^{13}C Solid-State NMR Determination of Cross-Linking Degree in Superabsorbing Cellulose-Based Networks

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Received August 16, 1999; Revised Manuscript Received November 22, 1999

ABSTRACT: ^{13}C solid-state NMR analysis has been performed on microporous superabsorbing networks based on hydroxyethylcellulose and sodium salt of carboxymethylcellulose in order to determine the *chemically effective* cross-linking degree. Microporous samples characterized by two different degrees of cross-link have been analyzed by performing ^{13}C cross-polarization magic angle spinning (CP-MAS) solid-state spectra and single-pulse excitation (SPE) experiments. Cross-linking degrees, expressed as number of cross-links per monomer, have been evaluated from the area of resonance due to methylene carbon atoms present on reacted cross-linker molecule (divinyl sulfone) and area of resonances due to anomeric carbon atoms C-1 of the polysaccharide rings. Optimization procedures for both CP-MAS and SPE experiments are also reported.

Introduction

Swelling properties of cross-linked hydrophilic polyelectrolytes in aqueous solutions are determined by several chemical and structural factors. In fact, there are different contributions to the free energy change associated with the swelling process.[1−10] In turn, the degree of cross-link is a structural parameter of primary importance to evaluate the swelling properties of a polyelectrolyte network in an aqueous medium.

Generally, the determination of *elastically effective* cross-linking density can be performed, among other techniques, by using equilibrium swelling measurements or by performing uniaxial compression tests on swollen networks.[1,11−14] However both techniques allow a straightforward determination of cross-linking density if the chemical structure is quite "simple" and structural complexities, like fixed ionic charges, are absent. Interpretation of experimental data is further complicated by the eventual presence of microporosity.[7]

As a consequence, the availability of an alternative experimental technique, able to supply a value for the *chemically effective degree of cross-linking*, obtained independently of the knowledge of other chemical−physical and structural parameters (such as density of charges, degree of ionization, and polymer/solvent interaction parameter), could be an important aid for the characterization of cross-linked systems.

Despite the interest in these materials, few methods suitable for their characterization are currently available. In principle, as a result of chemical and/or enzymatic hydrolysis of the network, low molecular weight, soluble products can be obtained and characterized with commonly used techniques allowing the determination of the cross-linking degree. However, degradation processes may involve and heavily modify the chemical bridges responsible for the cross-links; hence, soluble products might not be representative of the original structure of the network.

In turn, solid-state NMR spectroscopy offers a nondestructive approach, allowing an insight into the chemical structure of these amorphous, insoluble materials.

Since cross-linked polymers are involved in many industrial processes, numerous studies have been carried out on the application of solid-state NMR spectroscopy for characterizing polymeric networks. Among other examples are phenolic resins,[15,16] epoxy resins,[17,18] styrene-based resins,[19−22] formaldehyde-based resins,[23−25] methacrylate-based resins,[26,27] cross-linked polydivinylbenzenes,[28] and polysaccharide-based networks.[29−32]

In this paper we propose the use of ^{13}C solid-state NMR technique for the determination of the *chemically effective degree of cross-linking* in the case of a microporous superabsorbing network. This material was obtained by cross-linking a mixture of hydroxyethylcellulose and sodium salt of carboxymethylcellulose in aqueous solution with divinyl sulfone, followed by water extraction with acetone.

Experimental Section

Specimen Preparation. Highly absorbing cellulose-based hydrogels synthesized in this work have been obtained by cross-linking water solutions of carboxymethylcellulose sodium salt (referred in the following as CMCNa) and hydroxyethylcellulose (referred in the following as HEC) using divinyl sulfone as cross-linking agent (referred in the following as DVS). CMCNa is a cellulose ether where substituent groups are methylcarboxylic groups and is used as suspending agent or emulsifier in detergent, food, and textile industries.[34] Also, the other component, HEC, is a common commercial product. It is a cellulose ether, where substituent groups are oxyethylene chains. Structures of CMCNa and HEC along with the carbon atoms labeling are reported in Scheme 1. The degree of substitution and the relative distribution of substituents in the C-2, C-3, and C-6 position in cellulose ethers may strongly affect the properties and the behavior of these polymers.[35]

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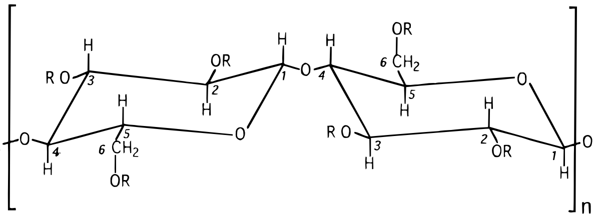
10.1021/ma9914117 CCC: $19.00

Scheme 1. Schematic Structure of CMCNa and HEC; Carbon Atoms Labeling Is Also Reported



CMCNa: R = H; $CH_2COO^-Na^+$

HEC: R = H; $CH_2CH_2(OCH_2CH_2)_mOH$

CMCNa (cod. 41,933-8), HEC (cod. 30,683-3), and DVS (cod. V370-0) were purchased from Aldrich Chimica s.r.l. Milano and used as received. According to the supplier, the degree of substitution (DS) of CMCNa is about 0.9 and the weight average molecular weight is 700 000. The molar substitution (MS) for HEC is about 1 and DS is about 1, while the weight average molecular weight is 250 000. Actually different values for DS have been determined for CMCNa by performing both high field NMR and conductometric titration according to procedures reported elsewhere.[36] In fact, both techniques gave results that are in good agreement and equal to 0.66 ± 0.03. Moreover, also the distribution of substituents at C-2, C-3, and C-6 positions of the anhydro D-glucose moiety has been determined by ^1H and ^{13}C NMR in solution;[36] the substituent groups (CH_2COO^- Na^+) turn out to be ≈40% in position 3, ≈40% in position 6, and ≈20% in position 2. Intrinsic viscosities of polymers in water have also been determined using an Ubbelohde capillary viscometer at 25 °C. Tests have been performed on filtered solution of polysaccharides and distilled water. The values obtained were 55.31 and 3.37 dL/g, respectively, for CMCNa and HEC.

