollen volume/dry volume. Measurements in triplicate were precise to ±0.01.

Results

Identification of meta and para isomers of (chloro-

Table I
Line Widths (Hz) in ^{13}C NMR Spectra of Soluble Poly[(halomethyl)styrene]

		δ, ppm[a]					
substituent	MHz	145	137	135	128	46.4	40.4
p-CH_2Cl	75	69		27	69	14	38
	25	20		8	25	5	12
p-CH_2Br	75	72		38	52	26[b]	37
	25	20		12	20	9[b]	14
m- + *p*-CH_2Cl	75	68	32	26	48	18	36
	25	23	9	9	19	7	13
m- + *p*-CH_2Cl[c]	75	103	44	*d*	212	25	43
	25	35	15	*d*	71	8	18

[a] Peak assignments are as follows: 145 ppm, quaternary aromatic bound to backbone; 137 ppm, quaternary aromatic bound to *m*-CH_2Cl; 135 ppm, quaternary aromatic bound to *p*-CH_2Cl or *p*-CH_2Br; 128 ppm, largest band of overlapping protonated aromatics; 46.4 ppm, CH_2Cl; and 40.4 ppm, backbone methine. [b] CH_2Br at 33.9 ppm. [c] 0.5% DVB cross-linked. [d] Peak distorted by overlap with broadest aromatic peak.

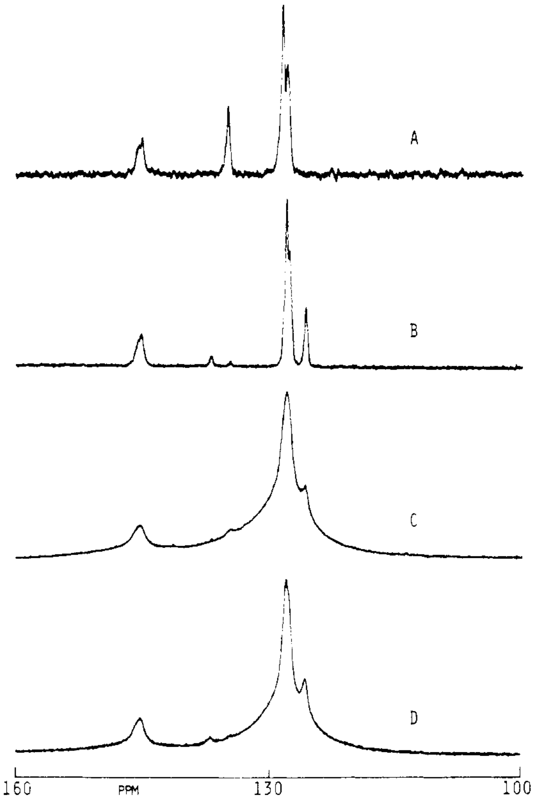


Figure 1. ^{13}C NMR spectra of the aromatic carbons of (A) soluble poly[*p*-(chloromethyl)styrene], (B) soluble poly[styrene-*co*-(chloromethyl)styrene] (25 wt % (chloromethyl)styrene), (C) 1 wt % DVB-cross-linked (0.92 wt % DVB after chloromethylation) polystyrene chloromethylated to 1.6 mequiv/g, and (D) 0.97 wt % DVB-cross-linked poly[styrene-*co*-(chloromethyl)styrene], 1.6 mequiv/g.

methyl)styrene repeat units was made by comparison of spectra of a soluble poly[(chloromethyl)styrene] and of poly[*p*-(chloromethyl)styrene]. Poly[*p*-(chloromethyl)-styrene] and poly[*p*-(bromomethyl)styrene] each gave a single peak for the quaternary aromatic carbon bound to the halomethyl group at 135 ppm as shown in Figure 1A and Table I. A soluble copolymer of *m*- and *p*-(chloromethyl)styrene gave peaks for the meta and para isomers at 137 and 135 ppm in a 7:3 area ratio (vs. the reported 6:4 mixture of isomeric monomers[10]) (see Figure 1B). A similar analysis of chloromethylated linear and 0.095% DVB-cross-linked polystyrene has been reported.[16] The CH_2Cl carbon peak at 46.4 ppm of the copolymer from the isomeric mixture of monomers was not resolved into two peaks even at 75 MHz, although the line width in the copolymer spectrum was greater than that in the poly-[*p*-(chloromethyl)styrene] spectrum (see Table I). As little as 0.5% DVB in the copolymer increased all of the line widths in the spectra. In Table I the line widths at 75 MHz are nearly three times the line widths at 25 MHz for every peak in the ^{13}C spectra.

