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^{13}C NMR INVESTIGATION OF CROSSLINKING IN ORGANIC AEROGELS

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ABSTRACT

Organic aerogels are a special type of low density foam produced from the supercritical drying of resorcinol-formaldehyde (RF) gels. These aerogels have continuous porosity, ultrafine cell/pore sizes (< 1000 Å), and a microstructure composed of interconnected colloidal-like particles with diameters ranging from 30-175 Å. The particle size, surface area, density, and mechanical properties of the aerogels are largely determined by the catalyst concentration used in the sol-gel polymerization. In order to gain some insight into the crosslinks between RF particles, aerogels were labeled with C-13 formaldehyde at various times in the polymerization. CPMAS and IRCP techniques were used to correlate the relaxation behavior of the C-13 enriched aerogels with their different microstructures.

INTRODUCTION

The aqueous, sol-gel polymerization of resorcinol with formaldehyde is a proven synthetic route for the formation of organic aerogels [1-4]. In this reaction, resorcinol (1,3 dihydroxybenzene) serves as a trifunctional monomer capable of electrophilic aromatic substitution with formaldehyde in the 2,4, and/or 6 ring positions. These intermediate products condense into polymeric "clusters" with diameters ranging from 30-175 Å. The presence of surface functional groups (e.g. $-CH_2OH$) on the resorcinol-formaldehyde (RF) "clusters" leads to additional crosslinking and eventual gel formation.

RF gels are supercritically dried to obtain organic aerogels. These low density materials have high porosity (> 80%), high surface areas (400-900 m^2/g), and ultrafine cell/pore sizes (< 1000Å). SEM and TEM reveal that the aerogel microstructure consists of interconnected colloidal-like particles. The RF particles are derived from the "clusters" formed in solution.

Previous studies have shown that the [Resorcinol]/[Catalyst] ratio is the major process variable which controls the RF polymerization and determines the final aerogel microstructure. As expected, the microstructure affects the macroscopic properties (e.g. compressive modulus) of these materials. In order to gain some insight into the interconnections between RF particles, C-13 labeled formaldehyde was introduced into the polymerization after "cluster" formation but prior to gelation. These solutions were permitted to gel, and then they were processed into aerogels in the usual manner. By selectively labeling surface groups which can form covalent linkages between RF "clusters", solid state NMR should allow us to quantify the <u>inter</u>-particle crosslinking density of the corresponding aerogels.

The principle approach to obtaining microstructural (morphological) information about polymeric materials is to measure relaxation parameters, since changes in molecular dynamics are reflected in relaxation times. An important question that needs to be addressed in the case of organic aerogels is: How large must a change in microstructure be in order to reveal a difference in relaxation properties? Crystalline and amorphous components of semicrystalline polymers have been distinguished by relaxation studies, and it is expected that regions of different crosslinking densities could be resolved in totally amorphous materials [5,6]. Thus, this study examines two different RF aerogels to see if the relaxation properties of these materials can be correlated with preparative methods and known structural characteristics, Table I.

EXPERIMENTAL

The preparation of RF gels and aerogels has been described in detail [2,4]. In this study, aquagels were prepared with the same solids content (5%) but different catalyst concentrations. The "high" catalyst formulation contained 0.29 M resorcinol, 0.52 M formaldehyde, and 6 mM sodium carbonate. The "low" catalyst formulation contained 0.29 M resorcinol, 0.52 M formaldehyde, and 1.5 mM sodium carbonate. These formulations have [Resorcinol]/[Catalyst] ratios of 50 and 200, respectively.

The C-13 labeled formaldehyde was added to a specific formulation after polymerization at 95 °C for 0, 4, or 8 hours. The concentration of labeled formaldehyde (Cambridge Isotope Laboratories; ^{13}C; 99%) was 0.06 M in each case. Previous work has shown that RF "cluster" formation is completed after ~3 hours of polymerization, and thus, C-13 labeled formaldehyde introduced at later times should only be present at the surface of the "clusters" [2].

The labeled gels were cured for a total of 7 days at 95 °C. Upon removal from their containers, the gels were placed in a dilute acid solution to maximize crosslinking. These gels were then exchanged into an organic solvent and supercritically dried from carbon dioxide (T_C= 31 °C; P_C= 1100 psi). The resultant ^{13}C enriched aerogels gave a total of 3 samples at a given [Resorcinol]/[Catalyst] ratio.

