Contribution of the Methine Group to the Transverse ^{1}H NMR Relaxation in Vulcanized Natural Rubbers

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Received March 19, 2004; Revised Manuscript Received May 12, 2004

ABSTRACT: Transverse ^{1}H NMR relaxation experiments in vulcanized natural rubber (NR) samples above the glass transition temperature (T_g) are reported on. Natural rubber samples with the same initial chemical composition but different times of cure were studied. The distinct feature of this study as compared to previous works is that the contribution to the total transverse ^{1}H magnetization of the methine group of the monomeric unit and the contribution of the methyl and methylene functional groups are analyzed independently. The results of these experiments show that for short delay times the decay of the ^{1}H transverse magnetization of the methine groups is slower than that of the methyl/methylene groups. Consequently, the methine ^{1}H contribution to the total transverse magnetization can be distinguished from the contribution of the other functional groups. A slow relaxing contribution to the total transverse ^{1}H magnetization in NR samples, similar to the one reported on in this work, has been described in the literature.[1] However, the contribution was attributed to ^{1}H in dangling chain ends experiencing fast anisotropic motions. Here, we show that, on the contrary, the contribution is indeed produced by the methine groups in cross-linked chains. Values for the residual dipolar second moment, fraction of dangling chain ends, and spin−spin relaxation constant time T_2 were obtained from the fit of the transverse ^{1}H relaxation curves of the methine and methyl/methylene groups independently. The values obtained for these parameters suggest that the protons in the polymer chains sense the same microscopic properties of the material independently of the functional group where they are. The slower decay of the methine magnetization is caused in part by a weaker dipolar interaction for the methine proton with its nearest ^{1}H neighbors as compared to the intragroup dipolar couplings in methyl or methylene groups.

Introduction

Technical elastomers are a very important class of materials considering the large number of applications that they have. The study of the fundamental properties of these materials, at the molecular level, is therefore of great interest. The understanding of these properties allows to control and modify the macroscopic properties of the elastomers as needed for different applications. Particular interest has the study and measure of the cross-links in polymer chains since they are very important for the mechanical properties of the rubber product.

NMR techniques are suitable to unravel the fundamental properties of polymers.[2,3] For cross-linked elastomers above the glass transition temperature, T_g, NMR provides information on the structure and on the dynamics of the polymer chains in the bulk.[4−10] Several ^{1}H NMR experiments like transverse ^{1}H relaxation (Hahn spin echoes),[4−6] pseudo solid spin echoes,[7] 2D exchange experiments,[8] and multiple quantum coherence[9] have been used to probe different aspects of the structure and dynamics of the polymer chains at the molecular level. Also, ^{13}C NMR has been used to detect and quantify the sulfur bridges in nonlabeled samples.[5]

Among the NMR experiments used to characterize elastomers, transverse ^{1}H NMR relaxation studies is of particular relevance. It provides quantitative information on the density of cross-links and on the fraction of dangling chains in the sample. Also, qualitative information on the dynamics of the polymer chains can be extracted. On the other hand, the measurements are easy and fast to perform and can be carried out in low-cost, low-frequency (less than 100 MHz) NMR spectrometers. Moreover, nowadays, superficial NMR scanners like the NMR-MOUSE[11] can directly carry out transverse ^{1}H NMR relaxation measurements ex situ in final rubber products like, for example, automobile tires.[11]

The interaction exploited in transverse ^{1}H NMR relaxation experiments is the spin dipole−dipole coupling between pair of ^{1}H. The dipolar interaction is partially averaged out by fast motions of the chain segments. The extent of this average depends on the characteristics of the motions, which in turn depends on the constraints imposed to those motions by the chemical and physical cross-links of the chain segments. These constraints, depending on their type, cause different relaxation behaviors for the transverse ^{1}H magnetization of the polymer chains. According to the type of constraints, the chains are usually classified as cross-link chains, dangling chain ends, or free sol chains.[4,5] The contribution to the transverse magnetization of protons in cross-link chains has a characteristic fast solidlike decay. The contributions of the dangling chains and free sol chains, on the other hand, have a slow liquidlike decay.

