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Functional Polymers Containing Dimethylene Spacers. Characterization by Solid-Phase ^{13}C-NMR

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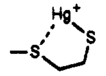
Insoluble functional polymers in which reactive functionalities ("X") have been covalently bound to particles of cross-linked polystyrene ("Ps") have found many chemical applications as easily-recovered (and often recyclable) solid-phase reagents, catalysts, protecting groups, and sequestering agents.[1-3] Especially stable and active are those in which "spacers" of two or more methylene groups have been interposed between heteroatoms of the functional groups and aryls of the polymer backbone (i.e., "Ps–CH$_2$CH$_2$–X"): such have previously been prepared via alkylation of cross-linked polystyrene[4] and are now readily available by a new method of radical-catalyzed anti-Markovnikov addition of thiols (or some other types of small molecules) across the pendant vinyl groups remaining in beads formed by suspension polymerization of a divinylbenzene-rich monomer mixture (Ps—CH═CH$_2$ + H—SR → Ps—CH$_2$CH$_2$—SR).[5] Here we show how, in the cross-linked products of this new procedure, the presence and mode of attachment of a new functional group can be verified, and even its mobility characterized, by solid-phase ^{13}C-NMR.

Ps—CH═CH$_2$ was typically prepared by stirring (1000 rpm) 20 g of a commercial 55:45 divinylbenzene/ethylstyrene mixture (Dow "Divinylbenzene 55-S") with 325 mL of water, 20 mL of toluene, 0.20 g of 2,2′-azobis(isobutyronitrile) (AIBN), and 0.10 g of cellulose ether (Dow "Methocel K100LV") together at 70 °C for 2 h under nitrogen, with the solid product then being filtered, washed with 4% benzoquinone/toluene and then acetone, subjected to Soxhlet extraction with acetone overnight under nitrogen, filtered, and vacuum-dried at 60 °C overnight to give white beads which FTIR showed[6] to contain 30–35 mol % residual vinyl groups. Portions thereof were then suspended in toluene and gently stirred with excess thiol H–SR (Table I) and 1 wt % AIBN at 70 °C under nitrogen for 1–2 days and then washed and dried in the same way. FTIR of the products Ps–CH$_2$CH$_2$–SR showed a decrease or disappearance of the peak at 1630 cm^{-1} (–CH═CH$_2$);[6] elemental analyses showed amounts of sulfur corresponding to 25–30 mol % degree of functionalization (some vinyls would have been consumed by further cross-linking). Ps–CH$_2$CH$_2$–SH was obtained by the acid-catalyzed hydrolyses of a portion of Ps–CH$_2$CH$_2$–SCOCH$_3$.[7]

^{13}C CP-MAS NMR spectra were obtained at 25.1 MHz on a Chemagnetics Inc. M-100 instrument with a contact time of 1 ms, a pulse delay of 3 s, a spin rate of 3–4 kHz, high-power proton decoupling during acquisition, referencing to hexamethylbenzene (17.4 ppm), and, in the ^{13}C CP-MAS-DD experiments, a dephasing time τ of 45 μs, except where varied from 22.5 to 150 μs as indicated. Variable-temperature ^{13}C CP-MAS-DD experiments were performed on a Chemagnetics Inc. CMX-300 spectrometer with a contact time of 1 ms, a pulse delay of 1.5 s, a dephasing time of 45 μs, and a spin rate of 2–3 kHz; temperature control in the sample was achieved by preheating or precooling the N$_2$ gas used for spinning the sample tube, equilibrating before the start of data acquisition.

Table I
^{13}C-NMR Peaks from Ps–CH$_2$CH$_2$–SR after Dipolar Dephasing

–SR	C (ppm)	CH$_3$ (ppm)	CH$_2$ (ppm)
–SCH$_2$CH$_2$COOH	178, 144	16	
–SC$_6$H$_5$	144, 131	16	
–SC(CH$_3$)$_3$	144, 42	34, 16	
–SCOCH$_3$	193, 144	30, 16	
–SH	144	16	
–SCH$_2$CH$_2$OH	144	16	62, 35
–S(CH$_2$)$_3$CH$_3$	144	16	33, 22
–SCH$_2$CH$_2$SH	144	16	35, 25
	144	16	
–S(CH$_2$)$_3$SH	144	16	36–34, 25
–S(CH$_2$)$_4$SH	144	16	34, 30, 24