Table II
Properties of FC-Cross-Linked Poly[(chloromethyl)styrene]

polymer	reacn time, h	swelling ratio[a]	% Cl	% of rings CH_2Cl subst[b]
0.5% DVB	0	5.82	23.02	99
1	1	5.76	21.73	92
2	3	4.26	20.94	88
3	9	2.90	18.40	75
4	21	2.46	16.91	67
5	49	2.38	16.21	64

[a] Swollen volume in $CDCl_3$/dry volume. [b] Calculated from Cl analyses.

Table III
Line Widths (Hz) in ^{13}C NMR Spectra of $SnCl_4$-Treated 0.5% DVB-Cross-Linked Poly[(chloromethyl)styrene] at 75 MHz

	polymer[a]					
δ, ppm	0.5% DVB	1	2	3	4	5
145	102	176	*b*	*b*		
137	46	*b*	*b*	*b*	3737[c]	4376[c]
128	209	262	445	941		
46.4	24	28	36	80	572[d]	1141[d]
40.4	40	52	61	[b]		

[a] Polymers are identified in Table II; peaks are assigned in Table I. [b] Could not be measured. [c] One broad peak in the aromatic region. [d] One broad peak in the aliphatic region.

Table IV
Ratios of Line Widths at 75 and 25 MHz in ^{13}C NMR Spectra of FC-Cross-Linked Poly[(chloromethyl)styrene]

	polymer[a]			
δ, ppm	0.5% DVB	1	2	3
145	2.97	2.52	*b*	*b*
137	2.80	*b*	*b*	*b*
128	3.01	2.78	2.14	1.35
46.4	3.13	2.89	2.69	1.89
40.4	2.56	1.67	1.11	*b*

[a] Polymers are identified in Table II. Peaks are assigned Table I. [b] Could not be measured.

A series of copolymers cross-linked by intrapolymer Friedel–Crafts alkylation was prepared by treatment of chloroform-swollen 0.5% DVB-cross-linked poly[(chloromethyl)styrene] with stannic chloride for various reaction times. Increase in reaction time decreased the chlorine contents and the swelling ratios of the polymers as shown in Table II and increased the ^{13}C NMR line widths as shown in Table III and Figure 2. All peaks except the backbone methine carbon peak in the spectra of the

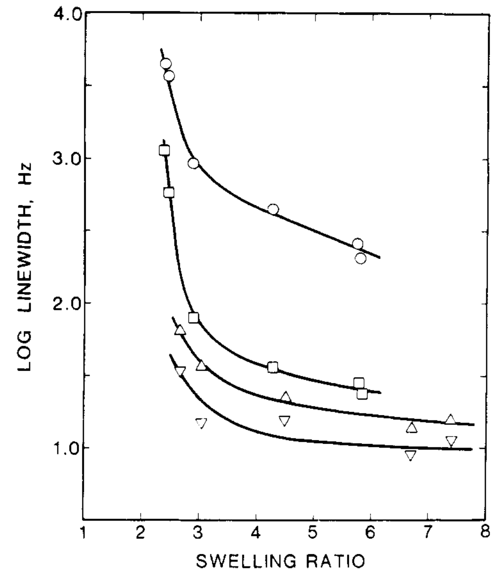


Figure 2. ^{13}C NMR line widths and swelling ratios in $CDCl_3$ of DVB-cross-linked poly[styrene-*co*-(chloromethyl)styrene] (25 wt % (chloromethyl)styrene) at 25 MHz and FC-cross-linked poly[(chloromethyl)styrene] at 75 MHz. Data are for polymers in ref 13 and in Tables II and III. (○) 128 ppm, aromatic, FC; (□) 46.4 ppm, CH_2Cl, FC; (▽) CH_2Cl, DVB; (△) 40.4 ppm, backbone CH, DVB.