Within that model, no distinction for protons belonging to different functional groups, i.e., methyl, methyl-

10.1021/ma049451k CCC: \$27.50 © 2004 American Chemical Society
Published on Web 06/29/2004

ene, or methine groups for NR, is made. Therefore, to validate the model and to gain a better understanding of the relaxation behavior of the transverse ^{1}H magnetization, we carried out new NMR studies in vulcanized NR, where the contribution of the methine group and the contribution of the methyl/methylene functional groups to the transverse magnetization were analyzed independently. The study was possible due to the fact that the ^{1}H NMR spectrum of NR samples, measured at 300 MHz, exhibit two partially resolved resonance lines. One NMR line corresponds to the ^{1}H of the methine group while the second one corresponds to the contribution of protons in methyl/methylene groups.

Our study shows the existence of a contribution to the total ^{1}H transverse magnetization in NR, produced by the methine groups at short delay times ($\tau \lesssim 8$ ms). This result is very important since it indicates that the contribution of the methine groups is not negligible. Also, it is important since a similar contribution to the total magnetization was reported in ref 1, but it was attributed to dangling chains experiencing anisotropic motions. In our work it is shown that at short delay times the decay of the methine magnetization is slower than the decay of the magnetization of the CH_3/CH_2 groups and makes its contribution to the total magnetization nonnegligible. It is also demonstrated that this slower decay is caused in part by a weaker dipolar interaction due to the relative long distance between the methine ^{1}H and its nearest neighbor.

The study also shows that the structural information about the system obtained from the analysis of the CH_3/CH_2 relaxation curves is the same as the one obtained from the analysis of the CH relaxation curves. This brings us to the conclusion that in NR samples protons located in the same chain segment sense the same microscopic properties, regardless of their functional group.

Theory

The model proposed by Schneider et al.[4,5] was used to analyze the NMR relaxation data. Here we summarize the main results of the model. As mentioned in the Introduction, the interaction exploited in transverse ^{1}H NMR relaxation experiments is the spin−spin dipolar coupling between pair of protons. This interaction is partially averaged out by the fast motions of the chain segments. The extent of the average of the dipolar interaction depends on the characteristics of the motion of the chains, which in turn depends on their topological constraints.

According to the type of constraint, the chain segments are usually classified as cross-link chains, dangling chain ends, and free sol chains.[4,5] The cross-link chains are polymer chains cross-linked to the network by the two end points. These chains experience fast (correlation times $\tau_f \sim 10^{-8}$ s) anisotropic motions that do not completely average out the dipolar second moment of the resonance line. A residual dipolar second moment of the order of 10^{-4} ms^{-2} remains. Thus, the contribution of cross-link chains to the magnetization has a solidlike behavior, characterized by a fast Gaussian type decay. Dangling chain ends are linked to the network only by one end. Hence, they experience fast isotropic motions that completely average out the dipole−dipole interaction. The decay of the magnetization associated with these chains has a liquidlike behavior characterized by a slow exponential decay. In these cases, the dipole−dipole interaction only contributes to the spin−spin relaxation mechanism (T_2), i.e., to the homogeneous broadening of the NMR lines. Similar behavior experience the free sol chains since they are not linked to the network at all.

It is important to note that entanglements or topological interactions behave as cross-linking points, and the chains between them will behave as cross-link chains. For this reason only the unentangled part of the pendant chains are considered as dangling chain ends.[12] Similar effects are expected for the free sol chains. If they are entangled to the network, then they will contribute (depending on the number of cross-link points) as cross-link chains and/or dangling chain ends. Therefore, only free isolated chains are considered as free sol chains.

The magnetization decays of dangling chains and of the free sol chains could have different T_2 constants.[4,5] However, in our experiments, no evidence of two different decays were observed. Thus, to explain the relaxation behavior of the transverse ^{1}H magnetization in vulcanized NR, only two components were considered. One corresponds to the contribution of the cross-link chains and the second to the contribution of the dangling chain ends and free sol chains. The following equation was used to describe the ^{1}H transverse magnetization decay in these cases:[4,5]

$$M(\tau) = A \exp(-\tau/T_2 - qM_2^{\mathrm{RL}}\tau_s^{\,2}[\exp(-\tau/\tau_s) - 1 + \tau/\tau_s]) + B \exp(-\tau/T_2) \quad (1)$$