Cross-linking reaction has been performed according to procedures reported in the literature.[37] For this study a mixture of CMCNa and HEC, with a weight ratio equal to 3/1, was first dissolved in a solution of DVS and distilled water by stirring gently at room temperature until a clear solution was obtained. The total polymer weight fraction in the solution was 2%. Two different DVS concentrations were used in order to obtain samples with two degrees of cross-linking: 0.04 and 0.133 mol of DVS per liter of solution. The presence of HEC is necessary to promote quantitatively intermolecular rather than intramolecular cross-linking. In fact, poor cross-linking efficiency is reported[37] if only CMCNa is used, seemingly due to the electrostatic repulsion between charged macromolecules and to the fact that few hydroxyl groups remain available for reaction at C6, the most reactive position. After the mixing stage, an aqueous solution of KOH was added as catalyst to the polymer solution until a pH = 12.5 was reached. Hydrogel formation occurred in few hours at room temperature. A schematic representation of cross-linked chemical structure is reported in Figure 3.

Following the reaction stage, a partially swollen hydrogel was obtained that was subsequently cut in small pieces with an approximate volume equal to 1 cm^3. To remove unreacted DVS and the KOH ("washing" stage), these small pieces of hydrogel were then soaked in distilled water, reaching equilibrium swelling under continuous stirring. Water was used in volumes greatly exceeding that of hydrogel and was changed several times. In one case this stage was performed without changing water surrounding the gel with the purpose of detecting the eventual presence in it of unreacted polysaccharide macromolecules. No traces of unreacted HEC or CMCNa were found, at least in the limits of the adopted UV measurement technique[38] based on sulfuric acid reaction for the identification of cellulose derivatives.

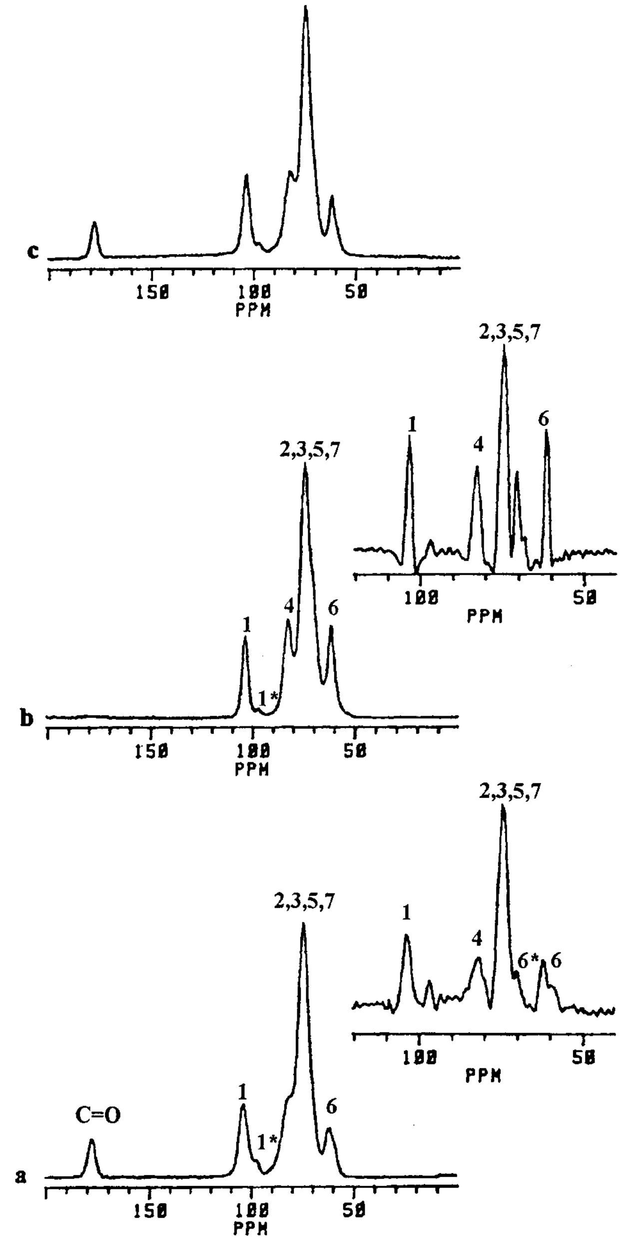


Figure 1. ^{13}C CP-MAS NMR spectra of: (a) Carboxymethylcellulose−Na salt; the methylenic group of the carboxylated side chain is labeled 7. (b) Hydroxyethylcellulose; side chain oxyethylenic groups labeled 7. (c) Physical mixture carboxymethylcellulose−Na salt/hydroxyethylcellulose (75/25 w/w). In the inset of (a) and (b) the spectral range 120−40 ppm is shown after applying a Gaussian apodization function (LB = −128, GB = 0.4).

After the "washing" stage, a dry product was obtained by desiccating hydrogel samples through phase inversion with acetone according to procedures reported in the literature.[39] According to this procedure, the swollen gel was soaked in pure acetone, which is a solvent for water and nonsolvent for the polymer. Two phases were then formed: a polymer-rich phase, with negligible residual amount of water, and a water/acetone liquid mixture. To further remove water, the cross-linked precipitate was then collected and again put in contact with pure acetone. These extraction cycles were repeated several times. The material, in the form of a white glassy polymer, was then kept under vacuum some hours to remove traces of residual acetone. Because of the high and connected microporosity induced by the fast water extraction, the previously described desiccation procedure guarantees a water swelling capacity of dry samples quite higher than the one obtained with samples desiccated by simple drying at atmospheric condition. The swelling ratio strongly depends on pH and ionic strength of the aqueous solution in contact with the material.