All NMR measurements were performed on a Bruker MSL-300 spectrometer. The carbon frequency was 75.423 MHz and the proton frequency 300.13 MHz. Samples were ground to a fine powder and routinely spun at 3750-4000 Hz. Adamantane or hexamethylbenzene was used as a secondary external chemical shift standard.

RESULTS AND DISCUSSION

The carbon backbone of organic aerogels is complex and yields a cross polarization magic angle spinning (CPMAS) C-13 NMR spectrum of four principle and one minor peak intermingled with spinning side bands, Figure 1. The NMR spectrum reflects the aromatic and aliphatic species within the aerogel. Although these peaks are indicative of carbon types, they reveal no major differences in the composition or microstructure of aerogels prepared under different conditions.

The four most prominent peaks in the NMR spectrum were used for relaxation measurements, and the amount of a particular carbon site was determined from peak amplitudes. The measured peaks have chemical shifts of ~ 150, 120, 60, and 20 ppm with respect to TMS. These peaks are assigned to aromatic carbons with an OH (150 ppm), aromatic carbons ortho to an OH (120 ppm), aliphatic carbons adjacent to oxygen (60 ppm), and methylene carbons (20 ppm) [7]. C-13 labeling at T=0 hours greatly increases the 20 ppm peak relative to the remaining peaks, whereas C-13 labeling at both T=4 and T=8 hours increases the 60 ppm peak as well. Peak intensity ratios comparing the enriched aerogels with unlabeled aerogels indicate that the 60 ppm peak primarily represents surface groups while the 20 ppm peak largely reflects groups buried within the RF particles. This finding was expected since a large excess of formaldehyde is available in the late stages of "cluster" formation to react with surface sites and form hydroxymethyl groups.

CPMAS measurements have been made as a function of contact time for each of the 6 samples [8]. The data were analyzed using a Bruker program, SIMFIT, to yield T_{CH} values for each carbon. Table II shows that two T_{CH} values are required to fit the CPMAS curves for the aliphatic carbons. These values differ by a factor of 15-40, and both values are appreciably shorter than $T_{1\rho}(H)$.

At the molecular level, T_{CH} is proportional to the inverse square of the dipolar C-H interactions within the aerogel. This dipole-dipole coupling scales as the sixth power of the distance between interacting atoms, and it can be used to elucidate separate motional environments for carbons having similar chemical shifts. The two T_{CH} components for the 60 ppm peak reflect methylene ether bridges, hemiformal groups, and hydroxymethyl groups which are in different environments at the surface of the RF particles [9]. The high T_{CH} component represents species which are loosely bonded or freely rotating at the surface, while the low T_{CH} component represents species that are highly crosslinked and immobile. A ratio of the intensities for the low T_{CH} component at 60 ppm to the 150 ppm peak shows that a larger fraction of surface groups are crosslinked in the aerogels synthesized with R/C=50. Intensity ratios were the same for aerogels labeled at T=4 and T=8 hours.

Inversion recovery cross polarization (IRCP) measurements, at a fixed contact time of 1 ms, were also used to examine the relaxation behavior of organic aerogels [8]. Figure 2 displays a semi-log plot of peak amplitude versus the length of time of the proton phase-inverted pulse for the 60 and 150 ppm peaks. The sharp break in the curve for the aliphatic peak necessitates a 2 component fit, while only a single component is present in the aromatic peak. Table II shows that the relaxation times of the aliphatic components differ by a factor of 10-25. For the aerogels labeled at T=4 and T=8 hours, a ratio of the intensities for the low T_{CH} component at 60 ppm to the 150 ppm peak shows that a larger fraction of surface crosslinks occur in the R/C=50 sample.

The IRCP and CPMAS data corroborate mechanical property measurements which show that R/C=50 samples are stiffer than R/C=200 samples at equivalent densities. The higher stiffness can be directly attributed to the larger fraction of surface crosslinks in the former aerogels.