where $A/(A + B)$ is the fraction of cross-link chains and $B/(A + B)$ is the fraction of dangling chain ends and free sol chains. The residual second moment of the dipolar coupling is $M_2^{\mathrm{Res}} = qM_2^{\mathrm{RL}}$, where q is the anisotropy parameter and M_2^{RL} is the second moment of the dipolar interaction in the rigid lattice. In turn, $M_2^{\mathrm{RL}} = (9/20)\Delta^2$, where $\Delta = \mu_0\gamma\hbar/4\pi r^3$, γ is the gyromagnetic ratio of the proton, μ_0 is the Bohr nuclear magnetic moment, and r is the distance between the proton spin pair. In eq 1, τ_s is a correlation time that takes into account slow motions involving larger chain segments.[4,5]

When the dispersion of the experimental data is high, an equation with fewer parameters can be used:

$$M(\tau) = A \exp(-\tau/T_2 - C\tau^2) + B \exp(-\tau/T_2) \quad (2)$$

where $C = {}^1\!/_2 qM_2^{\mathrm{RL}}$. This approximation is strictly valid for $\tau_s \gg \tau$, that is, when approaching the rigid lattice limit within the time scale τ.

The anisotropy parameter q can be written as $q = (K/n)^2$.[13,14] The factor K depends on the geometry of the molecule and takes the value 3/5 for a Gaussian chain, 3/10 for methylene groups, and 3/20 for methyl groups.[14] The number of Kuhn statistical segments, n, can be related with the average molecular mass of inter-cross-link chains M_c, $M_c = nM_s$. M_s is the molar mass of a statistical segment.[13,14] Finally, the relation between the density of cross-links μ, and the average molecular mass of inter-cross-link chains M_c is $\mu \approx 0.5\rho/M_c$, where ρ is the density of the rubber. Here, both physical and chemical cross-links were considered. To obtain the density of chemical cross-links (i.e., the elastic active cross-links), a correction to n must be applied to subtract the physical cross-links from the calculation.[1,4]

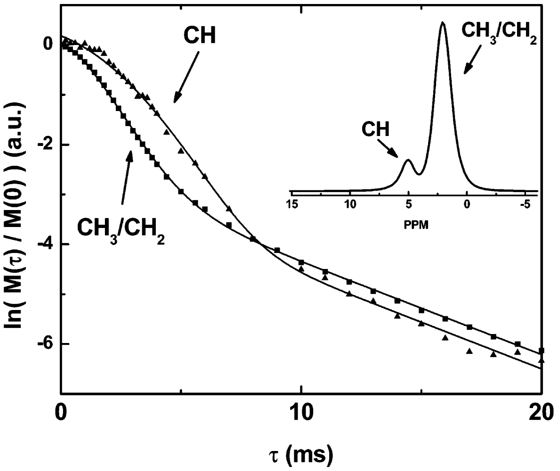

Figure 1. Transverse ^{1}H magnetization measured for the methyl and methylene (CH$_3$/CH$_2$) groups and for the methine (CH) group in the sample NR26. The solid lines are the fit to the data with eqs 1 and 2. Inset: ^{1}H NMR spectrum of NR26, obtained with a single 90° pulse, showing the two partially resolved lines; at ~2 ppm the methyl/methylene resonance and at ~5.2 ppm the methine resonance.

Experiments

The composition of the natural rubber (NR) samples studied in this work is as follows: SMR standard Malaysian rubber (SMR)-20 (100.0), zinc oxide (5.0), stearic acid (2.0), antioxidant (1.0), TBBS (0.5), sulfur (1.5); values are in phr. Samples were vulcanized at 414 K with different times of cure: 0 min (NR0, uncured sample), 23 min (NR23), 26 min (NR26), 34 min (NR34), 45 min (NR45), and 90 min (NR90, overcured sample). Details of samples preparation are given in ref 15. In this way, samples with different density of cross-links but having the same initial chemical composition were prepared.