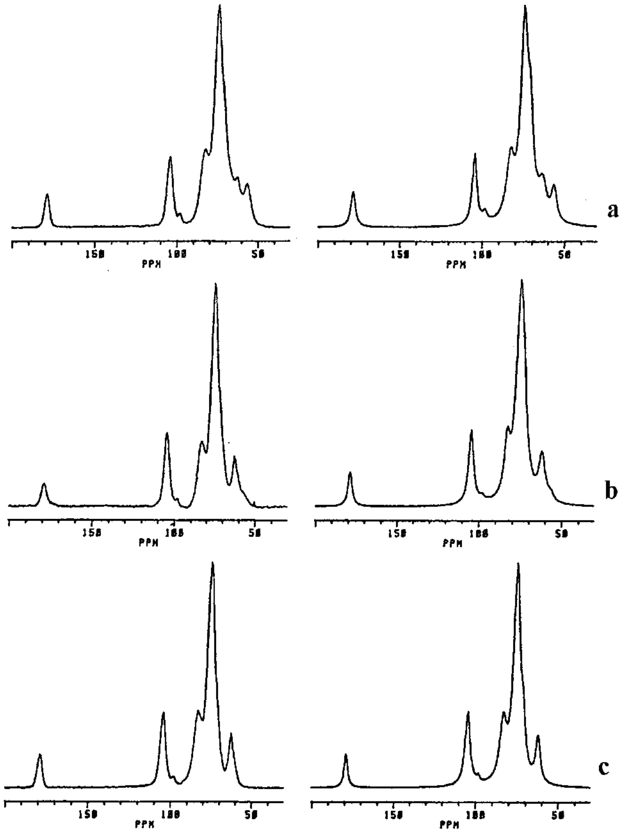


Figure 2. ^{13}C CP-MAS spectra of (a) sample H with a high degree of cross-link, (b) sample L with a low degree of cross-link, and (c) sample U, un-cross-linked sample. On the left are the experimental spectra, and on the right are the simulated ones showing the reliability of the quantitative analysis.

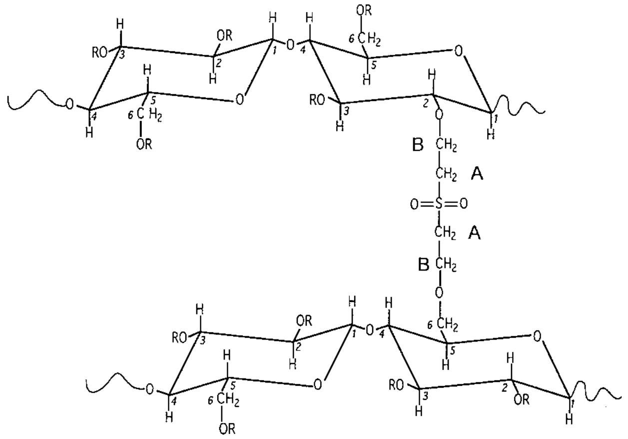


Figure 3. The possible structure of the chemical bridges responsible for the cross-links is shown.

Typical values of sorbed amounts in distilled water at room temperature were around 400 and 150 g of water per gram of dry polymer, respectively, in the case of a starting DVS concentration equal to 0.04 and 0.133 mol/L. These high sorption capacities, accompanied by a high water retention capability under compressive stress, make this material a good candidate as a potentially biodegradable superabsorbing system.

For the sake of comparison, un-cross-linked samples were also prepared. For this purpose the starting aqueous solution of CMCNa, HEC, and DVS (total polymer concentration 2 wt %, CMCNa/HEC ratio equal to 3/1 and DVS concentration equal to 0.133 mol/L) was put directly in contact with acetone and the precipitate collected.

NMR solid-state analyses have been performed both on the cross-linked and on the un-cross-linked samples. In the following cross-linked samples prepared with a starting DVS concentration equal to 0.04 and 0.133 mol/L will be referred to respectively as sample L (for low cross-linking degree) and sample H (for high cross-linking degree). The un-cross-linked sample will be referred as sample U (for un-cross-linked).

Cross-linked samples were found to be totally amorphous from wide-angle X-ray scattering[39] analysis.

Solid-State NMR Measurements. Samples H, L, and U were finely powdered, packed into 4 mm zirconia rotors and sealed with Kel-F caps. Solid-state ^{13}C CP-MAS spectra were performed on a Bruker AC-200 spectrometer, equipped with an HP amplifier for ^{1}H at 200 MHz, 120 W CW, and with a pulse amplifier M3205. The spin rate was always kept at 8 kHz. The $\pi/2$ pulse was 3.1 μs, the contact time for the cross-polarization experiment was 1 ms, and the relaxation delay was 4 s. Spectra were obtained with 1024 data points in the time domain, zero-filled and Fourier transformed with a size of 2048 data points; 19 000 scans were performed for each experiment.

As a function of the contact time, two series of experiment were performed. The intensity of resonances was reported against the contact time; from these data the cross-relaxation time between protons and carbons, T_{IS}, and the spin−lattice relaxation time of protons in the rotating frame, $T_{1\rho}(^1H)$, were obtained.

Single-pulse excitation (SPE) experiments were also performed; the recycle time was 40 s, and the ^{13}C $\pi/2$ pulse was 2.8 μs.

The spectral editing CP−SPI sequence[40,41] has also been applied. This sequence is the standard cross-polarization (CP) sequence combined with a simultaneous phase inversion (SPI) during the polarization inversion (PI). Properly choosing the pulse length for the simultaneous phase inversion, $\tau_{PI1} = \tau_{PI2} = 27\ \mu s$, a carbon spectrum can be obtained where methine resonances are zeroed and methylene resonances are inverted, while resonances due to methyls and nonprotonated carbon atoms are positive. Thus, a full spectral editing can be obtained. In this paper the sequence has been applied to sample H. In this way the resonance due to methylene carbon atoms involved in the cross-links are brought to evidence.