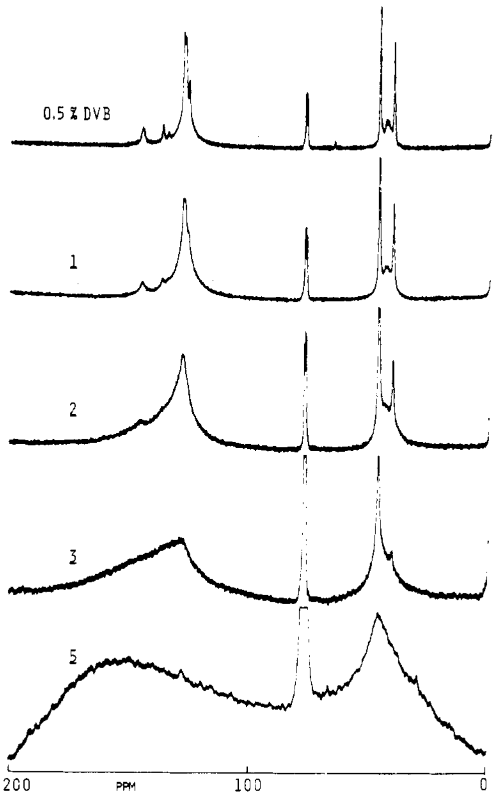


Figure 3. ^{13}C NMR spectra at 75 MHz of FC-cross-linked poly[(chloromethyl)styrene]. See Table II for sample characterizations.

starting 0.5% DVB-cross-linked poly[(chloromethyl)styrene] had line widths three times greater at 75 MHz than at 25 MHz (Table IV). The FC cross-linking reduced the 75 MHz/25 MHz ratio of line widths for every peak and eventually made every peak so broad that its width could not be measured, as can be seen in Table III and Figure 3.

Comparative effects of FC and DVB crosslinking on swelling are shown in Figure 4.

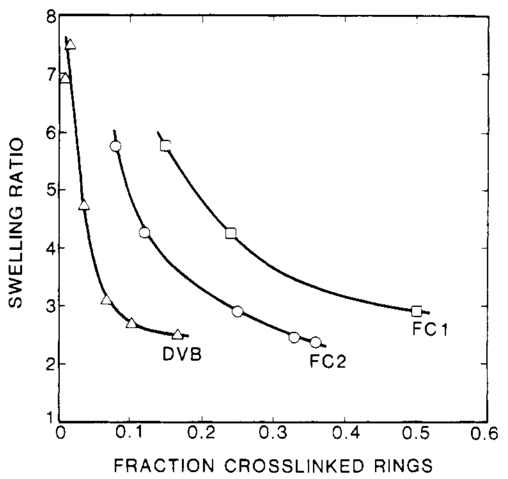
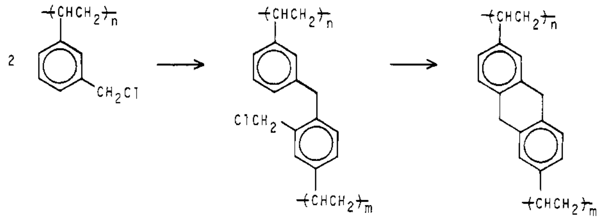


Figure 4. Swelling ratio in $CDCl_3$ vs. mole fraction of cross-linked repeat units in DVB-cross-linked poly[styrene-*co*-(chloromethyl)styrene][13] (25 wt % (chloromethyl)styrene) (△) and FC-cross-linked poly[(chloromethyl)styrenes] assuming (1) one methylene carbon cross-link (□) and (2) two methylene carbon cross-links per FC-cross-linked aromatic ring (○).

Attempts were made to identify cross-link carbon atoms in the spectra. Equation 1 shows diarylmethane and dihydroanthracene cross-link structures expected from intrapolymer alkylations. Model compounds **6** and **7** were prepared by treatment of 4-*tert*-butylbenzyl chloride with stannic chloride in chloroform and by similar treatment of a mixture of 4-*tert*-butylbenzyl chloride and *tert*-butylbenzene. The ^{13}C chemical shifts of methylene carbons in models of the cross-link structures of eq 1 are as follows: **6**, 38.3 ppm; **7**, 40.9 ppm; diphenylmethane, 42.0 ppm;[17] 9,10-dihydroanthracene, 37.7 ppm.[18] No new ^{13}C peak could be identified in the 38–41-ppm region of the spectra of the FC-cross-linked polymers. However, the line widths of such carbon peaks are expected to be large, and the peaks would overlap those of the backbone methine and methylene carbons.



