M_c Determination and Molecular Dynamics in Cross-Linked 1,4-*cis*-Polybutadiene: A Comparison of Transversal ^{1}H- and ^{2}H-NMR Relaxation

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Received August 30, 1991; Revised Manuscript Received February 18, 1992

ABSTRACT: A simplified theoretical model of the structure and dynamics of polymer networks is successfully applied to the transversal ^{1}H- and ^{2}H-NMR relaxation in 1,4-*cis*-polybutadiene networks produced by cross-linking a mix of conventional and partially deuterated chains with thiuram. For both independent relaxation methods the relaxation curves are qualitatively equal and their analysis provides a consistent picture of the characteristic network parameters. Especially, the M_c values, which were determined by both relaxation methods, are in good agreement with one another and with values which were obtained from stress-strain measurements on the same samples. Taking into consideration similar results of our previous papers, the theoretical treatment and comparison of the NMR results to mechanical experiments provide a firm basis for the continuing use of the approach to characterize M_c.

1. Introduction

Several papers[1-12,20,25] have shown that the measurement of the transversal ^{1}H-NMR relaxation is a successful method for an investigation of structural and dynamical parameters in polymer networks at temperatures well above the glass transition temperature T_g. Using the dipolar magnetic interaction of protons, a number of papers[3,4,8-11,20,25] describe and test an approach to the determination of the molecular mass of inter-cross-link chains.

The transversal ^{1}H-NMR relaxation rate depends on the strength of the interaction of the nuclear magnetic dipoles. If the relative motion of the interacting nuclei is fast enough (correlation time $\tau < M_2^{-1/2}$ where M_2 is the second moment of the dipolar interaction), the interaction averages to a certain degree and the rate decreases. Therefore, this can be used as a sensitive probe of local molecular dynamics which is closely related to chain dynamics and chain structure in polymer networks above T_g. Therefore, this NMR method can probe local and global molecular properties. A further advantage of this method is its applicability to unfilled as well as filled samples.

For the connection of NMR relaxation with molecular dynamics we use theoretical models which assume a single pairwise interaction and rotary diffusion of these pairs. However, the density of protons is very high in common polymer networks and the interaction is a many-particle problem which raises some difficulties for the theoretical description.

Hence, it is all the more surprising that until now the description of the relaxation succeeded well in the cited papers.[3,4,8-11,20,25] All resulting characteristic data, especially the M_c values and correlation times, were reasonable and in good accordance with values of other independent methods (stress-strain,[10,11,25] compression,[8,9] dielectric relaxation measurements,[16] ^{13}C MAS NMR[25]). We believe that the models used work since we can assume (according to ref 4) an interaction of mean dipoles in a chain segment.

In this paper we want to compare for the first time the transversal ^{1}H NMR dipolar relaxation with the transversal ^{2}H NMR quadrupolar relaxation measurements in partially deuterated polybutadiene networks (BR). The quadrupolar interaction is an extremely local and strong interaction of the electrical quadrupole moment of the ^{2}H nucleus with the electrical field gradient of the C-^{2}H bond and leads to a shift of the nuclear magnetic Zeeman levels. The shift depends on the angle between the C-^{2}H bond and the external magnetic field. For transversal relaxation this corresponds formally to a magnetic dipolar interaction of a single proton pair of a fixed distance where the ^{1}H-^{1}H direction corresponds to the C-^{2}H direction. The relaxation formalism used is the same in both cases.[13] Since the quadrupolar interaction fulfills the assumptions of the theoretical model more precisely, the quadrupolar relaxation can be used as a valuable test of this model. Furthermore, we can achieve a better understanding of the magnetic relaxation of proton dipoles.

