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^{13}C NMR Analysis of Polybutadiene via Cross Polarization and Magic Angle Spinning

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ABSTRACT: Changes in ^{13}C NMR spectra as a function of cross-link density have been investigated for polybutadiene. Increased cross-linking significantly increases the heteronuclear carbon proton dipolar coupling as measured by both ^{13}C T_2 relaxation measurements and combined cross polarization/magic angle spinning measurements (CP/MAS). The CP/MAS measurements provided much higher resolution spectra than T_2 relaxation experiments without the loss of information about low-frequency motions. High-speed MAS was shown to amplitude modulate the static carbon–proton dipolar interaction and frequency modulate the homonuclear proton dipolar coupling. The ability of the MAS to modulate the dipolar coupling is a measure of cross-link density.

Introduction

The analysis of structure in cross-linked polymers can be a very difficult problem. A good example of such a system is polybutadiene (PBd), which, at room temperature, is well above its glass transition point. It is commercially a very important rubber since it is widely used to modify glassy polymers.[1,2] One of the most common ways to measure cross-link density is by swelling in an appropriate solvent and calculating cross-linking from the swelling index using the Flory–Rehner equation.[3] In the case of a pure PBd, this works quite well. However, in a complex rubber modified thermoplastic, such as acrylonitrile–butadiene–styrene resins (ABS) or high-impact polystyrene (HIPS), there are a number of complicating factors such as occlusion levels[4] or grafting[5] that may interfere with the absolute measurement of cross-linking by swelling. In addition, the sample preparation requires separating the grafted rubber from the matrix, so that the rubber properties are not measured directly in the whole polymer.

^{13}C nuclear magnetic resonance (NMR) spectroscopy is a well-known tool for analysis of chemical structure in both liquids and solids. However, rubbery materials, i.e., polymers close to or above their glass transition temperature, are neither true liquid nor true solid. They exhibit some properties of both solids and liquids. High-resolution ^{13}C NMR spectra of these systems can be difficult to obtain since the lines are often very broad, and this broadening gets worse as the cross-link level is increased. It has been reported that useful ^{13}C NMR spectra could be obtained from solid PBd by using standard liquid NMR techniques in solid ABS.[6] The observed lines, however, were very broad unless the sample was spun by using high-speed magic angle spinning (MAS). It has also been reported that NMR relaxation measurements correlate with cross-link density.[7-13]

Although one can use T_2 measurements to make a qualitative analysis of cross-link densities, the extreme broadening in the most highly cross-linked samples does not give sufficient resolution to permit analysis of the cis, trans, and vinyl groups individually. Attempts to improve resolution by obtaining solution-state spectra are pointless since, by definition, a cross-linked sample cannot be dissolved. Swelling with an appropriate solvent might help resolution but would make obtaining reliable T_{2C} information very difficult because the rubber network would be so extended. A reasonable solution to the problems with resolution is to obtain high-resolution ^{13}C NMR spectra in cross-linked rubber by using high-speed magic angle spinning.[14] This, however, eliminates the desired line-width information since the line collapses to an isotropic value.

It is desirable to develop a technique that allows one to use the high resolution obtained with MAS and still be able to observe the effect of cross-linking on low-frequency motions of the rubber, which can be used to explain the physical properties. Measurement of the cross-polarization transfer rate (T_{IS}) is such a technique that is widely applied for NMR of solid systems. It has been difficult to obtain such cross-polarization spectra for rubbers because of poor signal intensity.

It has been reported for adamantane that the static C–H coupling is amplitude modulated by the MAS and that the homonuclear proton coupling is frequency modulated, giving rise to a dependence of transfer rate on the carbon spin locking radio frequency, ω_1. The maximum transfer rates occur when the carbon spin locking radio frequency is offset from the exact Hartmann–Hahn match by integrals of the spinning frequency.[15]

The results reported here will show how one can obtain good CP/MAS spectra of solid rubbers by using a Hartmann–Hahn mismatch. MAS produces some effects on T_{IS} that are not usually observed in glassy polymers. As with adamantane, the magnitude of T_{IS} varies as a function of the difference between carbon and proton ω_1's with maximum transfer rate observed when they differ by a multiple of the spinning frequency. The response of T_{IS}'s to spinning is explained in terms of the proton–carbon

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interaction. The rubber is a mobile material at the molecular level, resulting in both the proton and carbon lines being narrow compared to solids. In fact, PBd exhibits even sharper lines than adamantane, and the modulation effect on polarization transfer is much more pronounced.