Transverse ^{1}H NMR relaxation measurements were performed on a Bruker MSL-300 spectrometer with a Doty ^{1}H dedicated probe. The Hahn spin-echo pulse sequence ($\pi/2-\tau/2-\pi-\tau/2-$echo) was used to measure the transverse magnetization decay. A $\pi/2$ pulse of 4 μs, a recycled delay of 2 s, and 34 averages were used to record the spin echo. The time delay τ was varied from 100 μs to 20 ms. Only the right half side of the spin echo was recorded and Fourier transformed. Thus, a set of ^{1}H NMR spectra as a function of the delay time τ were obtained for each sample. In these experiments, the integrated area of each NMR line is proportional to the transverse ^{1}H magnetization of the ^{1}H associated with the line.

All the measurements were taken at a temperature of 330 K. The temperature was controlled with a VT-100 Bruker unit.

Results and Discussion

^{1}H NMR spectra in vulcanized elastomers usually exhibit a single NMR line. However, the ^{1}H NMR spectra of cured or uncured samples of NR, measured at 300 MHz, exhibit two partially resolved NMR lines, as shown in the inset of Figure 1. The NMR line at ~2 ppm corresponds to the protons of the two methylene groups (CH$_2$) and the methyl (CH$_3$) functional group of the *cis*-isoprene unit. The NMR line at ~5.2 ppm corresponds to the ^{1}H of the methine (CH) group of the monomer. In this case, then, it is possible to study the transverse ^{1}H magnetization of the methyl and methylene groups independently of that of the methine group. In Figure 1, the transverse magnetization curves of the CH$_3$/CH$_2$ groups and of the CH group, obtained for the sample NR26, are displayed. The areas of the two NMR lines were calculated using a standard deconvolution procedure.

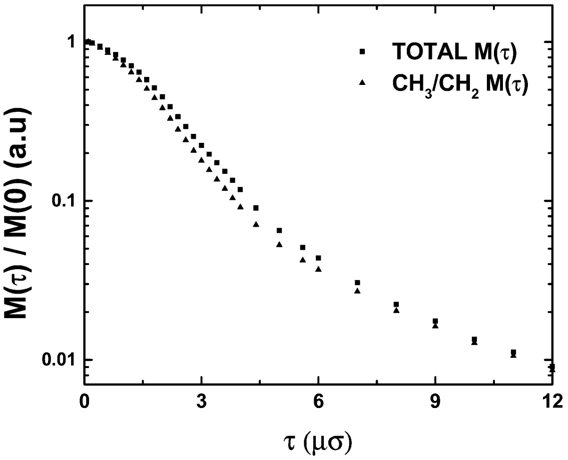

Figure 2. Experimental total transverse ^{1}H magnetization (■) measured in sample NR26 is compared with the methyl/methylene contribution (▲). The difference between the two curves corresponds to the contribution of the methine groups to the total transverse ^{1}H magnetization.

As observe in Figure 1, the two relaxation curves have similar behavior. At short delay times ($\tau \lesssim 6$ ms) they exhibit a fast solidlike decay that corresponds to the contribution of ^{1}H in cross-link chains. At long delay times, the relaxation curves show a much slower liquidlike decay that corresponds to the contribution of the protons in the dangling chain ends and free sol chains. This behavior of the ^{1}H transverse magnetization, showing two main components, is characteristic of elastomers above T_g. However, as observed in Figure 1, the decay of the methine magnetization at short delay times ($\tau \lesssim 6$ ms) is slower than the decay of the CH$_3$/CH$_2$ magnetization. This finding clearly indicates that the contributions to the total magnetization from protons in different functional groups of the monomer unit may have different behaviors. This was not discussed in previous works, and as it will be shown below, it is important to explain the total magnetization decay.

In previous works,[1,4,5] the contribution of the methine magnetization to the total transverse magnetization was not taken into account. The reason for this is that in a standard ^{1}H NMR spectrum (i.e., $\tau = 0$) the ratio of the areas (and the magnetization as well) of the methine NMR line to the CH$_3$/CH$_2$ NMR line is one to seven (1:7). However, a slower decay of the methine magnetization would imply an increase of this ratio for ^{1}H NMR spectra taken with delays $\tau > 0$. This is the case we observe for delays in the range $0 < \tau \lesssim 6$ ms. The contribution of the methine group to the total transverse magnetization can be visualized in Figure 2. In this figure, the total transverse magnetization curve and the transverse magnetization of the CH$_3$/CH$_2$ groups, for sample NR26, are compared. The two curves were normalized ($M(\tau{=}0) = 1$) in order to observe the difference between them. The total and the CH$_3$/CH$_2$ relaxation data can be measured very accurately. Hence, the dispersion of these data is very small (as shown in Figure 2), which makes it possible to distinguish the differences between the two curves. Since the total magnetization is proportional to the sum of the areas of the two NMR lines, then any difference between the total area and the area of the CH$_3$/CH$_2$ line corresponds to the area of the methine NMR line (see the inset in Figure 1). In turn, as already mentioned, the area of the methine NMR line is proportional to the transverse magnetization of the methine groups.