2. Experimental Section

CH_2-deuterated butadiene was polymerized by a conventional Ziegler-Natta polymerization at 40 °C in a glass reactor with hexane as solvent. The microstructure was determined by ^{13}C-NMR and showed a cis content of more than 97%. Molecular weights were determined by GPC: $M_n \approx 32$K and $M_w/M_n \approx 4.5$. The product was mixed (1:10) with undeuterated commercial CB10 (1,4-*cis*-polybutadiene, $M_n \approx 160$K, $M_w/M_n \approx 4.1$). The incorporation of carbon black (DEGUSSA N330) and the cross-linking reaction with tetramethylthiuram disulfide (TMTD) were performed by DEGUSSA AG (Wesseling) under standard conditions.

All cross-linked butadiene rubber samples (BR) were extracted with toluene for 24 h.

The un-cross-linked sample was dissolved in toluene and subsequently dried.

The NMR relaxation experiments were carried out on a Bruker SXP4-100 spectrometer at a resonance frequency of 90 MHz for protons and on a Bruker CXP 300 spectrometer (300-MHz proton resonance frequency) at a resonance frequency of 46 MHz for deuterons. The transversal magnetization decay of both nuclei was measured by the common Hahn spin-echo technique which eliminates inhomogeneities of the magnetic field and the chemical shift (which however do not influence the dipolar and quadru-

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0024-9297/92/2225-3624$03.00/0

Table I
Characteristic Parameters for All Samples

		BR0	BR2	BR3	BR2/25	BR2/50
thiuram, phr		0	2.0	3.0	2.0	2.0
filler, phr		0	0	0	25	50
sol,[a] %	^1H	0.83	0.24	0.30	0.17	<0.1
	^2H	1.72	1.34	1.90	0.68	0.32
$B/(A+B)$, %	^1H	7.96	13.2	10.8	15.6	13.2
	^2H	23.4	17.1	14.0	23.8	42.3
τ_s, 10^{-4} s	^1H	4.90	8.29	7.03	10.7	9.12
	^2H	7.17	6.32	3.37	7.34	4.53
τ_f, 10^{-9} s	^1H	3.40	12.5	16.4	14.0	16.7
	^2H	0.436	0.994	0.990	0.595	0.775
qM_2,[b] ms^{-2}	^1H	0.551	0.892	1.28	0.758	0.768
qQ_2,[c] ms^{-2}	^2H	2.04	4.13	7.00	4.37	4.58
M_c(NMR), $\times 10^{-3}$	^1H		8.32	5.69	10.7	10.4
	^2H		9.49	6.16	9.00	8.61
M_c(mech), $\times 10^{-3}$			8.81	5.51	7.96	7.85

[a] For cross-linked samples after extraction. [b] $M_2 = 1.23 \times 10^{10}$ s^{-2} (see section 3.4). [c] $Q_2 = 1.19 \times 10^{11}$ s^{-2} (see eq 7).

polar interactions). The signal-to-noise ratio must be as great as possible at each point of the relaxation curve in order to get a good correlation ($r > 0.985$, where r is the correlation coefficient) with fitted curves for all parts of the relaxation curve and to minimize the error bars of the parameter values to less than ±10%. In addition, a statistical error of about ±5% must be taken into consideration as a result of repeated measurements on the same sample at different times.

The measuring temperature of 60 °C is an optimum. On the one hand, it was chosen in order to accentuate differences in cross-link densities as much as possible. On the other hand, at this temperature additional thermal cross-linking and/or destruction is prevented.

The samples were also investigated by stress–strain experiments. These experiments were carried out at room temperature on an Instron 1122 mechanical tester with a strain velocity of 10 mm/min. Analysis of the data was made by using a modified Mooney plot and a tube model which includes a constraint-dependent microstructure factor.[14,15,23]

For filled samples a mean-strain amplification by undeformable particles, additional cross-links on the carbon black surface, and a finite extension factor in the upturn region were taken into account. The achieved fit was excellent in all cases. A detailed description of such an analysis is found in ref 23. The resulting M_c(mech) values are listed in Table I.

3. Theory

As a first step we want to recapitulate the basic ideas for the interpretation of the relaxation of the transversal proton magnetization in polymer networks well above T_g in terms of a modified single-chain approximation following refs 3, 4, and 6–12.

The second step will be a comparison with the deuteron relaxation.