The heteronuclear dipolar coupling is a static interaction. Maximum polarization transfer is achieved when ω_{1H} and ω_{1C} are matched. For solids, this condition requires the same ω_1 for both nuclei. However, with PBd, as in adamantane, MAS amplitude modulates (AM) the C–H dipolar coupling. A plot of CP efficiency as a function of ω_{1C} gives pairs of sidebands offset from the Hartmann–Hahn match by 1 and 2 times the MAS frequency. There is also frequency modulation (FM) of the homonuclear proton coupling, giving rise to a complicated FM pattern of multiple peaks. As the sample becomes more rigid, the homonuclear coupling becomes even stronger, giving rise to additional mismatch sidebands as well as a weak center band. It is possible to extract information about the nature of the rubber from the sideband pattern by deconvoluting the AM and FM pattern. This allows one to use MAS to give high resolution and use the size and number of mismatched CP pattern sidebands to measure molecular mobility.

We will demonstrate how T_{2C} measurements are useful for low-level cross-linking in polybutadiene, while CP/MAS using a Hartmann–Hahn mismatch gives excellent results for highly cross-linked materials.

Experimental Section

A. Synthesis of Cross-Linked Polybutadiene Networks. Materials. The polybutadiene used in these experiments was commercial Diene 35 NFA (Firestone). This polymer has a reported M_w/M_n of 202/96. Dicumyl peroxide (DiCup) was commercial Luperox 500R (Lucidol). All solvents were reagent grade.

Procedure. Stock solutions of 10% (w/w) Diene-35 and 1% DiCup in methylene chloride were used. Solution blends of peroxide and rubber were prepared as follows:

sample	rubber soln, g	DiCup soln, g
1	20	2.0
2	20	4.0
3	20	8.0

Each solution was poured into 6-cm-diameter aluminum weighing pans and allowed to air dry with gentle heating until evaporated (about 1 h). The samples were then placed in a vacuum oven at 180 °C for 10 min.

The swelling index of the samples was determined by placing an accurately weighed piece of the cross-linked rubber film (about 0.1 g) in a micro ultra centrifuge tube and allowing it to swell overnight in tetrahydrofuran. The sample was then spun at 22 500 rpm and the supernatant decanted. The quantity of dissolved rubber sol, determined by evaporating the supernatant to dryness, was negligible. The swelling index (SI) was calculated by

$$\text{SI} = (\text{wt of swollen rubber gel})/(\text{wt of dry rubber})$$

B. NMR Experiments. Equipment. The instrument used was a home-built spectrometer, having a resonant frequency of 100 MHz for protons and 25.14 MHz for carbons, with a dual airbearing magic angle spinner. During the MAS experiments, the rotor frequency was maintained at 1922 ± 5 Hz. ω_{1C}'s and ω_{1H}'s were calibrated twice daily by using a static reference sample of polybutadiene. ω_1 values were measured at five different levels of attenuation, and the desired ω_1 was selected from a curve of attenuation vs. ω_1. Throughout the ranges used, the amplifiers had a linear response. There was almost no observable change in ω_1 vs. attenuation throughout the course of these experiments.

Boron nitride rotors were used for the high-speed MAS experiments. T_2 measurements were made both with boron nitride rotors and in 10-mm glass NMR tubes purchased from the Wilmad Glass Co. There was no difference in results between the two types of sample holders.

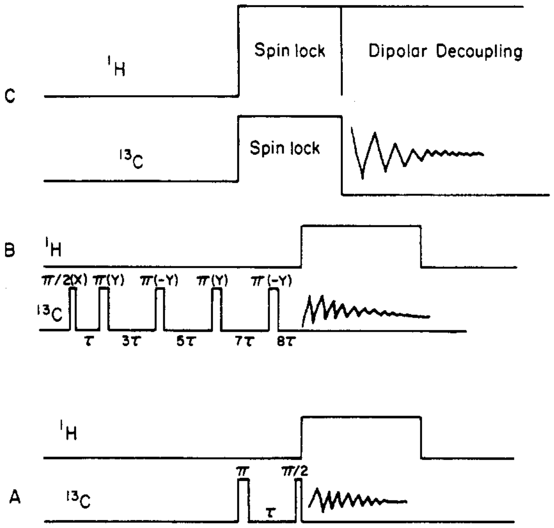

Figure 1. Pulse sequences used for (A) T_1 and (B) T_2 in the liquid-state-type experiments and (C) $T_{IS}/T_{1\rho H}$ in the CP/MAS experiments.