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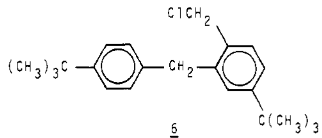

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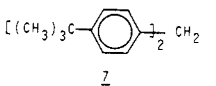

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Friedel–Crafts cross-linking decreased the peak areas in the ^{13}C spectra relative to an internal standard as shown in Figure 5. Cross-linking creates more rigid structures in the network that are dipolar coupled or have large chemical shift anisotropies, making some of the carbon atoms indetectable in a scalar-decoupled ^{13}C NMR spectrum. This phenomenon was observed earlier with DVB-cross-linked polystyrenes.[13] The percent cross-linking in Figure 5 was calculated from chlorine contents of the polymers according to two assumptions: (1) Each FC-cross-linked aromatic ring is bound to only one methylene cross-link carbon, as shown in eq 1 and model structure **6**. (2) The average FC-cross-linked aromatic ring is bound to two methylene cross-link carbons. This second assumption permits cross-linked aromatic rings bound to

Table V
Fractions of Peak Areas Observed and Calculated in ^{13}C NMR Spectra of FC-Cross-Linked Poly[(chloromethyl)styrene][a]

polymer[b]	carbon atoms *not* detected	calcd fraction detected: assumption 1	calcd fraction detected: assumption 2
1	x	0.85	0.92
	$x + y$	0.82	0.91
	$x + y + z$	0.56	0.77
	exptl: aromatic 0.84, aliphatic 0.84		
2	x	0.76	0.88
	$x + y$	0.71	0.86
	$x + y + z$	0.34	0.65
	exptl: aromatic 0.77, aliphatic 0.64		
3	x	0.50	0.75
	$x + y$	0.25	0.68
	$x + y + z$	−0.25	0.30
	exptl: aromatic 0.41, aliphatic 0.30		

[a] See text for definitions of x, y, and z and explanation of models used for calculated values. Experimental peak areas are compared with that of poly(ethylene glycol) of mol wt 1500 as internal standard.[13] [b] Described in Table II.

only one or to three or more methylene cross-link carbons as long as the average number is two. The dihydroanthracene structure in eq 1 is one special case of a structure with each aromatic ring bound to two methylene cross-link carbons.

One further assumption, that all chloromethyl groups in the network are equally reactive (that FC-cross-linking occurs randomly), allows calculation of distributions of microstructures. Let A and B be un-cross-linked and cross-linked repeat units, x be the mole fraction of B units, y be the fraction of A units in BAB triads, and z be the fraction of A units centered in BAA triads. Calculated distributions of microstructures are compared with the observed aromatic and aliphatic peak areas in Table V.

Line widths and aromatic/aliphatic peak area ratios from ^{13}C NMR spectra and swelling ratios of 1% DVB-cross-linked polystyrenes containing varied amounts of chloromethyl groups are in Table VI. One sample was a copolymer prepared from styrene, *m*- and *p*-(chloromethyl)styrenes, and DVB in our laboratory. The others were prepared by chloromethylation of 1% DVB-cross-linked polystyrene. In the spectra of the chloromethylated samples no distinct peak at 137 ppm due to *m*-chloromethyl-substituted aromatic carbon atoms was observed. Spectra of the two most nearly comparable samples prepared by the two methods are in Figure 1, parts C and D.

Although the data for the (chloromethyl)styrene copolymer in Table VI are from 100/200-mesh beads, use of four different bead sizes ranging from 20/40 mesh to 100/200 mesh gave only random errors of 2% in line widths, 5% in aromatic/aliphatic peak area ratios, and 1% in swelling ratio.