Since transversal ^{1}H-NMR relaxation is determined by the dipolar magnetic interaction of protons, a motional averaging of this interaction and, consequently, the nuclear motion itself are detectable in this way. Therefore, at $T > T_g$ a "contrast" in such a "relaxation picture" of a polymer network can be formed by different mobile molecular parts which produce separate relaxation signals of different form and/or length. In Figure 1 a rough sketch illustrates the principal different mobile parts. Most of the chains are inter-cross-link chains. As a first step they could be thought of as fixed at both ends. In this case the motional statistics provide a mean, small anisotropy of the fast local motion[4] (correlation time $\tau_f \approx 10^{-8}$ s) of the chain segments. Consequently, a small, mean residual part q ($q \approx 10^{-4}$) of the second moment M_2 of the dipolar interaction in the "rigid lattice"[13] ($T < T_g$) remains. The residue can only be destroyed by an overall isotropic motion of the whole inter-cross-link chain. This motion is much slower ($\tau_s \approx 10^{-3}$ s) as a result of the larger size of the moving object.

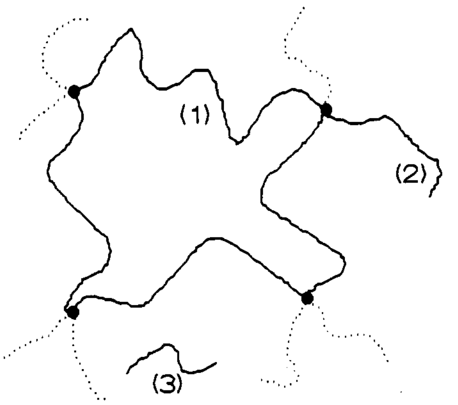

Figure 1. Principal sketch of the different mobile molecular parts in an elastomeric network: (1) inter-cross-link chains, (2) dangling chain ends, (3) sol molecules.

Dielectric measurements[16] gave direct evidence of the existence of the two relaxation mechanism by exhibiting two peaks in the correlation time spectrum of polyisoprene melts where the role of cross-links is assumed by entanglements.

For dangling chain ends a reason for an anisotropy of the local motion (also τ_f) does not exist ($q = 0$), and so τ_s cannot be detected.

Connecting this dynamical model with the NMR theory of the transversal magnetic relaxation, a sum of two relaxation components follows according to the two dynamical types of chains of a network.

3.1. Dangling Chain Ends. Since $x^2 = (2\pi f_0 \tau_f)^2 < \approx 1$ (liquidlike, f_0 = resonance frequency) and $q = 0$ is valid for chain ends, this component of the decay can be described by BPP (Bloembergan, Purcell, and Pound)[17] theory. Consequently, this component is a purely exponential function of the type $\exp(-t/T_2)$ with the transversal relaxation rate $1/T_2$ (BPP formula):

$$1/T_2 = M_2 \tau_f [1 + (5/3)/(1 + x^2) + (2/3)/(1 + 4x^2)] \quad (1)$$

We want to emphasize that this formula was established by assuming an intramolecular interaction of single-spin pairs and a rotary motion of these pairs. The real case of more than two interacting nuclei is taken into consideration by assuming that spins are fixed at the Kuhn statistical segments.[4] Under these circumstances the resulting decay should remain exponential (according to a similar case in ref 17).

Therefore, the τ_f values, which are derived according to eq 1, are effective values and represent an average over several closely attached interacting spin pairs mainly along the monomeric unit.