C. Pulse Sequences. Figure 1 shows the various pulse sequences used for the T_2, T_1, and $T_{1\rho}$ measurements. T_{2C} values were measured by using the Meiboom–Gill modification of the Carr–Purcell (CPMG) sequence[16] to avoid possible complications due to field inhomogeneity or pulse imperfections. The 90° pulse was 7.5 μs long. The delay times in the CPMG sequence varied between 50 μs and 15 ms in all the measurements reported here. Analysis of selected samples using longer delays, up to 100 ms, showed no difference compared with the faster measurements.

All cross-polarization measurements were made by using a 12-kHz ω_{1H}. ω_{1C} was varied as desired. The contact times were varied between 10 μs and 35 ms. The spectral width was 10 kHz, and 2K points were acquired. A 5-Hz exponential line broadening was used to smooth the spectrum. Since the line widths are typically greater than 50 Hz, this smoothing has very little effect on the data.

D. Sample Preparation. Sample preparation is simple. Flexible samples (low cross-link density) were rolled to form a cylinder, while brittle samples were broken up into small pieces. Both types of sample were packed as tightly as possible into the sample tube to maximize sensitivity. These packed tubes were then analyzed directly. Samples were analyzed at ambient temperature. The room temperature was 27 ± 3 °C.

Results

The cross-linked rubber networks exhibited swelling indices that varied regularly with the amount of peroxide as shown below:

sample	DiCup/rubber, %	SI	M_c
1	1.0	6.4	6810
2	2.0	3.5	2730
3	4.0	1.9	1020

The average molecular weight between cross-links (M_c) was calculated from the Flory–Rehner equation[3]

$$(\text{SI})^{5/3} = [1/(2 - \chi)]\nu M_c[1 - (2M_c/M)]^{-1}v_1^{-1}$$

where ν is the specific volume of the polymer (1.12 cm^3/g), v_1 is the molar volume of solvent (80 cm^3/mol), and χ is the Flory interaction parameter (0.3). The polymer molecular weight was taken to be 100 000.[17]

T_2 Measurements. Figures 2 and 3 illustrate the effect of cross-linking on the line width ($1/T_2$) in a ^{13}C NMR spectrum of polybutadiene. The spectra range from an un-cross-linked rubber, Figure 2A, to a highly cross-linked rubber, Figure 2D. Even the un-cross-linked rubber does not show truly liquid-like resolution, since the molecular weight is above the entanglement limit. As the sample is cross-linked, structural information is obscured by the loss

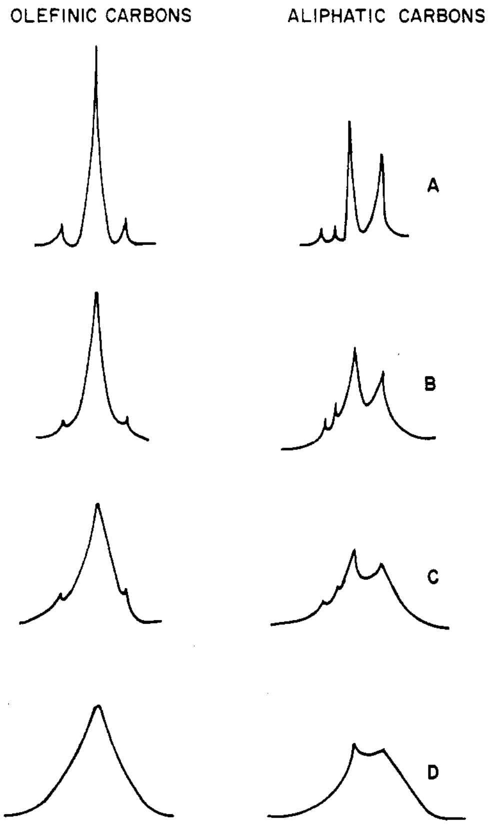

Figure 2. Spectra of polybutadiene with varying cross-link density: (A) un-cross-linked; (B) M_c = 6810; (C) M_c = 2730; (D) M_c = 1020.