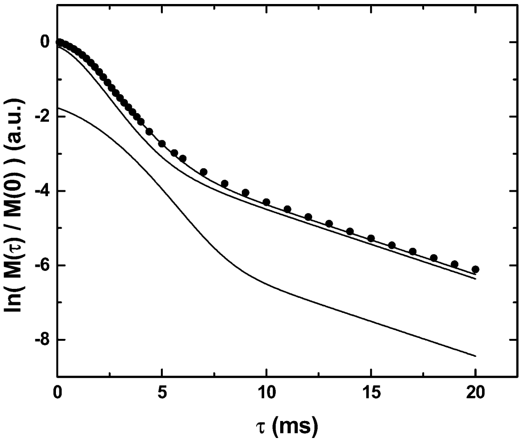

Figure 3. Total transverse ^{1}H magnetization of sample NR26 is compared to the sum of the fits of the CH_3/CH_2 and of the CH contributions shown in Figure 1 (see text for details).

As expected, the methine contribution is appreciable at short delay times. Similar results to those shown in Figure 2 were obtained for all the samples, independently of the time of cure of the sample.

To further analyze the data, the relaxation curve of the CH_3/CH_2 groups was fit to eq 1, and the relaxation curve of the methine group was fit to eq 2. The solid lines in Figure 1 correspond to the fit of the CH_3/CH_2 and CH curves with eqs 1 and 2, respectively. Equation 2 was used to fit the methine data because of the high dispersion of those data. The good agreement between the data and the fits indicates that the model detailed in the Theory section is suitable to explain the experimental data. The model only considers two contributions to explain the behavior of the transverse magnetization: a solidlike contribution due to cross-link chains and a liquidlike contribution due to dangling chain ends and free sol chains. Similar agreements between the relaxation data and the fits, as those shown in Figure 1, were obtained for all the samples. It is important to note here that the parameters B and T_2 are completely determined by the behavior of the magnetization at long delay times ($\tau \gtrsim 8$ ms), while A, qM_2, τ_s (for the CH_3/CH_2 relaxation curves), or A and C (for the CH relaxation curves) are determined by the behavior of the magnetization at short delay times ($\tau \lesssim 8$ ms).

The influence of the methine contribution on the behavior of the total magnetization can be further visualized in Figure 3. There, a curve (solid line), obtained by adding the fit to the CH_3/CH_2 data and the fit to the CH data (shown in Figure 1) in a ratio of seven to one, is compared to the total transverse magnetization experimental data. As observed in Figure 3, the contribution of the methine proton affects the shape of the total magnetization decay mainly at short delay times. This is the same result found in the analysis of the experimental data shown in Figure 2. Hence, it was concluded that a more accurate model to explain the total transverse ^{1}H magnetization of NR should include a third term to account for the methine contribution at short delay times. Furthermore, since the CH magnetization curve has a solidlike behavior at short delay times, this third component should have a Gaussian shape.

A third solidlike contribution to the transverse magnetization has just been considered in other works[1] in order to explain the relaxation data in vulcanized NR samples. However, a different explanation for the origin of this contribution was given. It was proposed that the contribution corresponds to dangling chain ends experiencing fast anisotropic motions. In that case, some residual second moment remains and would produce a solidlike contribution to the total magnetization. In our work, however, it is clearly demonstrated that the third contribution to the total magnetization corresponds to the contribution of the methine ^{1}H.