The ^{13}C CP-MAS spectrum of dry Ps—CH═CH$_2$ is shown in Figure 1a. Peaks here at 114 and 137 ppm can be respectively assigned[8] to pendant –CH═CH$_2$ and –CH═CH$_2$. Peaks at 129 and 144 ppm are from CH and C of polystyrene phenyls. Peaks at 16 and 30 ppm are due to CH$_3$ and CH$_2$ of the ethyl group from ethylstyrene units. The large peak at 41 ppm comes from CH$_2$ and CH carbons in the polymer backbone. These assignments were tested by dipolar-dephasing (^{13}C CP-MAS-DD) experiments, in which the ^{1}H decoupler was turned off for 45 μs before data acquisition started, a treatment which typically[9] quenches signals due to solid-phase CH$_2$ and CH (which have strong dipolar interactions with linked protons) and not those from CH$_3$ (whose rapid rotation—even in solids—attenuates ^{13}C–^{1}H dipolar interactions therein) and nonprotonated C: as expected, all peaks except those at 16 and 144 ppm were mostly or completely quenched, giving a simplified spectrum (Figure 1b).

The ^{13}C CP-MAS and ^{13}C CP-MAS-DD spectra of the product of Ps—CH═CH$_2$ with HSCH$_2$CH$_2$COOH (3-mercaptopropanoic acid) are illustrated in parts a and b of Figure 2, and Table I. Peaks at 114 and 137 ppm are now absent, indicating <1 mol % remaining vinyls (by comparison with spectra from "known" Ps—CH═CH$_2$/polystyrene mixtures), and a new peak due to the added functional group appears at 178 ppm which persists in the DD spectrum (R–CO–O), together with the old 16 ppm peak due to Ps–CH$_2$CH$_3$. No new peak arises in the methyl region, indicating exclusive β-addition across vinyl, as expected for radical addition of H–SR.[10]

Similar "normal" DD spectra, in which only C and CH$_3$ peaks appear, were obtained with –SR = –SC$_6$H$_5$, –SC(CH$_3$)$_3$, –SCOCH$_3$, and –SH (Table I). However, with sulfide-linked *n*-alkyl (–SR = –SCH$_2$CH$_2$CH$_2$CH$_3$), *n*-hydroxyalkyl (–SR = –SCH$_2$CH$_2$OH), and *n*-mercaptoalkyl (–SR = –S(CH$_2$)$_{2-4}$SH) products, those carbons distal to the sulfide linkage were unexpectedly *not* quenched by dipolar dephasing, as shown in parts c and d of Figure 2 for –SR = –SCH$_2$CH$_2$OH (62 ppm) and –SCH$_2$CH$_2$OH (35 ppm). This suggests that these methylenes, being less encumbered and farther from the polymer backbone, are sufficiently mobile for ^{13}C–^{1}H dipolar interactions here to be attenuated, as occurs with CH$_2$ in solution or –CH$_3$ in solution or solid. The hypothesis of a "liquid" (or at least, "rubbery") microenvironment for certain spacer-displaced functional groups in this "solid" dry material was tested by a variable-temperature ("VT") ^{13}C CP-MAS-DD study of –SR = –SC$^{\alpha}$H$_2$C$^{\beta}$H$_2$C$^{\gamma}$H$_2$C$^{\delta}$H$_3$ (Figure 3): here, "resid-

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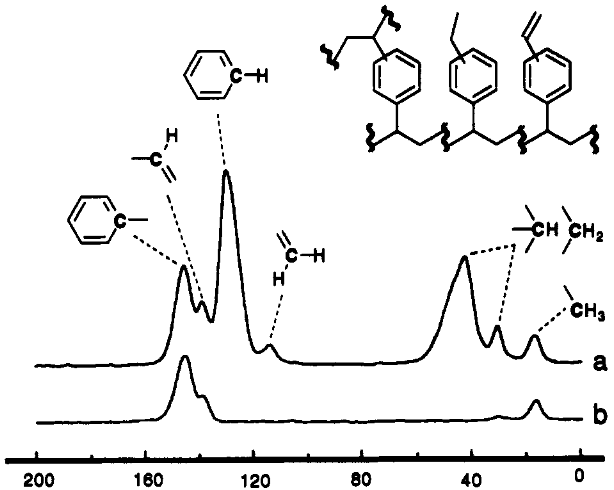

Figure 1. ^{13}C CP-MAS (a) and ^{13}C CP-MAS-DD (b) NMR spectra of Ps—CH═CH$_2$.