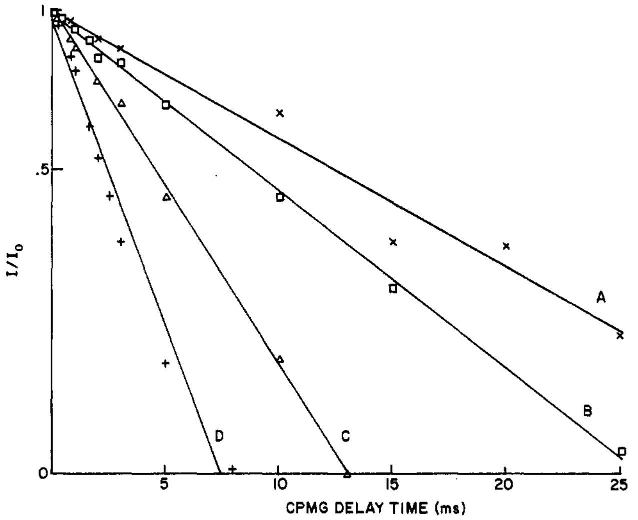

Figure 3. T_2 plots of signal intensity vs. delay time in the CPMG sequence for (A) un-cross-linked, (B) M_c = 6810, (C) M_c = 2730, and (D) M_c = 1020.

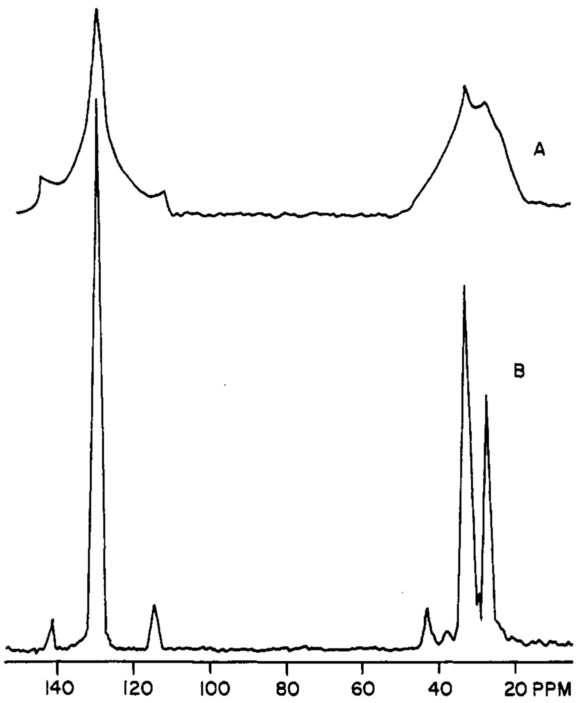

Figure 4. Illustration of the effect of magic angle spinning on resolution of sample with M_c = 6810: (A) no MAS; (B) MAS at 1.9 kHz.

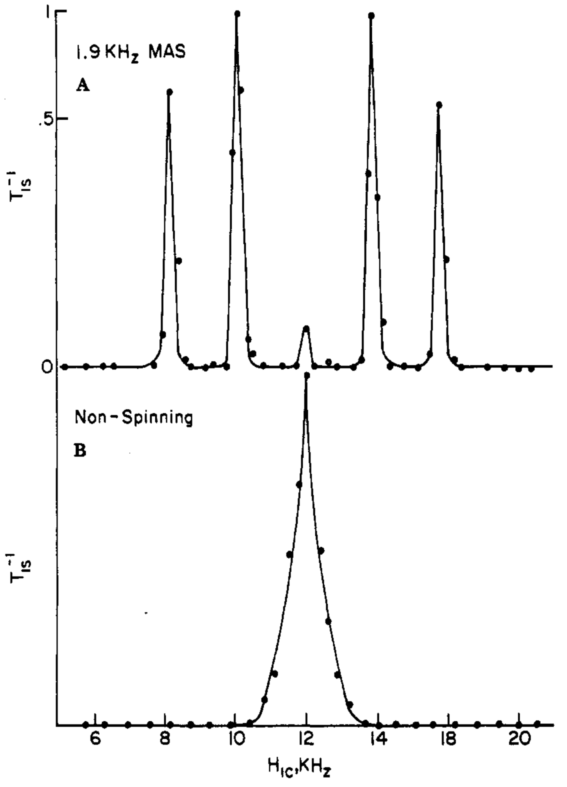

Figure 5. Plot of magnetization transfer efficiency vs. ω_{1C} with ω_{1H} maintained at 12 kHz for the un-cross-linked PBd.

of resolution due to lower T_2's.