3.2. Inter-Cross-Link Chains. The "inter-cross-link component" is influenced by the fast anisotropic motion as well as by the slow isotropic motion. Since $x^2 = (2\pi f_0 \tau_f)^2 < \approx 1$ (liquidlike) and $(2\pi f_0 \tau_s)^2 \gg 1$ (solidlike) is valid, the relaxation function has to be described by a combination of the BPP theory[13,17] and the Anderson–Weiss formula.[13] The latter takes into consideration the residual "solid" behavior ($q \neq 0$) and leads to a shortening of the decay and to an observable deviation from a simple exponential decay form (Gaussian-like). According to Anderson–Weiss the magnetization decay is given by

$$M(t) \sim \exp\left(-\int_0^\infty G(\tau)\,(\tau - t)\,\mathrm{d}\tau\right) \quad (2)$$

The correlation function $G(\tau)$ should reflect the fact that the fast local motion is anisotropic and cannot eliminate the dipolar interaction (M_2) totally:

$$G(\tau) = M_2[(1 - q) \exp(-\tau/\tau_f) + q] \exp(-\tau/\tau_s) = M_2 \exp(-\tau/\tau_f) + qM_2 \exp(\tau/\tau_s) \quad (3)$$

The latter expression is valid since $\tau_f \ll \tau_s$ and $q \ll 1$.

3.3. Total Relaxation Function. Including eqs 2 and 3 and all the above dynamical and structural assumptions, it follows for the total transversal magnetization decay that

$$M(t) = A \exp[-t/T_2 - qM_2\tau_s^2(\exp(-t/\tau_s) + t/\tau_s - 1)] + B \exp[-t/T_2] \quad (4)$$

with $1/T_2 = M_2\tau_f$. The latter expression is identical with the more general formula of eq 1 if $(2\pi f_0\tau_f)^2 \gg 1$ (slow motion). That is the point of the formal combination of BPP and Anderson–Weiss: $1/T_2$ will always be identified with eq 1. A and B are the portions of proton magnetization (equivalent to mass portions!) of the inter-cross-link chains and dangling chain ends, respectively.

Usually a second, very long exponential tail (liquidlike) of an amount smaller than 5% can be detected. This tail could be eliminated or reduced by an extraction procedure and, consequently, belongs to sol molecules or admixtures of high mobility. This was verified in some cases by high-resolution ^{13}C-NMR spectra of the extracted product or by proton-NMR spectra which were obtained by the Fourier transformation of the Hahn echo decay in the tail region.

In all subsequent cases we will only discuss the portions A and B which belong to the network. Remaining sol fractions were eliminated by a simple subtraction.

3.4. M_c Determination. It is possible to calculate from q the molecular mass of an inter-cross-link chain[4] if this chain can be described by a Kuhn chain[18] with N freely rotating segments and if intermolecular interactions are excluded:

$$M_c = Nc_\infty M_{ru}/n \quad (5)$$

with

$$N = 3/(5q^{1/2}) \quad (6)$$

c_∞ is the number of backbone bonds in a Kuhn segment,[19] and M_{ru}/n is the mass of the chemical repeating unit per number of backbone bonds in this unit. In former papers[9,10] we approximated c_∞ by the characteristic ratio C_∞. The more exact value $c_\infty = g^2C_\infty$ can be used if the ratio g of the contour length of the real chain to the Kuhn chain is available. The necessary molecular-statistical data for 1,4-*cis*-polybutadiene can be taken from refs 19 and 24. Hence, it follows that $g^2 = 1.1$.

For real networks q must be replaced by $q - q_0$ in order to consider only the contribution of the chemical junctions. q_0 can be obtained by eq 4 using an un-cross-linked sample having a qualitatively equal relaxation curve. q_0 takes into account the integral interaction of physical hindrances (entanglements) at the NMR time scale. The validity of this special calibration for N was found experimentally[9–11,20] by comparing the NMR M_c results with the results of other methods for a number of different elastomers with different cross-link densities.

In order to determine q, the parameter qM_2 must be divided by M_2, which can be obtained at $T < T_g$ by a simple analysis of the free induction decay (FID) with the common Gauss form[13] $M(t) = M(0) \exp(-M_2t^2/2)$.