Analysis of NMR resonances was performed using the simulation program “GLINFIT”.[42] This program can perform the full deconvolution of overlapped lines with Gaussian and/or Lorentzian shapes. Errors in the integrals are less than 10% of their nominal value.

Results and Discussion

Before studying the nature of the chemical bridges in the network, CMCNa and HEC were separately investigated by solid-state NMR. Moreover, since the full assignment of ^{1}H and ^{13}C spectra in solution of CMCNa and HEC was incomplete, a full high-field NMR study was performed, obtaining not only a full assignment of the spectra but also for CMCNa the degree of substitution and its positional distribution.[36] As by notation adopted in ref 36, we will label with a “n*” any glucose monomer carrying a substitution in position Cx(n), with $n = 2, 3, 6$. According to this notation C-1 (2*) means the anomeric carbon atom of a glucose unit carboxylated in position 2.

Carboxymethylcellulose−Na Salt. In Figure 1a the ^{13}C CP-MAS spectrum of CMCNa is shown, along with the assignment of resonances: at 178.6 ppm the resonance of carbonyl carbons of substituent groups $-CH_2COO^-$ is observable; at 104. 6 ppm the resonance of anomeric carbon C-1 of anhydro D-glucose units unsubstituted in C-2 position is observed, while at 97.2 ppm the signal of the anomeric carbon C-1(2*) belonging to anhydro D-glucose units substituted in position 2 is observed. The upfield shift of the resonance of C-1(2*) is possibly due to a γ-gauche effect.[36,43] In fact, in solution the effect on C-1 of a chemical substitution in C-2 is almost zero, while in the solid state a $\approx$7 ppm upfield shift is observable. From the ratio between the area of resonance C-1(2*) and the area of resonance C-1, the degree of substitution in position 2 can be obtained; it is $\approx$0.15. Note that, even if cross-polarization is not a directly quantitative technique, in this case we take into account for the same anomeric methine carbon atom, the presence or the absence of substituent in position 2 being the unique difference. The obtained value is in excellent agreement with the corresponding value obtained in solution.[36] The broad resonance centered at $\approx$82.5 ppm is mostly due to C-4; however, other resonances might also contribute.[36] At $\approx$75.2 ppm a very intense resonance is observed, resulting from the overlapping of resonances of different carbon atoms: C2, C3, C5, and methylene carbons of substituents in positions 2, 3, and 6 certainly contribute. The resonance at 71.1 ppm is possibly due to C-6 as assigned from spectra in solution.[36] In fact, in the presence of the substituent $-CH_2COO^-Na^+$ in position 6, C-6 undergoes an additive β contribution,[44] so that a resonance shift downfield, $\approx$8 ppm, is observed. In the absence of any substitution the resonance due to carbon C-6 is at 62.7 ppm.

Hydroxyethylcellulose. In Figure 1b the ^{13}C CP-MAS spectrum of a sample of HEC is shown. At 104.2 ppm the resonance of anomeric carbon C-1 of anhydro D-glucose units unsubstituted in the C-2 position is observed, while at 97. 8 ppm the signal of the anomeric carbon C-1(2*) belonging to anhydro D-glucose units substituted in position 2 is observed. Again the degree of substitution in position 2 can be obtained from the ratio of the area of resonances C-1(2*) and C(1); it is $\approx$0.05. The resonance at 83.3 ppm is mostly due to C-4; however, other resonances might contribute. Applying a strong resolution enhancement to the spectrum, see inset in Figure 1b, three resonances can be easily distinguished at 75.3, 71.5 and 69.1 ppm. The assignment of these resonances is quite difficult; in fact, C-2, C-3, C-5, and also resonances due to the oxyethylene chains of substituents resonate in this range of frequency. However, the resonance at 69.1 ppm might be partly due to C-6*; in fact, the carbon atom in position 6, if substituted, gets a β contribution.[44] Hence, its resonance shifts downfield. In the absence of substituent groups, the resonance of carbon C-6 resonates at 62.3.

Physical Mixture. Finally, in Figure 1c is shown the ^{13}C CP-MAS spectrum of a physical mixture obtained by simple mechanical mixing of CMCNa and HEC powders (3/1). The reported spectrum is similar to the one obtained overlapping the spectra previously reported in Figure 1a,b.

Cross-Linked Samples. The ^{13}C CP-MAS spectrum of sample H is reported in Figure 2a; for comparison, in Figure 2c the spectrum of sample U is also shown. Therewith, since DVS is soluble in CH_3COCH_3, no free DVS is present in both samples. Note that the ^{13}C chemical shift of the resonance of the methine carbon of DVS is at $\delta = 137.2$ ppm while the chemical shift of the methylene is $\delta = 129.7$ ppm (from tetramethylsilane).[45] Since both spectra reported in Figure 2 do not show any carbon resonance in both ranges of frequency, the presence of unbound DVS can be excluded for both samples. On the same basis, the presence of DVS as a pendant group can also be excluded. The resonance at 56 ppm observed in the spectrum of the cross-linked compound is due to methylene carbon atoms of type A (see labeling reported in Figure 3), i.e., adjacent to the sulfoxide group, while methylene carbon atoms of type B (see labeling reported in Figure 3) resonate in the same crowded range of frequency of polysaccharides (70−80) and cannot be resolved in solid-state spectra. It is worth noting that the resonance at 56 ppm is fully absent in the spectrum of sample U (see Figure 2c), confirming the previous assignment.