Magic Angle Spinning. Figure 4 shows how the use of magic angle spinning improves the resolution of the spectrum of the most highly cross-linked sample. MAS restores the structural information since the lines are now much narrower than in the T_{2C} analysis. Unfortunately this complicates T_{2C} characterization of the samples.

Cross Polarization/Magic Angle Spinning. CP efficiencies that depend on static, 0 Hz, couplings should reflect the same mobility effects as T_{2C}. With decreased rubber mobility, the CP transfer rate will be higher. In glassy polymers, the transfer rate is not significantly affected by MAS. This is not the case in the rubbers. In a static sample, as illustrated in Figure 5B, the maximum transfer rate is at the Hartmann–Hahn match. A plot of transfer rate as a function of carbon ω_1 expectedly shows the maximum polarization transfer rate at an exact Hartmann–Hahn match and slower polarization transfer with increasing mismatch.

This is not the case, however, in the same sample spun at 1.9 kHz, at the magic angle, as shown in Figure 5A. There is a very slow transfer of polarization at the Hart-

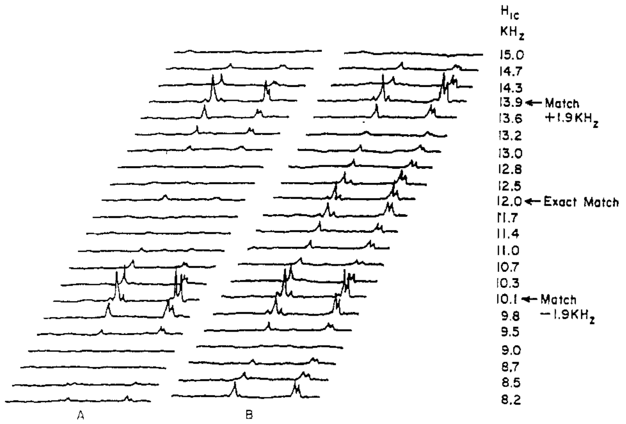

Figure 6. Spectra obtained by using a 2-ms contact time as ω_{1C} is varied with 1.9-kHz sample MAS: (A) un-cross-linked; (B) M_c = 1020.

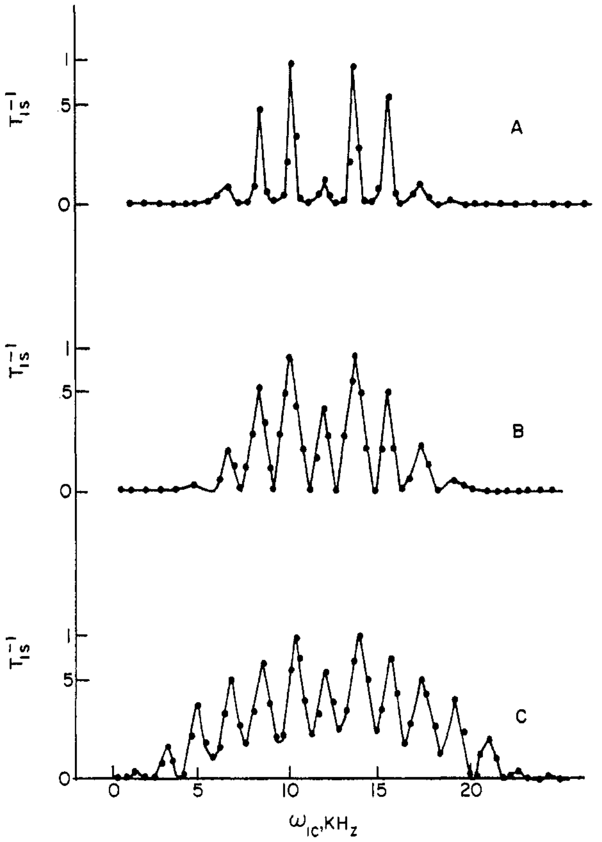

Figure 7. Illustration of the effect on cross-linking on the efficiency of polarization transfer: (A) M_c = 6810; (B) M_c = 2730; (C) M_c = 1020.

mann–Hahn match, where the transfer is expected to be most rapid. A modulation of the polarization transfer occurs with the maximum transfer rate observed with a deliberate mismatch of the ω_{1C} and ω_{1H}. There is a series of maxima in the plot of T_{IS} vs. ω_{1C} occurring when ω_{1H} and ω_{1C} are mismatched by a multiple of the spinning frequency, 1.9 kHz in this case.