CONCLUSIONS

NMR relaxation studies have been performed on C-13 labeled organic aerogels that have dramatically different microstructures and physical properties. Analysis of the CPMAS and IRCP C-13 relaxation data suggests a difference in inter-particle crosslinking density for aerogels synthesized with [Resorcinol]/[Catalyst] ratios of 50 and 200. Further studies are in progress to measure additional C-13 parameters such as $T_{1\rho}$, T_1, and T_2.

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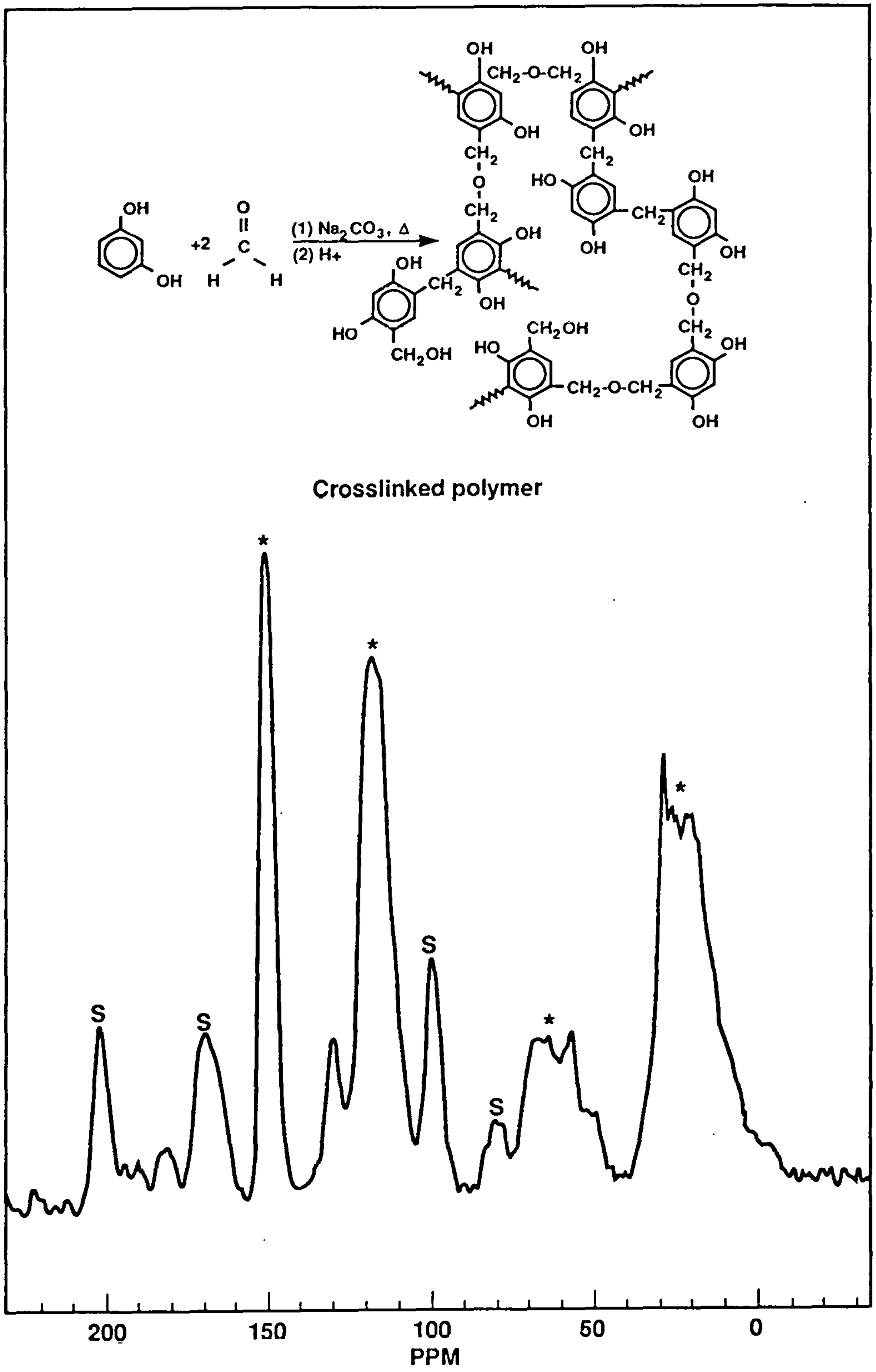