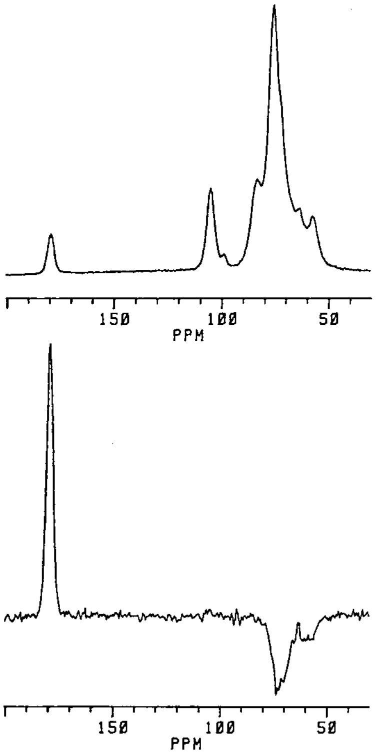


Figure 4. (top) ^{13}CP-MAS spectrum of sample H; the resonance at 56 ppm is due to methylene carbon atoms of type A (see Figure 3). (bottom) Spectrum obtained after applying the CP−SPI sequence: all resonances of methine carbons are zeroed, while resonances of methylene carbons are inverted. Note that the resonance at 56 ppm is inverted, confirming the attribution to methylene carbons.

The spectrum of the cross-linked compound is poorly resolved showing a broader spectrum with respect to the one of sample U; in particular, the C-4 and C-6 resonances are noticeably broad, possibly due to differences in the chemical environment changed by the presence of cross-linked units. It must be observed that carbon resonances belonging to the groups 2* and 3* resonate quite close to the resonance of C-4 and might contribute to its broadening, while the broadening observed on C-6 might be due to γ-gauche effects. The ^{13}C CP-MAS spectrum of sample L is shown in Figure 2b. At $\approx$56 ppm the resonance due to methylene carbon A appears as a broad shoulder of the resonance due to C-6. All other resonances are quite unaffected.

For a further confirmation of the assignment of the resonance at 56 ppm to methylene carbon atoms of type A, the spectral editing sequence CP−SPI has been applied to sample H. As a result, a ^{13}C spectrum has been obtained where methine carbon resonances are zeroed and methylene carbon resonances are inverted, while resonances due to quaternary and methyl carbon atoms are positive. The spectrum is shown in Figure 4, bottom, for the case of sample H, while in the top the ^{13}C CP-MAS spectrum of the same sample is reported for comparison. Note that for improving the resolution a Gaussian apodization function has been applied to both spectra; typical parameters for the shifted Gaussian apodization are line broadening (LB) = −8 and amount of shift expressed as a fraction of total data length (GB) = 0.2.[46] All methine resonances are nicely zeroed, while resonances at 56 and 62.5 ppm are negative, confirming the assignment to methylene carbon atoms, A and C-6, respectively. At ≈70 and ≈72 ppm methylene resonances due to oxyethylene chains are also observable; however, a detailed assignment is not possible.

^{13}C CP-MAS NMR and Related CP Dynamics. During the cross-polarization process, the polarization of proton spins can be dissipated to the lattice by relaxation under the spin-locked condition at a rate $1/T_{1\rho}$, or it can be transferred to a dilute spin system with a rate $1/T_{IS}$. As a consequence, the cross-polarization process is effective if $\tau_{CP} < T_{1\rho}$. In turn, if contact times are too long, the polarization is lost from the dilute spin system to the abundant spin system and finally to the lattice again. Hence, at short contact times, the intensity of the resonances increases exponentially with increasing the time, with a time constant T_{IS}, the cross-relaxation time between protons and carbons. Thus, an optimum contact time exists which should be carefully searched on each sample.

To match this requirement, CP-MAS experiments were performed at variable contact times τ_i, with τ_i ranging from 20 to 12000 μs.

In parts a and b of Figure 5, the intensity of resonances is reported against the contact the time for sample U and sample H, respectively.

In simple cases, the kinetics of the cross-polarization process is described by the following equation:[47,48]

$$S(\tau_i) = \frac{G(\tau)}{\lambda} S(0) \tag{1}$$

$$G(\tau) = \exp\left(\frac{-\tau_i}{T_{1\rho}(^1\mathrm{H})}\right) - \exp(-\tau\gamma) \tag{2}$$

where

$$\lambda = 1 + \beta \tag{3}$$

$$\beta = \frac{T_{IS}T_{1\rho}(^1\mathrm{H}) - T_{IS}T_{1\rho}(^{13}\mathrm{C})}{T_{1\rho}(^{13}\mathrm{C})\ T_{1\rho}(^1\mathrm{H})} \tag{4}$$

$$\gamma = \frac{T_{1\rho}(^{13}\mathrm{C}) + T_{IS}}{T_{IS}T_{1\rho}(^1\mathrm{H})} \tag{5}$$

$S(0)$ is the intensity of the resonance for the total CP transfer, and $S(\tau_i)$ is the intensity of the resonance measured as a function of the contact time.

Using this equation, a best fit of $S(\tau_i)$ was performed. T_{IS}, $T_{1\rho}(^1\mathrm{H})$, and $S(0)$ are parameters obtained from the best fit procedure. Note that both $T_{1\rho}(^1\mathrm{H})$ and $T_{1\rho}(^{13}\mathrm{C})$ can be measured in proper experiments.[49] Moreover, $T_{1\rho}(^1\mathrm{H})$ can also be obtained from the slope $1/T_{1\rho}(^1\mathrm{H})$ of the straight line at long contact times (see Figure 5).

In Table 1 $T_{1\rho}(^1\mathrm{H})$ values measured on both sample U and sample H are reported.