The practical consequence of this effect is illustrated in Figure 6, where the observed spectra for a 2-ms contact time is shown for a number of carbon spin locking radio frequencies for the un-cross-linked sample (A) and a highly cross-linked PBd (B). There is virtually no signal observed by using an exact Hartmann–Hahn match. Mismatching ω_{1C} and ω_{1H} by multiples of the MAS frequency, however, produces excellent signal intensity, with maximum transfer efficiency in mismatched sideband 1.

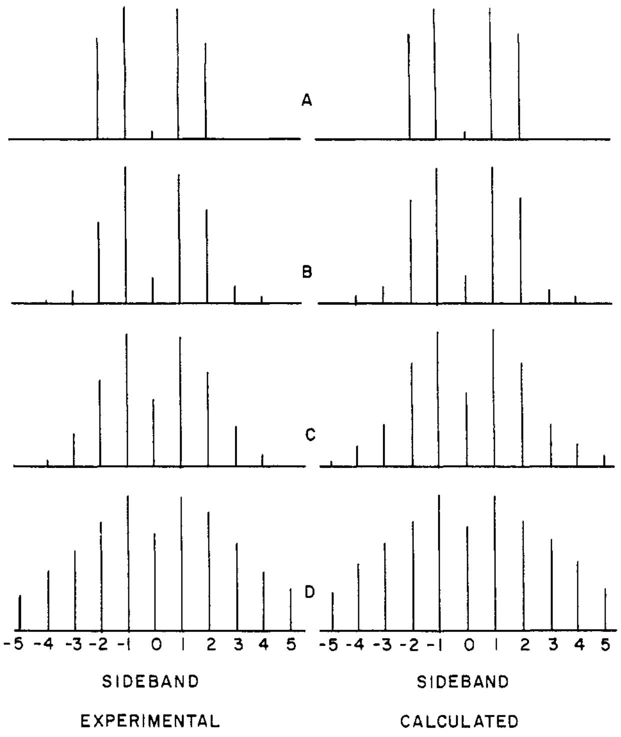

Figure 8. Comparison of experimental and calculated Hartmann–Hahn mismatch sideband patterns for (A) un-cross-linked, (B) M_c = 6810, (C) M_c = 2730, and (D) M_c = 1020.

Table I

M_c	FM index	% FM character
Diene 35	2.31	2
6810	2.40	8
2730	2.65	70
1020	2.88	92

Figure 7 shows a strong dependence of T_{IS} on ω_{1C}. The strength of this dependence is controlled by cross-link density, being more pronounced in the case of the un-cross-linked rubber and less critical for a cross-linked PBd. In all cases it is important to select ω_1 carefully, or one could miss the signal completely.

The series of maxima and minima observed in T_{IS} as a function of carbon ω_1 is in fact a combination of an amplitude-modulated pattern due to carbon proton heteronuclear coupling and a frequency-modulated pattern due to proton homonuclear coupling.

Since the heteronuclear coupling, which produces the Hartmann–Hahn mismatched AM sidebands in pure PBd, is static for all samples, it produces exactly the same pattern in all the rubbers giving two mismatch sidebands in an intensity ratio of 1:0.7, i.e., a standard AM pattern.[18] The interesting part of the pattern is the change produced by increased homonuclear proton coupling as a function of cross-linking. By separating the two parts of the pattern it is possible to use the FM pattern to characterize the physical mobility of the rubber. The sideband intensities in an FM pattern are determined by a series of bessel functions of the first kind

$$J_n(\delta)$$

where n is the number of the sideband and δ is the modulation index.[18] If the intensities of three successive sidebands are known, the recurrence relation[19]

$$J_{n-1}(\delta) + J_{n+1}(\delta) = (2n/\delta)J_n(\delta)$$

determines the modulation index. Once the FM index is known, the entire pattern can be calculated (Figure 8). The cross-link density can then be related to both the FM index and the % FM character of the pattern (Table I).