It is important to note here that the “extra” contribution to the transverse ^{1}H magnetization discussed in this work is observed in the range $1 \leq \tau \leq 8$ ms in natural rubber samples. This is the same time interval of the contribution reported in ref 1. This effect should not be confused with recent reports about the solidlike behavior of dangling chain ends, observed in molten polybutadiene and poly(ethylene oxide) at delay times $\tau > 10$ ms.[16,17] In those studies it was reported that solid echoes are formed for delay times larger than 10 ms, where the magnetization is largely due to dangling chain ends. The formation of solid echoes would indicate a remaining residual dipolar coupling for protons in those chains. The works suggest that a fraction of the dangling chain ends should have a solidlike behavior. However, no findings of a solidlike behavior of the dangling chain ends in the transverse ^{1}H relaxation curves were observed by the authors. Moreover, they found the decay of the magnetization for $\tau > 10$ ms to be exponential, which is the same behavior observed in this work for the dangling chain ends of NR samples.

To understand the cause of the slower decay of the methine magnetization at short delay times, the parameters obtained from the fit of the data with eqs 1 and 2 were analyzed. The values for $B/(A + B)$, qM_2^{RL}, T_2, and $2C$ are tabulated in Table 1. It can be observed in Table 1 that the values of B and T_2 obtained from the fit of the CH_3/CH_2 and the CH curves are very similar. On the other hand, the residual second moments measure for CH_3/CH_2 (qM_2^{RL}) are larger than those measured for CH ($2C$). However, as shown in Figure 4, it was found that qM_2^{RL} and $2C$ have similar behavior as a function of the time of cure of the sample. The residual second moments increase with the time of cure of the sample until a maximum is reached, and then they start to decrease again. As described in the Theory section, the anisotropy parameter q is proportional to the square of the density of cross-links, $q \propto \mu^2$. Thus, the results shown in Figure 4 indicate an increase of the density of cross-links with the time of cure of the sample until a maximum is reached. This maximum corresponds to the sample with the optimum time of cure. Then, a decrease in the density of cross-links occurs as expected for the overcured sample. This is the same behavior that we observed when we measured these samples using the swelling technique in *n*-decane.[15]

The finding that a similar behavior for qM_2^{RL} and $2C$ as a function of the time of cure is observed and, given the similarity of the values for $B/(A + B)$ and T_2 obtained for the CH_3/CH_2 and the CH data sets, seems to indicate that the properties of the bulk sensed by the ^{1}H nucleus do not depend on the functional group where it is located. Within the model depicted in the Theory section, only n, the number of Kuhn statical segments, should depend on the time of cure of the sample. Then, if the same parameter n is sensed by all the ^{1}H, the ratio $qM_2^{\mathrm{RL}}/2C$ has to be independent of the time of cure of

Table 1. Values for the Parameters Obtained from the Fit of the Relaxation Curves of the Methyl/Methylene Groups with Eq 1 and for Those of the Methine Group with Eq 2

sample	cure time [min]	$B/(A+B)$ (CH_3/CH_2)	$B/(A+B)$ (CH)	$T_2(CH_3/CH_2)$ [ms]	$T_2(CH)$ [ms]	qM_2 [ms^{-2}]	$2C$ [ms^{-2}]
NR0	0	0.14	0.15	5.8	5.5	0.2	0.038
NR23	23	0.11	0.08	5.6	6	0.3	0.054
NR26	26	0.08	0.05	5.4	5.3	0.6	0.112
NR34	34	0.05	0.06	5.6	4.0	0.97	0.17
NR45	45	0.05	0.04	5.6	4.0	1.1	0.192
NR90	90	0.06	0.05	5.7	4.3	0.93	0.154

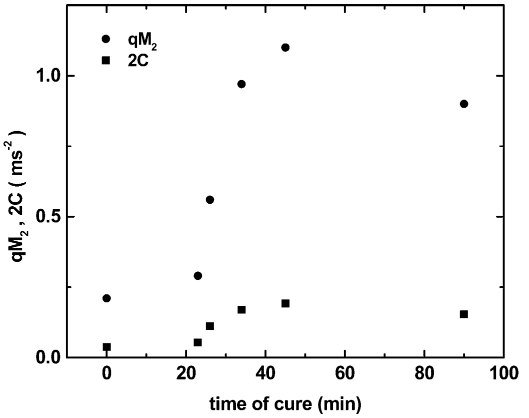

Figure 4. Values of the residual second moments for the CH_3/CH_2 groups (qM_2) and for the CH group ($2C$) plotted as a function of the time of cure of the sample. These values were obtained from the fit of the CH_3/CH_2 and CH magnetization curves with eqs 1 and 2, respectively.