The Gotlib model requires that qM_2 and M_2 originate only from intramolecular magnetic interactions of proton dipoles. While this is fulfilled for the residual second moment qM_2 at the measuring temperature $T > T_g + 150$ K (liquidlike motion), the second moment of the "rigid lattice" $M_{2,0}$ ($T < T_g$) usually contains an intermolecular contribution of about 40% in common polymers. We tried to eliminate this portion by measuring samples at $T \approx 150$ K $< T_g$ which were swollen (cross-linked samples) or solved (un-cross-linked samples) in CCl_4. Both procedures provided the same "intramolecular" M_2 result ($M_2 = 1.23 \times 10^{10}$ s^{-2}) which is used in this paper in contradistinction to the total value of the second moment $M_{2,0} = 1.50 \times 10^{10}$ s^{-2} (dry samples) which was used in a former paper[8] as an approximation.

In spite of this correction and the correction of c_∞, the resulting change of M_c is negligible for BR since the corrections have a contrary direction: $g^2(M_2/M_{2,0})^{1/2} = 1.0$. The use of the "intramolecular" M_2 is also more exact in the BPP theory (eq 1).

For the transversal ^{2}H-NMR quadrupolar relaxation the principal formalism,[13] including the measuring procedure, is the same. However, from the theoretical point of view the advantage of this relaxation is the fact that most of the formulas (eqs 1–6) (with changes indicated below) are valid more strictly since the quadrupolar interaction is restricted to the C–^{2}H bond and corresponds to a "single proton pair" interaction.

According to ref 13 the second moment of the dipolar interaction M_2 must be replaced by the second moment of the quadrupolar interaction, symbolized here by Q_2:

$$Q_2 = (9/20)\pi^2(e^2Qq_{CD}/h)^2 = (4/5)\pi^2(\delta\upsilon)^2 \quad (7)$$

Q is the quadrupole interaction constant, e is the value of the elementary charge, and q_{CD} is the electrical field gradient in the carbon–deuteron bond. The frequency $\delta\upsilon$ is the distance of the two maxima in the NMR powder spectrum[13] which can be measured below T_g. For CH_2 in BR we obtained $\delta\upsilon = 123$ kHz and, consequently, $Q_2 = 1.19 \times 10^{11}$ s^{-2}.

A second change is the change of the value of f_0, the resonance frequency, in our case from 90.00 MHz for protons to 46.00 MHz for deuterons.

4. Data Analysis, Results, and Discussion

Figure 2 shows the proton and deuteron relaxation curves for unfilled and filled samples and the fit curves according to eq 4 for protons or eq 4 with changes mentioned above for deuterons. Table I contains the quantitative values of all parameters of the fit curves.

We can state the following results:

1. There are no principal differences between the ^{1}H- and ^{2}H-NMR relaxation curves of protonated and partially deuterated polybutadiene, respectively. The correspondence with the theoretical curves is excellent in both cases.

2. Within an error of ±15% the NMR M_c values of both independent methods agree very well with one another and with stress–strain results (M_c(mech)) which were obtained according to the tube concept[14,15,23] providing the "chemical" M_c. Using experiences of ref 23 with SBR, we expected smaller M_c(mech) values in the filled samples. Obviously the applied carbon black type has a low activity in BR which leads to less cross-links on the carbon black surface.

3. The "slow" correlation times τ_s do not differ very much among each other. Differences by a factor 2 between both methods are not very significant if we take into account an error of ±15% and the fact that we used a simplified dynamical model without a correlation time distribution.