$T_{1\rho H}$. It is known that T_{1H}, which measures megahertz frequency interactions, is sensitive to cross-linking.[13] One would expect therefore the $T_{1\rho H}$, which measures kilohertz frequencies, might also be affected. We do observe changes in $T_{1\rho H}$ with cross-linking. However, the effect is not as pronounced as the changes in T_{2C} or T_{IS}. $T_{1\rho H}$ and T_{1H} are less sensitive to cross-link density than T_{2C} and T_{IS} because the major change in molecular mobility is at very low frequencies, near 0 Hz. The changes observed for $T_{1\rho H}$ and T_{1H} are due to increased proton homonuclear coupling and faster spin diffusion in a cross-linked rubber. The effect is, however, not as dramatic as the changes in long-range low-frequency motions. With very high cross-link densities, the local environment will change enough to effect major changes in $T_{1\rho H}$, T_{1H}, and T_{1C}, but the cross-link levels used here are still fairly low. All the measured $T_{1\rho H}$ values for a given sample were the same no matter which carbon ω_1 was used. $T_{1\rho H}$ were obtained by using the maximum transfer rate, i.e., a mismatch of the Hartmann–Hahn condition for carbon ω_1 by 1.9 kHz, the rotor frequency. This gives maximum CP signal intensity since the $T_{1\rho H}$ decay does not dominate the early part of the intensity vs. time plot as in the case where the transfer rate is very slow. The $T_{1\rho H}$ results were consistent with a homogeneous sample since only a single $T_{1\rho H}$ relaxation is observed. The effect of cross-linking on carbon $T_{1\rho}$'s was not investigated.

Discussion

T_{2C} Results. The strong effect of cross-linking on the ^{13}C NMR spectrum illustrated in Figure 2 provides valuable information about the physical state of the rubber. What one macroscopically observes is that, as the cross-link density increases, the PBd becomes more brittle; in the case of the most highly cross-linked sample, there is very little rubbery nature at all. The relationship between cross-link density and $1/T_{2C}$ is not surprising since the changes in T_{2C} are influenced primarily by long-range low-frequency motions. T_{2C} values are also affected by high-frequency motions, but since measurements of T_{1C} relaxation times, which are influenced only by high-frequency motions, show no dependence on cross-linking, the changes in T_{2C} must be due to low-frequency motions. One can explain the fact that T_{1C} shows no dependence on cross-linking because the very short range motions which contribute to T_{1C} effects are primarily due to localized phenomena. Even in the highest cross-link density investigated here the M_c is over 1000, so very few monomer units are close enough to a cross-link point to be restrained by it.

There is one major problem with T_{2C} measurements. Even in the samples studied, where the cross-link density is reasonably low, the line widths are sufficiently large to destroy spectral resolution. As Figure 4 clearly demonstrates, MAS significantly enhances the resolution. The combination of a Hartmann–Hahn mismatched CP measurement with MAS retains high resolution and information about the molecular motion of the rubber.

CP/MAS using a Hartmann–Hahn mismatch is ideally suited to characterization of rubber systems like PBd. One would expect that if the system were cross-linked sufficiently, the mismatch sideband pattern should essentially disappear, and the more familiar pattern with a single maximum would appear, i.e., a solid-state-type response. Conversely, if the rubber molecular weight was lower than the entanglement molecular weight or the linear PBd was in solution, there would be insufficient interaction to allow any cross polarization. In either case, the Hartmann–Hahn mismatch sideband pattern would not be observed. This technique is very well suited for chemical and physical studies of rubbers. The use of MAS gives high resolution, while the size and number of mismatched CP pattern sidebands is a measure of molecular mobility.

The deconvolution of AM and FM parts of the modulation pattern and the determination of the FM index are straightforward. The modulation index is a measure of the extent of proton homonuclear coupling as is the % FM character of the pattern. The modulation index appears to be much more sensitive to cross-linking than the % FM. This is to be expected, especially in samples with low FM or AM character, since the error in accurately measuring the FM or AM intensities becomes large relative to the signal size.

The major difficulty with the CP/MAS measurements is in obtaining a full curve, as shown in Figures 6 and 7, which requires approximately 1 week per sample. However, once the shape of the patterns has been confirmed for standards, it is only necessary to measure the maxima at mismatch sidebands 1, 2, and 3 to determine the modulation index and calculate the entire pattern. This provides the needed information in 2–3 h without the loss of resolution inherent in other measurements.

Conclusions

It has been demonstrated that if one uses the proper conditions it is possible to obtain ^{13}C NMR spectra of rubbers either by traditional liquid-state methods or by solid-state methods. One can observe the effect of rubber cross-linking on line widths by direct pulse and acquire methods. Alternatively, one can use CP/MAS to obtain similar information without loss of resolution in the spectrum.