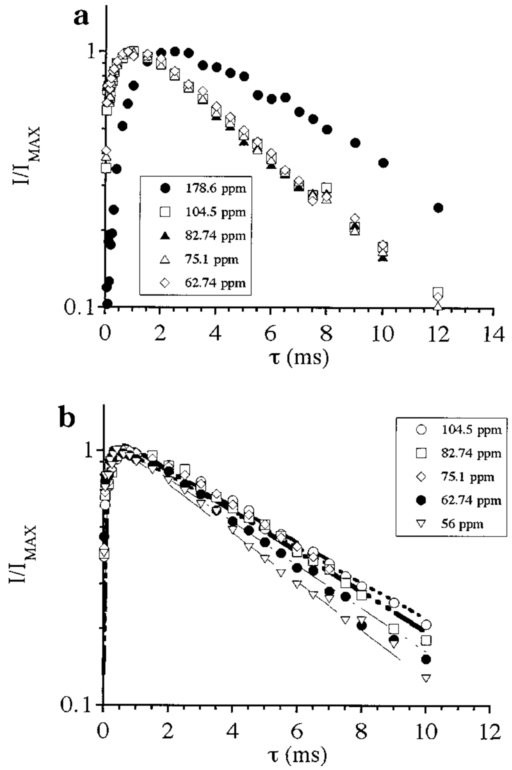


Figure 5. Correlation between the intensity of resonances of ^{13}C CP-MAS NMR spectra and the contact time τ for the CP-MAS experiment: (a) intensity of resonances of the ^{13}C CP-MAS spectrum of sample U vs the contact time; (b) intensity of resonances of the ^{13}C CP-MAS spectrum of the sample H. Lines through experimental points are obtained applying a best fit procedure to eq 1. All parameters obtained from the best fit procedure are reported in Table 2.

Table 1. $T_{1\rho}(^1\mathrm{H})$ [ms] Values Measured for Same Selected Resonances Are Reported, for an Un-Cross-Linked (U) and a Highly Cross-Linked (H) Sample

ppm	sample H	sample U	ppm	sample H	sample U
178.9	13 ± 1	5.9 ± 0.4	75.4	6.2 ± 0.3	4.9 ± 0.2
104.3	6.0 ± 0.3	5.0 ± 0.2	62.5	5.0 ± 0.3	5.2 ± 0.3
82.5	5.5 ± 0.4	4.8 ± 0.3	56.0	4.6 ± 0.3	

Note that $T_{1\rho}(^1\mathrm{H})$ is not very sensitive to motion of single molecular groups, since it is averaged within domains up to a size as large as 1−2 nm. In the presence of sufficient dipolar coupling among the protons, able to provide efficient spin-diffusion over a range of 1−2 nm, $T_{1\rho}(^1\mathrm{H})$ can be treated as a “phase” quantity,[50] indicating that the system can be considered homogeneous in that spatial range. Therefore, since in both sample U and sample H all resonances due to carbon atom with attached protons show $T_{1\rho}(^1\mathrm{H})$ values quite similar within the experimental error, both samples should be considered homogeneous, with an efficient spin-diffusion process averaging $T_{1\rho}(^1\mathrm{H})$ values.

In Figure 6 the intensities of the carbonyl carbons resonance are reported vs the contact time, for both sample U and H. In the same figure the best fit curve is given as a solid line. From the best fit procedure the following parameters have been obtained:

sample U

$$S_0 = 1.50 \pm 0.06 \text{ au}; \quad T_{1\rho}(^1\mathrm{H}) = (6.0 \pm 0.4) \text{ ms}; \quad T_{IS} = 1.3 \pm 0.1 \text{ ms}$$

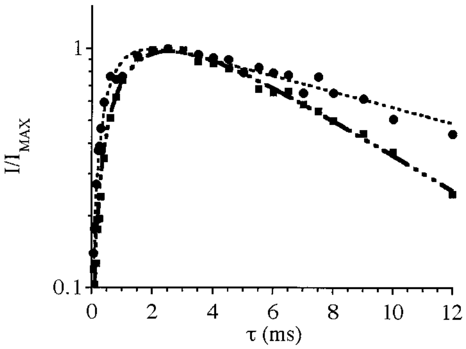


Figure 6. Intensity of resonance of carbonyl carbon atoms vs the contact time: sample H (■) and sample U (●). Lines through experimental points are obtained applying a best fit procedure to eq 1. Note that, after the reaction, due to a change in the chemical environment of same carbonyl carbon atoms, $T_{1\rho}(^1\text{H})$ shortens from ≈13 ms down to ≈6 ms.

sample H

$$S_0 = 1.16 \pm 0.04 \text{ au}; \quad T_{1\rho}(^1\text{H}) = 13 \pm 1 \text{ ms}; \quad T_{IS} = 0.60 \pm 0.05 \text{ ms}$$

Thus, in the network a net $T_{1\rho}(^1\text{H})$ lengthening and a net T_{IS} shortening are observed.

This effect can be rationalized on the basis of a change of the chemical environment of carbonyls. In fact, after the cross-linking reaction, a large variation in mobility and first neighbor proximity of the carbonyl group is likely to occur.

Degree of Cross-Linking. As mentioned, in characterizing cross-linked polymers, the important question arises of evaluating the actual degree of cross-linking. In many cases resonances due to carbon atoms involved in chemical bridges responsible for the cross-links can be directly observed in ^{13}C CP-MAS NMR spectra. However, since the signal enhancement by cross-polarization implies that signal intensities are affected by the kinetics of the transfer of magnetization, the quantitative reliability of the intensity of resonances in ^{13}C CP-MAS NMR spectra must be interpreted with caution. In fact, the rate of the process is strongly dependent on the number of abundant spins near dilute spin S and their distance from S. Thus, the problem exists of quantifying resonances due to carbon nuclei of different types at least in the ideal case where the system is homogeneous and $T_{1\rho}(^1\text{H})$ is single valued. Such a situation is quite common in simple organic systems but not always in polymers.

One possibility consists of investigating the dynamics of the cross-polarization; see eq 1 and Figure 5.

Equation 1 describes the rise of the ^{13}C magnetization with a time constant λ^{-1} T_{IS} during the contact of the ^{13}C nuclei with the proton reservoir which is cold with regard to the spin temperature. Superimposed to this process is the heating of the proton reservoir due to the relaxation of the protons with a time constant $T_{1\rho}(^1\text{H})$.