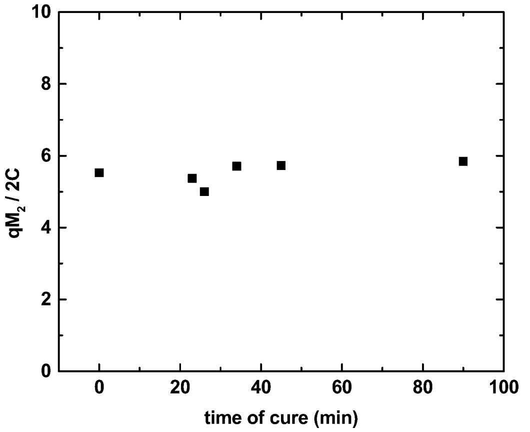

Figure 5. Ratio of the residual second moments qM_2 (CH_3/CH_2) and $2C$ (CH) displayed in Figure 4 as a function of the time of cure of the sample.

the sample and only dependent on the second moments in the rigid lattice and the K factors:

$$qM_2^{RL}/2C = qM_2^{RL}(CH_3/CH_2)/qM_2^{RL}(CH)$$
$$= K^2M_2^{RL}(CH_3/CH_2)/K^2M_2^{RL}(CH)$$

The ratio $qM_2^{RL}/2C$ was calculated for each sample and displayed in Figure 5. As observed in Figure 5, the ratio $qM_2^{RL}/2C$ as a function of the time of cure of the sample is mainly constant in agreement with the model. Also, the data in Figure 5 indicate that $qM_2^{RL}/2C$ is ~5.5(3), which explains the slower decay of the CH magnetization. The value for the ratio of the residual dipolar couplings is consistent with the value of ~6.3 estimated for the methine/methylene residual dipolar couplings ratio obtained from the spinning sideband intensities of MAS ^{1}H NMR experiments.[9]

A smaller residual dipolar coupling for the methine group is expected since the distance between the single proton of the methine group and the nearest protons from the methyl and methylene groups is longer than the intragroup distance in methylene or methyl groups. Thus, the dipolar second moment (M_2^{RL}) for the methine group should be smaller than the methyl or methylene M_2^{RL}.

Conclusions

It is shown in this work that the study of the contribution of different functional groups to the transverse ^{1}H magnetization in vulcanized natural rubber was necessary to understand the relaxation behavior of the total magnetization. Our results show a slower decay of the methine contribution at short delay times $\tau \lesssim 6$ ms as compared to that of the CH_3/CH_2 contribution. This makes its contribution to the transverse ^{1}H magnetization nonnegligible. As a consequence, the model for the analysis of the total magnetization has to include an extra solidlike component to account for the methine contribution. On the other hand, our results demonstrate that this extra contribution is not caused by dangling chains experiencing fast anisotropic motions, as proposed in ref 1.

Besides, the good agreement between the data and the fits with eqs 1 and 2 indicates that the decay of the magnetization of the methyl/methylene or methine groups can be modeled considering only two contributions: one that accounts for the cross-link chains and the other for the dangling chain ends and free sol chains.

Finally, the values obtained for the fraction of dangling chains, the time constant T_2, and the residual dipolar couplings show that the methine proton senses the same microstructural properties of the bulk as the protons in the methyl/methylene functional groups. The differences in the values of the residual dipolar coupling are explained in part by the smaller intergroup dipolar coupling for the methine proton as compared with the intragroup dipolar coupling in methyl or methylene groups. This, also explains the slower decay of the methine magnetization.

Acknowledgment. We express our gratitude to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), The Agencia Nacional de Promoción Científica y Técnica (ANPCyT), Secretaría de Ciencia y Técnicas, Universidad Nacional de Córdoba (SECYT-UNC), Universidad Nacional de Buenos Aires (Investigation project X-150), and the Fundación Antorchas which supported this work.

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MA049451K