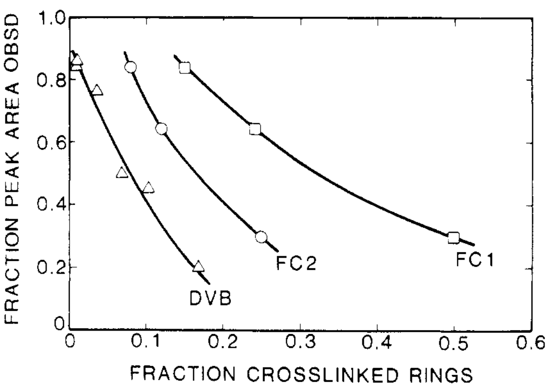

Figure 5. Fraction of aliphatic peak areas observed in ^{13}C NMR spectra (relative to poly(ethylene glycol), mol wt 1500, as internal standard) vs. mole fraction of cross-linked repeat units. Spectra of DVB-cross-linked poly[styrene-*co*-(chloromethyl)styrene][13] (25 wt % (chloromethyl)styrene) are at 25 MHz and those of FC-cross-linked poly[(chloromethyl)styrene] are at 75 MHz. (△) DVB; (□) FC assumption 1; (○) FC assumption 2.

Discussion

Isomer contents of soluble (chloromethyl)styrene copolymers and of 0.5% DVB-cross-linked poly[(chloromethyl)styrene] can be determined from the peak areas in ^{13}C NMR spectra at 137 and 135 ppm due to meta and para quaternary aromatic carbons bound to chloromethyl groups.[16] The analysis is not possible with ≥1% DVB-cross-linked chloromethylated polystyrene or styrene–(chloromethyl)styrene copolymers because the breadth of the base of the protonated aromatic carbon signal centered at 128 ppm obscures the much weaker peaks at 137 and 135 ppm. (See Figure 1.)

The factor of 3 difference in line width between peaks in 75- and 25-MHz ^{13}C spectra of the soluble and 0.5% cross-linked polymers (Tables I and IV) demonstrates that those line widths are determined almost entirely by chemical shift dispersions. This confirms earlier results.[19] Only the 75 MHz/25 MHz line width ratio of the methine carbon peak of the 0.5% DVB-cross-linked poly[(chloromethyl)styrene] at 40.4 ppm shows broadening from a non-field-dependent mechanism, such as dipolar coupling or fast transverse relaxation (short T_2). FC-cross-linking of that polymer (Table IV) caused a systematic decrease in the 75 MHz/25 MHz line width ratio of every signal. Part of each FC-cross-linked sample must have either large dipolar couplings or very short T_2, because the signal areas also decreased with increased cross-linking (Figure 5). Similar line broadening occurs in both ^{13}C and ^{1}H NMR spectra of DVB-cross-linked polystyrenes.[13,19,20]

Table VI
^{13}C NMR Spectral Line Widths and Peak Areas of 1% DVB-Cross-Linked Chloromethyl Polystyrenes at 75.43 MHz

	chloromethylated polystyrene[a]				copolymer[b]
mequiv of Cl/g	0.0	0.7	1.3	1.6[c]	1.6
line width, Hz[d]					
145 ppm	103	105	121	135	113
128 ppm	98	112	125	140	110
46.4 ppm			29	29	28
40.4 ppm	48	50	54	57	47
aromatic/aliphatic peak area					
calcd	3.00	2.89	2.80	2.76	2.75
found	3.26	3.03	2.94	2.75	2.73
swelling ratio	4.84	4.40	4.53	4.43	5.21

[a] Merrifield resins from Lab Systems, Inc. [b] 25 wt % (chloromethyl)styrene, 0.97 wt % DVB, 100/200 mesh. [c] Corresponds with 0.92 wt % DVB assuming starting copolymer contained 1.00 wt % DVB. [d] Peak assignments are in Table I.

Comparisons of experimental peak areas with peak areas calculated from models of cross-linking (assumptions 1 and 2 in the Results) in Table V permit interpretation of which carbon atoms are *not* detected in the spectra of the more highly cross-linked samples. The extent of dipolar coupling in the ^{13}C spectra is assumed to decrease in the following order: (1) cross-linked repeat units B, (2) un-cross-linked repeat units A in BAB triads, (3) A centered in BAA triads, and (4) A centered in AAA triads. Data in Table V indicate that carbon atoms in B units are not detected and that additional carbon atoms in the center A units of BAB and perhaps BAA triads also are not detected. The results for sample **1** fit best assumption 1 with only B not detected or with all B and A only in BAB triads not detected. The results for sample **2** fit assumption 1 with all B not detected in the aromatic region and with all B, A in BAB triads, and perhaps some A centered in BAA triads not detected. The results for **2** could also fit assumption 2 with all B, A in BAB triads, and some A centered in BAA triads not detected in the aromatic region and all A centered in BAA triads not detected in the aliphatic region. The results for **3** fit best assumption 1 with all B and some A in BAA triads not detected or assumption 2 with all B and A in BAB and A centered in BAA triads not detected. Since assumptions 1 and 2 involve exactly one and an average of two methylene cross-link carbons per FC-cross-linked ring, respectively, and the experimental peak area integrations have probable errors of 10%, more specific conclusions cannot be drawn. In principle, one would expect the fraction of rings with two methylene carbon cross-links to increase as the degree of cross-linking increases, and that is consistent with the comparisons of calculated and experimental results in Table V.