Figure 1. CPMAS spectrum of organic aerogel with (insert) reaction to produce crosslinked polymer network (s = spinning side band, * = measured peak)

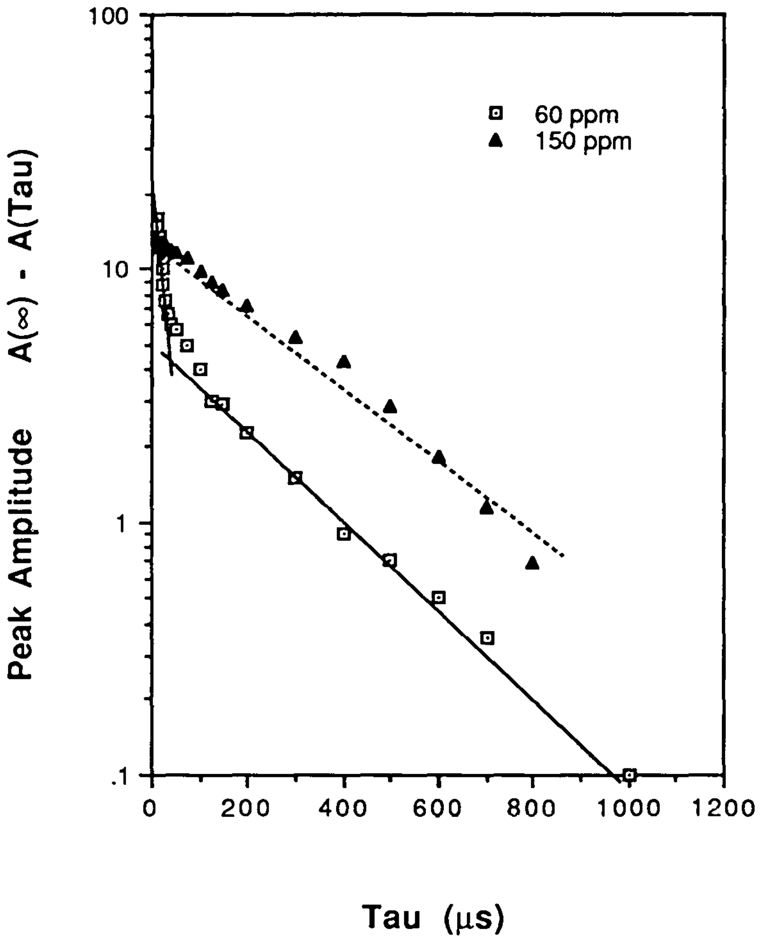

Figure 2. IRCP data for selected aliphatic and aromatic carbons. Aerogel was synthesized with R/C= 50 and labeled at T=4 hours.

TABLE I

	R/C = 50	R/C = 200
Target density (g/cc)	0.050	0.050
Actual density (g/cc)	0.088	0.057
BET surface area (sq.m./g)	905	580
TEM particle radius (Å)	17	59
Density dependence of compressive modulus	$E = 10^{3.21} \rho^{2.87}$	$E = 10^{2.35} \rho^{2.48}$

Table II

Cross Polarization *

Hours	R/C = 50				R/C = 200			
	150 ppm	120 ppm	60 ppm	20 ppm	150 ppm	120 ppm	60 ppm	20 ppm
0	---	----	---	635	---	---	---	485
				14				13
4	438 (11.4)	498	509	461	470 (12.4)	330	513	460
			18 (9.4)	16			19 (7.4)	14
8	650 (11.7)	549	322	218	493 (13.6)	353	438	532
			25 (8.9)	18			17 (8.3)	13

Inversion Recovery Cross Polarization *

Hours	R/C = 50				R/C = 200			
	150 ppm	120 ppm	60 ppm	20 ppm	150 ppm	120 ppm	60 ppm	20 ppm
0	---	---	---	255	---	---	---	258
				12				12
4	404 (5.6)	343	218	175	410 (7.2)	320	364	298
			15 (2.5)	10			21 (0.7)	14
8	730 (8.3)	628	248	160	398 (6.3)	328	165	203
			11 (3.8)	8			18 (1.0)	12

* $T1\rho(H)$ varies from 5600 to 7000 µs for all carbons.
All T_{CH} values are expressed in µs; intensities for selected T_{CH} components are shown in brackets.

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