

Investigation of partially deuterated poly(butadiene) elastomers. Part 1. ^1H and ^2H nmr transverse relaxation data

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Abstract

It is well known that deuterium nmr is a very sensitive tool for the investigation of order and orientation. ^1H and ^2H nmr measurements of partially deuterated poly(butadiene) elastomers with systematically varied elastic properties are presented. A combined study of proton and deuterium nmr relaxation and the behavior under mechanical deformation was performed. ^2H nmr transverse magnetization data are compared to the predictions of a model describing elastomer deuterium transverse magnetization data as a linear superposition of contributions from elastic chains and free dangling chain ends. The structural parameters are compared with results from mechanical and swelling measurements. The influence of microstructure, precursor chain length and their molar mass distribution as well as of the crosslink density on the transverse relaxation and the deformation behavior were studied. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction and background

Standard techniques for obtaining information about elastomer structure infer molecular-level structure from bulk properties, such as mechanical moduli (E -, G -modulus) or polymer swelling. A more refined understanding of elastomer structure requires the use of experimental techniques, which directly probe molecular-level elastomer properties. Chemical characterization of elastomers is difficult because of the small amount of crosslinks present in these materials. For this reason, the direct observation of the crosslinks using ^{13}C nmr [1] suffers from low sensitivity. On the contrary, the indirect observation of various crosslink densities through difference in molecular mobility has been reported in nmr relaxation [2–5] and imaging of elastomeric materials [6,7]. At higher temperatures, the transverse relaxation has shown to be the most sensitive to crosslinking. Transverse relaxation is mainly determined by dipole–dipole or quadrupolar interaction which is dramatically reduced by molecular motions for elastomers well above T_g . The observed residual interaction is due to rapid anisotropic segmental motion that is spatially inhibited by chemical crosslinks, topological chain constraints such as entanglements, or physical and

chemical interactions acting as anchors for the rapid short-range processes [8–10].

^2H nmr has emerged as a powerful tool for such investigations because it is sensitive to elastomer segment orientations and dynamics, through the deuterium quadrupolar interaction [11,12]. The quadrupolar interaction involves the asymmetric nuclear charge distribution, known as a quadrupole moment, which is associated with each deuterium nucleus. A quadrupolar moment experiences a torque in the presence of a local electric field gradient (EFG), which is determined by local molecular structure. The interaction between the quadrupolar moment and the EFG induces energy splitting whose magnitude depends on the orientation of the EFG. If the EFG is axially symmetric, the magnitude of the deuterium quadrupolar interaction is given by

$$\omega_Q = \frac{3}{4} \left(\frac{e^2 q Q}{\hbar} \right) (3 \cos^2 \Theta - 1) \quad (1)$$

where $e^2 q Q / \hbar$ is the quadrupolar coupling constant and Θ is the angle between the EFG and the external magnetic field B_0 . Typically, deuterium nuclei in labeled polymer samples are covalently bonded to carbon atoms and the EFG is oriented along the C–D bond axis. The orientation distribution of the C–D bonds in a deuterated elastomer is controlled by the orientation distribution of polymer backbone segments. For polymers at

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temperatures below their glass transition temperatures, these segments are randomly oriented and are fixed in space on the nmr time scale (in the order of 10^{-7} s). An isotropic distribution of fixed C–D bonds results in the well known Pake pattern, which is characteristic of rigid solids.

Above the glass transition temperature, each C–D bond orientation becomes time-dependent due to segmental motions. Then, the averaging of the quadrupolar interaction is described by its time average, i.e. the time average about $\cos^2 \Theta$.

Thus, motions average the quadrupolar interaction and narrow the ^2H nmr spectrum. In the limit of rapid, isotropic segmental motion the interaction is completely averaged, and the spectrum is reduced to a sharp line at central frequency.

In the few last years, ^2H nmr spectra have been reported for a variety of elastomers without stretching above their glass transition temperature [13–17], all represented by single lines. However, they are significantly broader than the spectra of the corresponding uncrosslinked polymer melts. Thus, elastomer ^2H nmr spectra represent residual, motion-averaged quadrupolar frequency distributions corresponding to rapid, but anisotropic segmental motions.

Recently, a model was proposed which describes the residual deuterium quadrupolar frequency distribution observed by ^2H nmr of elastomers as a linear superposition of two distinct components [3,18,19]. One component is attributed to elastic (intercrosslinked; fixed at both ends) chains, the other one is attributed to free dangling ends. According to this model, the free dangling chain ends move isotropically. Thus, their contribution to the residual quadrupolar frequency distribution is expected to experience more motional averaging than does the elastic chain component, due to differences in the mobility of the two distinct types of chains. Hence, this model predicts that the contribution of the dangling ends to the ^2H nmr spectrum is narrower than that of the intercrosslinked chains. Kornfield [19] has qualitatively tested this assumption using ^2H nmr measurements of polystyrene (PS) chains composed of deuterated and non-deuterated blocks. The position of the labeled PS-block was changed to create either pendant or elastic chains. The spectra of the labeled blocks near the chain ends were significantly narrower than that of the centered blocks.