Since the carbon atoms of the cross-linked repeat units cannot be detected in scalar-decoupled ^{13}C NMR spectra, the true identity of the cross-link structures is unknown. It should be possible to detect the cross-link carbon atoms in dipolar-decoupled cross-polarization ^{13}C NMR spectra of more highly cross-linked networks, particularly if the cross-link carbon atoms are ^{13}C-labeled.

Comparisons of the swelling ratios and ^{13}C NMR line widths and peak areas of DVB-cross-linked polymers with those of FC-cross-linked polymers in Figures 2, 4, and 5 show that it takes fewer DVB cross-links than FC cross-links to restrict motions in the networks. For example, Figure 4 indicates that 8 mol % of the assumption 2 cross-links or 15 mol % of assumption 1 cross-links achieve the same swelling ratio of about 5.8 attained with 1 mol % DVB cross-linking. Friedel–Crafts cross-linking takes place while the network is fully swollen, creating a polymer described as isoporous.[21,22] When the network is formed in a swollen state, that state is conformationally relaxed. Drying forces the polymer network into a conformationally strained state, and exposure of the dry polymer to fresh solvent allows it to revert to the relaxed state. With DVB cross-linking in the absence of solvent, the network is formed in a contracted state.[2,21–23] Solvent swelling of the dry polymer then strains the network. FC-cross-linked polystyrenes also have been prepared with unfunctionalized polystyrene and difunctional alkylating agents.[21,22,24–26]

Comparisons of 1% DVB-cross-linked chloromethylated polystyrene with 1% DVB-cross-linked poly[styrene-*co*-(chloromethyl)styrene] in Table VI show several interesting features. The copolymer swells more in chloroform than either the chloromethylated polystyrene with the same chlorine content (1.6 mequiv/g) or the unfunctionalized polystyrene, due to some unknown difference in the polymerization procedures. The decrease in swelling ratio from 4.8 to 4.4 with increased degree of chloromethylation from 0.0 to 1.6 mequiv/g indicates that either the chloromethyl group reduces the swelling tendency or chloromethylation occurs with additional cross-linking, as noted more than 30 years ago.[5,6] Table VI shows that the line widths of ^{13}C peaks in spectra of the chloromethylated resins increase with the degree of chloromethylation and with decreased swelling. Direct comparison of the 1.6 mequiv/g chloromethylated resin with 1.6 mequiv/g poly[styrene-*co*-(chloromethyl)styrene] shows that ^{13}C line widths of the chloromethylated resin are greater for every peak except the CH_2Cl, which is mainly para in the chloromethylated resin and is a 70/30 meta/para mixture in the (chloromethyl)styrene copolymer. The line width differences are most easily explained by FC cross-linking during chloromethylation. In our earlier work the chloromethyl carbon line widths at 46.4 ppm in spectra of several chloromethylated polystyrenes were smaller than that of equally cross-linked (chloromethyl)styrene copolymers, presumably because chloromethylation produces mainly the para isomer.[12] The mixture of meta and para isomers is expected to show a greater dispersion of chemical shifts.