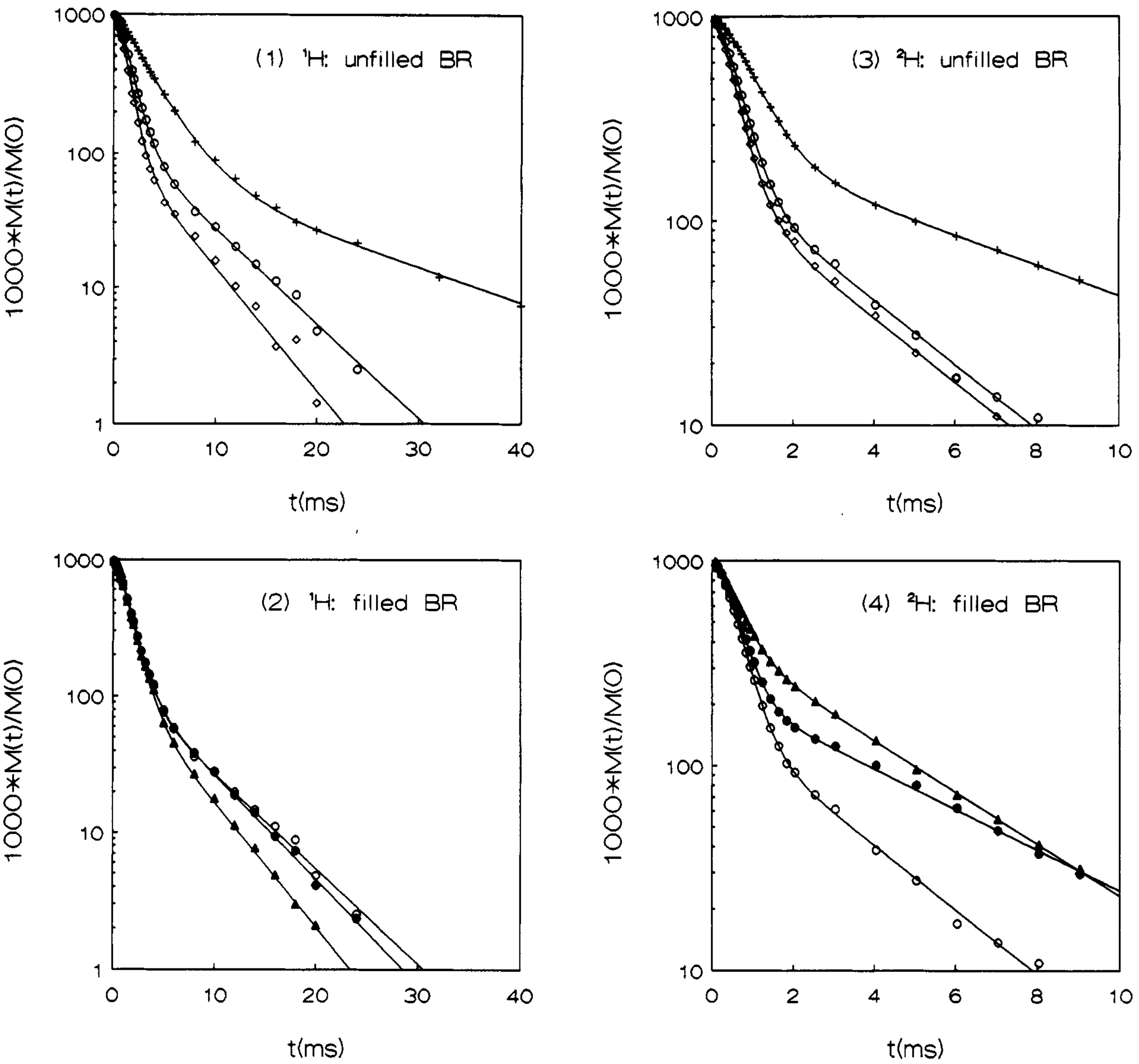

Figure 2. (1-4) Measured (symbols) and fitted (full lines) relaxation curves of the transversal magnetization in partially deuterated 1,4-*cis*-polybutadiene: (+) un-cross-linked, (○) 2 phr TMTD, (◇) 3 phr TMTD, (●) 2 phr TMTD + 25 phr N330, (▲) 2 phr TMTD + 50 phr N330.

4. The "fast" local correlation times τ_f involve some problems. The τ_f values from the ²H-NMR relaxation are about 10 times shorter than those from the ¹H-NMR relaxation. An increase of τ_f with decreasing M_c (beginning with the un-cross-linked state) was already found in ref 8 for 1,4-*cis*-polybutadiene and in ref 9 for PDMS. However, for SBR[10] τ_f was independent of M_c in accordance with expectations of a local motion.

All these problems are not clarified until now and will be objects of further investigations. We believe that we obtain only effective τ_f values and that the above-mentioned difficulties are a result of the simplicity of the BPP model if it is applied to a complicated motion of a number of interacting protons.