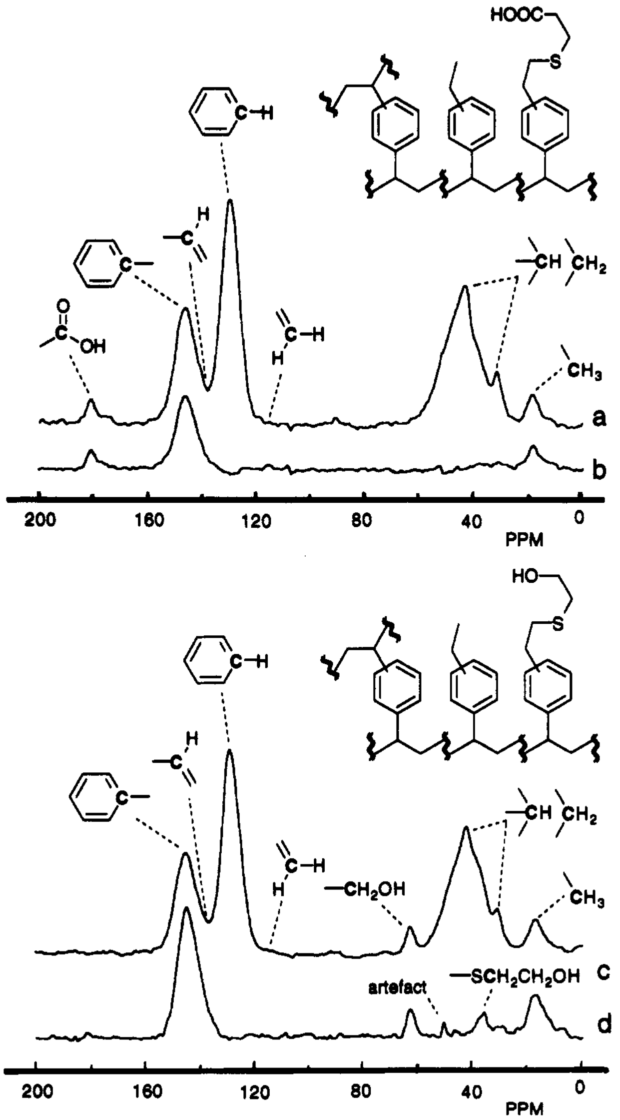

Figure 2. ^{13}C CP-MAS (a) and ^{13}C CP-MAS-DD (b) NMR spectra of Ps–CH$_2$CH$_2$–SCH$_2$CH$_2$COOH. ^{13}C CP-MAS (c) and ^{13}C CP-MAS-DD (d) NMR spectra of Ps–CH$_2$CH$_2$–SCH$_2$CH$_2$-OH.

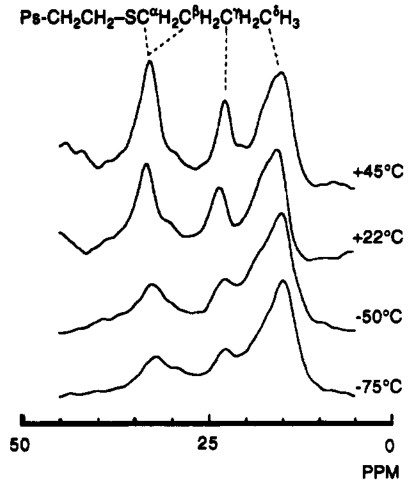

Figure 3. Variable-temperature ^{13}C CP-MAS-DD NMR spectra of Ps–CH$_2$CH$_2$–SCH$_2$CH$_2$CH$_2$CH$_3$.

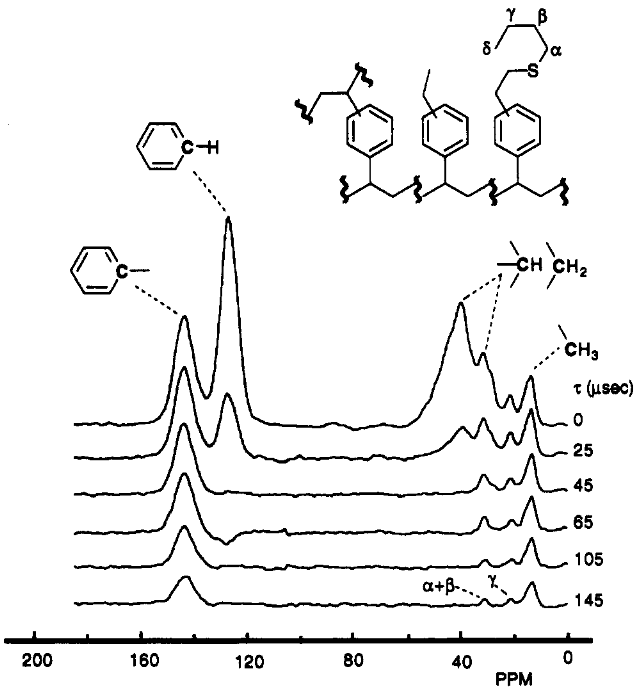

Figure 4. ^{13}C CP-MAS-DD NMR spectra of Ps–CH$_2$CH$_2$–SCH$_2$-CH$_2$CH$_2$CH$_3$ at different experimental dephasing times (τ).