Polybutadiene is an excellent candidate for such structural analysis by ^{13}C NMR. Its fast and relatively constant T_{1C} allows rapid signal acquisition. The high sensitivity of T_{2C} measurements to cross-link density augments the chemical information inherent in the spectrum with physical information about the state of the rubber, but it is limited to lightly cross-linked samples.

In a highly cross-linked rubber, however, the sensitivity of T_{2C} is a drawback since the extreme broadening of the lines diminishes the chemical information in the spectrum. In this case, magic angle spinning greatly improves resolution, while the use of a deliberate mismatch of the Hartmann–Hahn condition produces high sensitivity due to the modulation of the static dipolar coupling between carbons and protons by the MAS. This modulation is similar to that reported previously for materials having sharp proton lines, but in the rubber the effect is much stronger because of the extremely sharp lines in a rubber spectrum.

For highest resolution, CP/MAS is the technique of choice. If sufficient care is used to control ω_{1C} and ω_{1H}, the response of T_{IS} to frequency mismatches can be measured without obtaining the entire pattern. Results can be obtained more rapidly than with T_{2C} measurements, and the FM index and the % FM character of the pattern are measures of molecular mobility.

The techniques reported here are not limited to polybutadiene. Useful applications of the mismatch technique exist for the analysis of other systems that are molecularly more rigid than PBd but still above the glass transition temperature, for example, EPDM rubber, acrylate rubber, or adhesives. In these cases, the lines are too broad for good T_{2C} measurements but are sufficiently narrow to observe modulation of the dipolar coupling by MAS.

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Scattering Function of Polystyrene

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ABSTRACT: An improvement over previous determinations of the structure factors of polystyrene has been obtained from small-angle neutron scattering by using the isotopic labeling method. Atactic polystyrenes have been deuteriated in three different ways: in the backbone, in the phenyl rings, or in both. Their scattering functions, measured from dilute solutions in a good solvent, are found to be quite different beyond $q = 0.05$ Å^{-1}. Actually, the variations with contrast of the structure factor indicate that the monomer structure affects the scattering function of polystyrene beyond q values as low as 0.03 Å^{-1}. To interpret this result, the polystyrene is approximated by a curved cylinder, and the effect of its local structure is divided into two parts. First, the properties of the monomer species are smoothed along an infinitely thin curve. This object is represented by the Porod–Kratky chain model. Second, the effect of side groups on the scattering function is treated as a simple thickness; a corrective term $\Phi(q)$ is then added to the structure factor $S_0(q)$ of the thin thread. The cross-section term $\Phi(q)$ is determined for each type of deuteriated polystyrene. Remarkably, these functions are not compatible with a model where the chain has cylindrical symmetry; therefore, anisotropic correlations between the orientations of successive phenyl groups must be important. The structure factor of the thin thread follows the $q^{-1/\nu}$ decay of the self-avoiding random walk model up to $q = 0.06$ Å^{-1}; beyond this point the rigidity of the chain becomes important. A universal constant related to the amplitude of this $q^{-1/\nu}$ decay is determined.

I. Introduction

The only direct methods available for studying the conformational statistics of chain molecules are radiation scattering techniques.[1,2] They yield the structure factor $S(\vec{q})$, defined as the Fourier transform of the monomer density autocorrelation function $\langle \rho(\vec{r})\rho(0)\rangle - \langle \rho \rangle^2$.[3] In the static approximation, the magnitude of the scattering vector $\vec{q}$ is related to the wavelength of the radiation λ and the angle between incident and scattered beams θ by the relation

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \qquad (1)$$

For chain molecules that can take random orientations, we are concerned with the isotropic average $S(q)$ defined as

$$S(q) = \frac{1}{4\pi}\int_0^{4\pi} S(\vec{q})\, d\Omega$$

and the aim is to obtain this function for a single molecule at all q values. A reciprocal Fourier transform will then yield the pair correlation function of monomers $\langle \rho(\vec{r})\rho(0)\rangle$ which describes the average conformation of the chain.

From an experimental point of view, this procedure is unrealistic because the range of q values is always limited; its upper boundary sets the spatial resolution of the experiment.[3,4] Two distinct approaches are then used.

(1) The Guinier range, i.e., small q values: for homopolymers, we measure the mean square radius of gyration of the chain R_G^2. Some details about the chain statistics can be obtained by studying R_G^2 as a function of the molecular weight M_w. This requires well-characterized samples in a broad range of M_w values.

(2) The range of higher q values, i.e., for $qR_G > 1$: the spatial resolution is improved, and we observe the corre-

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