5. For the un-cross-linked sample the proton portion of dangling chain ends $B/(A + B)$ seems to be a little too small in comparison to cross-linked samples; however, it should be noted that the un-cross-linked sample was mixed mechanically in solution and not in the dry state as the other samples. This and the omission of the vulcanization lead to less chain cracks and, consequently, to a minimum of $B/(A + B)$.

The higher portion of sol molecules and of dangling chain ends in the "deuteron case" finds a natural explanation in our model. It is a consequence of a relatively low M_n of the precursor chains with a considerable portion of short chains. It should be noted that the "²H-sol portion" in Table I is divided by 10, since it is the sol content which is referred to the whole sample (mix 1:10; see the Experimental Section).

6. In ref 10 an addition of 50 phr carbon black N220 (PM 100) to SBR vulcanizates increases the mean $\tau_f(^1H)$ by a factor of 2. A similar type of carbon black N330,[21] which is added here, does not increase $\tau_f(^1H)$ so drastically. $\tau_f(^2H)$ seems even to decrease slightly. An explanation could be (similar to result no. 2) the low activity of N330 in BR (no motionally restricted surface layers of some nanometers).

The influence of the filler on the relaxation is mainly reflected by an increase of the portion $B/(A + B)$ of dangling chain ends. This corresponds with the ¹H-NMR relaxation of a former work[10] on SBR. The increase of $B/(A + B)$ points to chain cracks during the mechanical mixing by the rigid carbon black particles. The M_c values of the polymer matrix are not changed within the error ±15% in comparison to the respective unfilled samples in both cases, which also corresponds to experiences obtained with SBR.[10]

Finally, an important question which should be asked is the question of the error involved especially in the M_c

determination since the fit function in eq 4 depends on five parameters and since qM_2 and τ_s seem to be coupled. However, two parameters, B and T_2, are already determined by the exponential tail. Another parameter, A, is restricted by the total signal. If $\tau_s > \approx t \approx (qM_2)^{-1/2}$, the form of the "short" decay is Gaussian-like and q and τ_s are clearly separable. Otherwise, $qM_2\tau_s^2(\exp(-t/\tau_s) + t/\tau_s^{-1})$ tends to $qM_2\tau_s^2(t/\tau_s - 1)$ which indeed involves difficulties for a separation. However, according to our experiences, this case occurs only in melts or slightly cross-linked networks at high temperatures.

We can state that the parameter qM_2 is the most stable and reproducible one. This is clear since qM_2 mainly depends on the curvature $[\mathrm{d}^2M(t)/\mathrm{d}t^2] \approx (A + B)/T_2^2 - AqM_2 \approx -AqM_2$ for typical parameters at the beginning ($t \ll \tau_s$) of the relaxation function and is only slightly dependent on the decomposition of $M(t)$. All of our experience with a great number of elastomeric materials supports this.

In addition, the coincidence[8-11,25] of the $M_c(q)$ values with M_c values of other independent methods proves good reliability of $M_c(q)$. Taking into account all random uncertainties, the statistical error bar of the NMR M_c is about ±15%. According to uncertainties of c_∞ and M_2 a systematic error (error of scaling) of about 20% must be taken into consideration.

5. Conclusions

Using the Kuhn–Grün chain model,[18] the Gotlib ideas,[4] which concern the dynamical averaging of the nuclear interactions, the basic NMR relaxation models of BPP[13,17] and Anderson–Weiss,[13] several extensions,[3,8-11,20] some of which concern the separation of the influence of the "physical" and the "chemical" networks and others which concern the general relaxation curve structure of polymer networks, the proton and deuteron transversal NMR relaxation can be well described and interpreted consistently to a great extent. This consistency supports the applicability of the above model to the more complicated theoretical case of the multiple-spin system of protons. This is also interesting in so far as the "proton method" is now at the stage of a routine method for the M_c determination and takes less than half an hour on modern NMR spectrometers.