^{13}C NMR spectra demonstrate distinct differences between chloromethylated polystyrene and poly[styrene-*co*-(chloromethyl)styrene]. The chloromethylated Merrifield resins have mainly para CH_2Cl groups. The increases in line widths after chloromethylation (Table VI) indicate that FC cross-linking occurs during chloromethylation. Since the FC cross-links are formed with the polymer swollen, they cause only a small reduction in the swelling ability of the resin. The alternative (chloromethyl)styrene copolymers have no FC cross-links and a 70/30 mixture of meta/para CH_2Cl groups. Chloromethylation introduces functional groups initially only at sites accessible to external reagents, but the subsequent FC cross-linking could render some of the sites unreactive in later applications. Copolymerization of (chloromethyl)styrene with DVB may leave some functional groups in unreactive sites from the beginning, and the relative reactivities of the meta and para isomers are unknown. Reactivity differences between the various chloromethyl polystyrenes are not known at present. Comparisons of meta with para isomers and of chloromethylated resins with (chloromethyl)styrene copolymers in standard reactions such as quaternization with amines to form ion-exchange resins and conversion to polymer-supported peptides might explain some of the inconsistent results previously reported and show which type of functionalized polystyrene will give best performance in future uses.

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Carbon-13 Nuclear Magnetic Resonance Characterization of Random Ethylene–Vinyl Chloride Copolymers

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ABSTRACT: A complete series of ethylene–vinyl chloride (E–V) copolymers have been prepared by reductive dechlorination of poly(vinyl chloride) (PVC) with tri-*n*-butyltin hydride. ^{13}C NMR was employed to determine the microstructure of each E–V copolymer including the overall comonomer composition and sequence and the stereosequence of neighboring vinyl chloride (V) units. Our detailed analysis of E–V microstructure by ^{13}C NMR was made possible by comparison of the observed spectra with the ^{13}C NMR chemical shifts previously calculated for these copolymers based on γ-gauche shielding effects. Dechlorination was found to be an approximately random process in terms of comonomer sequence; however, VV dyads with a meso stereosequence were found to be significantly more susceptible to dechlorination than racemic VV dyads. GPC determination of molecular weights revealed that the reductive dechlorination of PVC to yield E–V copolymer does not result in chain scission or cross-linking. Consequently, we have produced a series of E–V copolymers with nearly the same chain lengths as the starting PVC, each with a well-characterized microstructure.

Introduction

Recently considerable effort has been applied to the study of poly(vinyl chloride) (PVC) microstructure.[1] A key step in much of this work is the reductive dechlorination of PVC to polyethylene (PE) with tri-*n*-butyltin hydride (Bu_3SnH). The structure of the starting PVC is then deduced from that of the resulting PE, principally by ^{13}C NMR analysis.

It is also possible to obtain ethylene–vinyl chloride (E–V) copolymers by the incomplete reduction of PVC.[2] A series of ethylene–vinyl bromide copolymers have already been obtained by Cais and Kometani[3] through the Bu_3SnH reductive debromination of poly(vinyl bromide).

Traditional means of obtaining E–V copolymers suffer from several shortcomings. Chlorination of PE[4] results in head-to-head (vicinal) and multiple (geminal) chlorination leading to structures which are not characteristics of E–V copolymers. Direct copolymerization of E and V monomers does not usually lead to random E–V copolymers covering the entire range of comonomer composition. Free-radical copolymerization[5,6] at low pressures yields E–V copolymers with V contents from 60 to 100 mol %. γ-Ray-induced copolymerization[7] under high pressure yields E–V copolymers with increased amounts of E, but it appears difficult to achieve degrees of E incorporation greater than 60 mol %.

Several factors serve to motivate our interest in E–V copolymers. First is the convenient means for obtaining these copolymers provided by the Bu_3SnH reduction of PVC. Second, our ability to assign the ^{13}C NMR spectra of E–V copolymers[8] means we can determine the details of their microstructure. Third, our interest in using electrical birefringence measurements (Kerr effect)[9-11] performed on dilute polymer solutions to characterize their structures and conformations prompts us to consider the Kerr effect study of the E–V system, because ^{13}C NMR provides us with an independent means to determine both of these characteristics. Fourth, we would like to measure several solid-state properties[2] of a well-characterized copolymer system with the view of eventually establishing structure–property relations.

In this paper we outline the preparation and characterization of E–V copolymers. Their physical properties, measured both in dilute solution and in the solid state, will be discussed in subsequent contributions.

Experimental Section

Preparation of E–V Copolymers. PVC obtained from Aldrich (No. 18958-8) was dissolved in tetrahydrofuran (THF) that had been passed through basic alumina. The PVC was next precipitated from cold methanol, filtered, and dried in a vacuum oven overnight at ambient temperature.

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