ual" 33 (C$^\alpha$ & C$^\beta$) and 22 (C$^\gamma$) ppm methylene peaks, prominent at room temperature (and still more at 45 °C), significantly decreased as many side-chain motions were frozen out at −75 °C, while 15 ppm peaks (Ps–CH$_2$CH$_3$ and Ps-CH$_2$CH$_2$-SCH$_2$CH$_2$CH$_2$C$^\delta$H$_3$ units, which still rotate freely at these low temperatures) did not change intensity. –SR = –S(CH$_2$)$_n$SH functionalities behaved similarly; for $n = 2$, methylenes could also be "immobilized" (peaks at 35–25 ppm made DD-quenchable) by addition of mercuric ion to form a cyclic complex.[11]

The relative mobilities of carbon atoms can be quantitated by observing changes in signal intensity with variation of experimental dephasing time τ. The characteristic dipolar dephasing time of a carbon atom, T_{dd}, which relates to the mobility of that atom in the sample, can be obtained from eq 1:[9]

$$\ln I_\tau = -\tau / T_{dd} + \ln I_0 \qquad (1)$$

where I_τ is the peak intensity for experimental dephasing time τ, and I_0 is the peak intensity in the absence of dipolar dephasing ($\tau = 0$).[12] A nonprotonated carbon, or one protonated but highly mobile, displays a longer T_{dd}, while that of a protonated and/or rigidly-held carbon is shorter. Figure 4 shows the ^{13}C CP-MAS-DD spectra of Ps–CH$_2$-CH$_2$–SBu at different τ, from which I_τ for each peak were measured (through deconvolution by computer fitting with

Gaussian functions) so that $\ln I_\tau$ could be plotted against $-\tau$ to obtain T_{dd} for each carbon. T_{dd} for nonprotonated aryl carbons (145 ppm) and for rapidly-rotating methyl groups (15 ppm) were found, of course, to be very large (110–150 μs; DD-persistent), while the short dephasing times (15–21 μs; DD-quenchable) for aryl CH (127 ppm) and methylene and methine carbons of the polymer backbone and spacer group (40 ppm) were also to be expected for such. However, peaks from methylene carbons in the dangling $-SC^{\alpha}H_2C^{\beta}H_2C^{\gamma}H_2CH_3$ moieties showed enhanced T_{dd} values of 42 μs for the α and β carbons (33 ppm peak) and 45 μs for the γ carbons (23 ppm), indeed indicating significantly increased mobility at room temperature of these functionalities with respect to the polymer backbone.

Solid-state ^{13}C NMR spectroscopy (CP-MAS and CP-MAS-DD) has been demonstrated to be a powerful technique to characterize structure and mobility within dry functionalized cross-linked polystyrene. Results indicate that the cross-linked polymer backbone generally behaves as a rigid network, while certain spacer-supported functionalities can show significant flexibility. Such mobility may be an important aspect of the polymer microenvironment affecting the accessibility and activity of these functional groups.

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References and Notes

(1) *Polymeric reagents and catalysts*; Ford, W. T., Ed.; American Chemical Society: Washington, DC, 1986.
(2) *Syntheses and separations using functional polymers*; Sherrington, D. C., Hodge, P., Eds.; Wiley: New York, 1988.
(3) Akelah, A.; Sherrington, D. C. *Polymer* **1983**, *24*, 1369–1386.
(4) Darling, G. D.; Frechet, J. M. J. *J. Org. Chem.* **1986**, *51*, 2270–2276.
(5) Gao, J. P.; Barghi, R.; Darling, G. D., in preparation.
(6) Bartholin, M.; Boissier, G.; Dubois, J. *Makromol. Chem.* **1981**, *182*, 2075–2085.
(7) Morse, B. K.; Tarbell, D. S. *J. Am. Chem. Soc.* **1952**, *74*, 416–419.
(8) Periyasamy, M.; Ford, W. T.; McEnroe, F. J. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 2357–2366.
(9) Yoshimizu, H.; Mimura, H.; Ando, I. *Macromolecules* **1991**, *24*, 862–866.
(10) Stacey, F. W.; Harris, J. F., Jr. *Org. React.* **1963**, *13*, 165–196.
(11) Gao, J. P.; Dong, X. M.; Darling, G., in preparation.
(12) It has been reported[13] that when carbons are strongly coupled to protons, the decay of signal is better described by the equation $\ln I_\tau = -\tau^2/2(T_{dd})^2 + \ln I_0$. We found no difference here.
(13) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697–6704.