Important network parameters are available, such as the molecular mass of inter-cross-link chains, the portions of these chains, of dangling chain ends, and of sol molecules, and typical, however, effective, correlation times.

Also, the influence of a filler on the network matrix and on its parameters can be studied, which is of interest for technical applications.

Acknowledgment. We thank Professor E. Straube for his valuable comments and for the analysis as well as the interpretation of our stress-strain data. The vulcanizates were prepared by Dr. S. Wolff and Dr. Freund of DEGUSSA AG (Wesseling).

References and Notes

(1) Cohen-Addad, J. P. *Phys. Rev. Lett.* **1974**, *33*, 940. Cohen-Addad, J. P. *J. Chem. Phys.* **1974**, *60*, 2440.
(2) Cohen-Addad, J. P.; Dupeyre, R. *Polymer* **1983**, *24*, 400.
(3) Fedotov, V. D.; Tshernov, V. M.; Khasanovitsh, T. N. *Vysokomol. Soedin. A* **1978**, XX, *4*, 919. The English version of this journal is entitled *Polym. Sci. USSR.*
(4) Gotlib, Yu. Ya.; Lifshitz, M. I.; Shevelev, V. A.; Lishanskij, I. S.; Balanina, I. V. *Vysokomol. Soedin. A* **1976**, XXVIII, *10*, 2299. The English version of this journal is entitled *Polym. Sci. USSR.*
(5) Cohen-Addad, J. P. *J. Phys.* **1982**, *43*, 1509.
(6) Doscocilova, D.; Schneider, B. *Pure Appl. Chem.* **1981**, *54*, 575.
(7) English, A. D. *Macromolecules* **1985**, *18*, 178.
(8) Simon, G.; Schneider, H.; Häusler, K.-G. *Prog. Colloid Polym. Sci.* **1988**, *78*, 30.
(9) Simon, G.; Birnstil, A.; Schimmel, K.-H. *Polym. Bull.* **1989**, *21*, 235.
(10) Simon, G.; Götschmann, B.; Matzen, D.; Schneider, H. *Polym. Bull.* **1989**, *21*, 475.
(11) Simon, G.; Schneider, H. 9th European Symposium on Polymer Spectroscopy. *Makromol. Chem., Macromol. Symp.* **1991**, *52*, 233.
(12) Brereton, M. G. *Macromolecules* **1990**, *23*, 1119.
(13) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, U.K., 1961; and references therein.
(14) Matzen, D.; Straube, E. *Colloid Polym. Sci.* **1992**, *270* (1), 1.
(15) Heinrich, G.; Straube, E.; Helmis, G. *Adv. Polym. Sci.* **1987**, *85*, 33.
(16) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585.
(17) Roth, H.-K.; Keller, F.; Schneider, H. *Hochfrequenzspektroskopie in der Polymerforschung*; Akademie-Verlag: Berlin, 1984; and references therein.
(18) Kuhn, W.; Grün, F. *Kolloid Z.* **1942**, *101*, 248.
(19) Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722. Aharoni, S. M. *Macromolecules* **1986**, *19*, 426.
(20) Fedotov, V. D.; Tshernov, V. M.; Wolfson, S. I. *Vysokomol. Soedin. B* **1978**, XX, *9*, 679. The English version of this journal is entitled *Polym. Sci. USSR.*
(21) Kleemann, W. *Mischungen für die Elastverarbeitung*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, FRG, 1982.
(22) Baumann, K. Thesis, University Freiburg, Germany, 1991.
(23) Straube, E.; Matzen, D. Lecture on the Internationale Kautschuktagung, Essen, Germany, 1991, published in *Kautsch. Gummi, Kunstst.* **1992**, *4*, 264.
(24) Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley & Sons: New York, London, Sydney, Toronto, 1969.
(25) Gronski, W.; Hoffmann, U.; Simon, G.; Wutzler, A.; Straube, E. Proceedings of the ACS Meeting, Toronto, 1991, published in *Rubber Chem. Technol.* **1992**, *65*, 63.