Even in highly homogeneous systems in order to quantify the measurements we should avoid the rising branch of the ^{13}C magnetization (see Figure 5).

In the presence of a single valued $T_{1\rho}(^1\text{H})$, the plots of intensity are almost parallel when the contact time is long (see Figure 5), and the intensity ratio should be quite correct, the price to be paid being a deterioration of the signal-to-noise ratio.

Table 2. Parameters Obtained from the Best Fit of Eq 1 for the Case of the Highly Cross-Linked (H) Sample

ppm	$S(0)$	$T_{1\rho}(^1\text{H})$ [ms]	T_{IS} [ms]	λ	γ
104.3	1.30 ± 0.03	6000 ± 300	130 ± 16	1.155	0.0089
82.5	1.31 ± 0.02	5500 ± 400	180 ± 10	1.092	0.0061
75.4	1.29 ± 0.02	6200 ± 300	160 ± 7	1.141	0.0015
62.5	1.24 ± 0.02	5000 ± 300	130 ± 5	1.084	0.0085
56.0	1.19 ± 0.02	4600 ± 300	130 ± 5	1.041	0.0082

Table 3. Distortion of Signal Intensities Due to the CP Procedure at Selected Contact Times for the Case of the Highly Cross-Linked (H) Sample

ppm	$[G(\tau)/\lambda]_{\tau=0.5\text{ms}}$	$[G(\tau)/\lambda]_{\tau=1\text{ms}}$	$[G(\tau)/\lambda]_{\tau=3\text{ms}}$	$[G(\tau)/\lambda]_{\tau=5\text{ms}}$
104	0.79	0.74	0.53	0.39
82.7	0.79	0.76	0.53	0.37
75.1	0.80	0.76	0.55	0.40
62.7	0.82	0.76	0.52	0.35
56.0	0.85	0.77	0.50	0.34

Table 4. Values of Average Distortion of Signal Intensity and of Δ at Selected CP Times for the Case of the Highly Cross-Linked (H) Sample

τ (ms)	$\langle G(\tau)/\lambda\rangle$	$\Delta = \langle G(\tau)/\lambda\rangle_{\max} - \langle G(\tau)/\lambda\rangle_{\min}$
0.5	0.81	0.06
1	0.76	0.04
3	0.53	0.04
5	0.37	0.04

It is worth noting that a best fit of eq 1 can provide information about the best contact time to use in the CP-MAS experiment for obtaining an almost quantitative spectrum.[51] In fact, eqs 2 and 4 can be used to calculate the scaling factor λ and $G(\tau)$ at a fixed contact time; the ratio $\lambda/G(\tau)$ is the factor by which the measured intensity must be multiplied for obtaining a "correct" intensity. In turn, the ratio $G(\tau)/\lambda$ provides the distortion of the signal intensity due to the cross-polarization procedure.[52] Since we were mostly interested in evaluating the degree of cross-linking, a best fit of eq 1 was performed on the intensity of all resonances due to carbon atoms with attached protons. In Figure 5b curves resulting from the best fit procedure are shown as solid lines through experimental points in the case of sample H.

Parameters obtained from the best procedure have been used to calculate λ and γ; data are shown in Table 2.

In Table 3, the distortion of the signal intensity $G(\tau)/\lambda$ has been reported; data have been obtained applying eq 2 at few selected cross-polarization times τ_i spanning the range of interest (see also Figure 5b).

The smaller the difference in $G(\tau)/\lambda$ for different carbon resonances, the better is the quantitative condition in the spectrum; i.e., the smaller is the Δ value, the better is the quantitative reliability of intensity of resonance (see Table 4). At longer contact times, the signal-to-noise ratio definitively decreases; in fact, the mean value $\langle G(\tau)/\lambda\rangle$ is 0.81 at $\tau = 500$ μs, while decreasing down to 0.37 at $\tau = 5000$ μs (see Table 4).

The best contact time for obtaining an almost quantitative CP-MAS spectrum is the time corresponding to the highest $\langle G(\tau)/\lambda\rangle$ value and to the lowest Δ. As a consequence, a contact time $\tau = 1$ ms was chosen.

As is well-known, the simplest experiment for obtaining quantitative measurements in high-resolution NMR of solid polymers is the single-pulse excitation (SPE).[53] A single $\pi/2$ pulse is applied to excite carbon signal which is recorded in the presence of MAS and dipolar decoupling (DD). The recycle time RD between successive scans must be long enough to allow all sites to relax

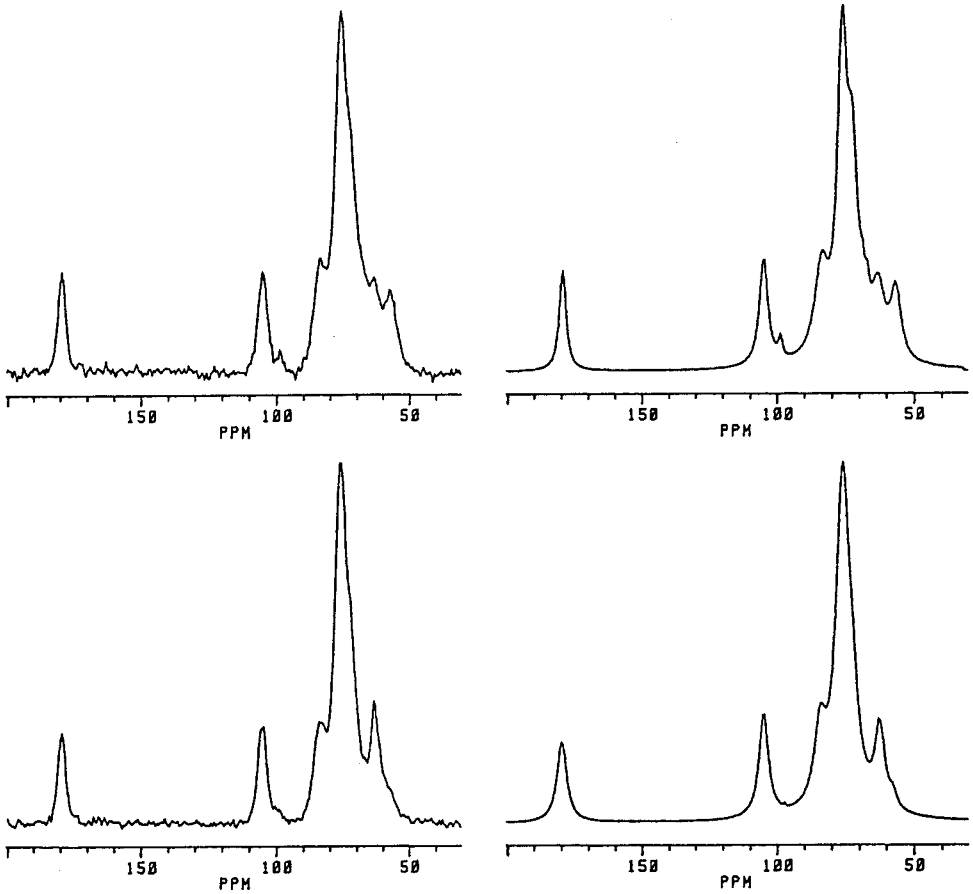


Figure 7. ^{13}C MAS SPE spectra of (top) sample H, high degree of cross-link and (bottom) sample L, low degree of cross-link. On the left experimental spectra are shown, while on the right, the simulated spectra are reported.

back to equilibrium. This time mostly depends on the $T_1(^{13}C)$ values for the relevant carbon sites and on the flip angle of the exciting pulse. The difficult with SPE is that in many rigid glassy or crystalline polymers $T_1(^{13}C)$ values may be very long up to 10^2-10^4 s. Note that measurements should obey to the condition recycle time (RD) $\geq 5T_1(^{13}C)$, with RD values sometimes of the order of hundredths of seconds. Thus, this approach may be unrealistic. However, in the cellulose ether-based network, a recycle time of 40 s was found, allowing all proton bearing C atoms to fully relax. This is due to the fact that these materials are fully amorphous.[39]

In the following, we will compare the degree of cross-linking as obtained by CP-MAS spectra performed with cross-polarization time $\tau = 1$ ms, with the degree of cross-linking as obtained by SPE spectra.

Both methods show some drawbacks. CP-MAS spectra, even if performed in the best experimental conditions, are not perfectly quantitative, while SPE spectra always show a lower signal/noise ratio.

Chemical shifts, line widths, and line shapes obtained from experimental spectra have been used as an input for a program performing full spectra simulation. Intensities and areas of all resonances have been obtained. In Figure 2, left, ^{13}C CP-MAS spectra are reported (sample U (c), sample L (b), sample H (a)), while on the right simulated spectra are reported for comparison. In Figure 7, left, SPE spectra are reported (sample L (bottom), sample H (top)), while on the right, simulated spectra are shown.

The degree of cross-linking, expressed as the number of cross-links per monomer, has been calculated from the ratio between one-half of the area of resonance at 56 ppm due to the two carbons of type A (see Figure 3) and the sum of the area of resonances due to anomeric carbons C-1(2) ($\approx$104 ppm) and C-1(2*) ($\approx$97 ppm) which has been used as a reference.

In the case of sample L, the ratio of integrals obtained from the simulation of the ^{13}C CP-MAS spectra and those obtained from simulation of SPE spectra provides the same result; i.e., the degree of cross-link is $\approx$0.04. In the case of sample H, the degree of cross-linking measured by CP-MAS is $\approx$0.24 with a standard deviation (SD) = 7% of nominal value, while its value measured by the SPE method is $\approx$0.33 with a SD = 10%. Thus, the agreement between the two sets of data is reasonable, but not excellent. As previously mentioned, both methods have some drawbacks. The ^{13}C CP-MAS spectrum, even performed with the proper contact time, might provide intensities not fully reliable. In turn, SPE spectrum gives broader resonances (possibly due to the contribution of mobile chain ends) and a lower signal/noise ratio, so that the simulation is affected by a higher uncertainty.

The actual value is probably in between, $\approx 0.28 \pm 0.09$.

It is worth noting that from the simulation of the CP-MAS as well as of the SPE spectrum a resonance at $\approx$66 ppm has been obtained. This resonance is fully absent in the spectrum of sample U (see Figure 2a, left), and it is probably undetectable in the spectrum of the sample at low degree of cross-linking. It is possibly due to methylenes carbon of type B (see Figure 3). However, since this resonance is fully hidden in a very crowded spectral range of frequencies, its area cannot be used for any calculation.

Conclusions

A ^{13}C solid-state NMR analysis procedure has been set up for the quantitative determination of the *chemically effective* cross-linking degree in polymer networks. This technique has been shown to be very effective in determining the degree of cross-linking, expressed as number of cross-links per monomer, in the case of cellulose-based chemically cross-linked networks characterized by a microporous structure and displaying superabsorbing capabilities coupled with high water retention under compressive stress. With proper adjustments, the procedure can be extended to the case of other chemically cross-linked macromolecular systems.

^{13}C CP-MAS spectra and SPE experiments have been performed for evaluating the ratio between one-half of the area of resonance at 56 ppm due to the two carbons of type A present on cross-linker molecule (DVS) after reaction and the sum of the area of resonances due to anomeric carbons, C-1(2) and C-1(2*), present on polysaccharide rings. Proper choice of cross-polarization time for ^{13}C CP-MAS spectra and of recycle time between successive scans for SPE experiments allowed quantitative evaluations.

Further work is in progress using ^{1}H NMR relaxometry for a better understanding of local motions possibly correlated to swelling properties.

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MA9914117