Simon et al. [3,18] have already obtained ^2H nmr data for randomly crosslinked *cis*-polybutadiene elastomers to quantitatively test the two-component representation. After a component attributed to soluble material was subtracted, the data were well represented by a sum of two distinct components representing intercrosslinked chains and free dangling ends. The authors [18] proposed a description of the total transverse magnetization decay which is valid for deuterons as well as for protons and is composed of all three

contributions:

$$M(t) = A \exp\left\{-\frac{t}{T_2} - qM_2\tau_{\text{slow}}^2\right\} \times \left[\exp\left(-\frac{t}{\tau_{\text{slow}}}\right) + \frac{t}{\tau_{\text{slow}}} - 1\right] + B \exp\left\{-\frac{t}{T_2}\right\} + C \exp\left\{-\frac{t}{T_{2,\text{sol}}}\right\} \quad (2)$$

The fractions A, B and C representing the parts of magnetization of protons/deuterons in intercrosslink chains, dangling ends and “sol”-fraction (soluble, free chains) correspond in first approximation to their molecular mass parts. In case of the deuterons, the second moment of dipolar interaction M_2 must be replaced by the second moment of quadrupolar interaction $Q_2 = (4/5)\pi^2(\Delta\nu)^2$. For the CD_2 in butadiene rubber (BR) $\Delta\nu = 125$ kHz was obtained and, consequently, $Q_2 = 1.19 \times 10^{11} \text{ s}^{-2}$.

For molecular masses between two crosslinks M_c ranging from approximately 5.5–8.8 kg/mol [18], as estimated from mechanical measurements, the nmr transverse magnetization decay for protons and deuterons was correlated to M_c . Based on GOTLIB's idea [20] of the factor q as the ratio between the second moments well above the glass transition temperature and those of the rigid lattice, respectively, the averaged molecular mass of intercrosslink chains M_c can be determined. It is assumed that the polymer chain consists of N_s KUHN statistical segments [21]. It follows

$$M_c = \frac{k}{\sqrt{q} - \sqrt{q_0}} c_\infty \frac{M_{\text{ru}}}{N} = N_s c_\infty \frac{M_{\text{ru}}}{N} \quad (3)$$

M_{ru}/N is the molecular mass of one monomer unit per number of backbone bonds in one unit. The quantity c_∞ is the number of backbone bonds in one KUHN-segment. The factor k depends on the direction between the spin–spin connecting vector and the segment direction. If they are perpendicular to each other then $k = 3/10$ or in the parallel case $k = 3/5$ is valid. The value q_0 corresponds to the correction due to entanglements and is determined by fitting Eq. (2) to the relaxation decay of the corresponding non-crosslinked melt.

On the contrary, it is well known that the mechanical properties of vulcanizates depend not only on the crosslink density, but also to a large extent on the vulcanization conditions such as curing agent, curing time and temperature [22]. The presence of a filler also contributes significantly to the mechanical properties. A deeper understanding of the mechanical properties of vulcanized elastomers may be gained from structural characterization of their networks. On the basis of the relationship between motional and structural parameters, an insight into the structural features of these materials should be available from those nmr parameters which are influenced by molecular mobility and order.

Table 1
Characterization of precursor poly(butadiene) PB-d₄

Sample	A	B	C	D	E
$M_n(1,4\text{-PB})$	120.000	125.000		61.000	
$M_w(1,4\text{-PB})$	450.000	129.000		64.000	
U (1,4-PB)	3.75	1.03		1.05	
$M_n(1,4\text{-PB-d}_4)$	190.000	152.000	135.000	70.000	50.000
$M_w(1,4\text{-PB-d}_4)$	700.000	162.000	140.000	72.000	52.000
U (1,4-PB-d ₄)	3.68	1.06	1.04	1.03	1.04
Microstructure	97% 1,4- <i>cis</i>	<i>cis/trans</i>	<i>cis/trans</i>	<i>cis/trans</i>	<i>cis/trans</i>

To further assess the sensitivity of ²H nmr to elastomer structure and to examine the proposed two-component model [18] for elastomer ²H nmr spectra, we have obtained proton and deuteron transverse magnetization decays as well as ²H nmr spectra for partially deuterated polybutadiene elastomers with systematically varied elastic properties. We have produced randomly crosslinked polymer networks with different microstructure, precursor chain length and crosslink density with molecular weights between crosslinks M_c which vary from 2 to 10 kg/mol. The M_c -values were also determined independently by mechanical measurements.

2. Experimental

The validity of the theory was already shown by conventional measurements of the transverse relaxation times in rubber samples with well-known crosslink densities [18,23,24].

All experiments were carried out on a Varian Unity 400 widebore spectrometer. The measurement of the transverse relaxation was performed using standard Hahn echo sequence operating at 40 or 61.3 MHz for protons or deuterons, respectively, to eliminate the influence of magnetic field inhomogeneities and of chemical shift on the transverse decay, while the dipolar/quadrupolar interaction is not affected. All relaxation measurements were performed

at $T = 60^\circ\text{C}$, for which the condition $T = T_g + 120\text{ K}$ (T_g is the glass transition temperature) is fulfilled.

The elastomeric networks under study were based on partially CD₂-deuterated poly(butadiene) with different microstructure, molar mass and mass distribution due to the polymerization process (see Table 1). They were mixed in a ratio 1:9 with a corresponding commercial poly(butadiene) with nearly the same parameters. Dicumyl peroxide (DCP) was used as the crosslinking agent in variable amounts between 0.5 and 3 phr. The samples were vulcanized in a vulcameter press at 145°C and 100 bar for 1 h. The samples B–E contain about 10% 1,2-vinyl poly(butadiene).

3. Results and discussion

3.1. Characterization of undeformed elastomers

To investigate the relationship between the nmr data and the network structure, spectral features of polybutadiene-d₄ networks were compared to structural parameters resulting from macroscopic properties. The ²H nmr spectra as well as the transverse magnetization decays for protons and deuterons were obtained. The ²H nmr spectra of sample series A crosslinked with different amounts of DCP are shown in Fig. 1. An increasing amount of the crosslinker DCP increases the portion of intercrosslinked (elastic) chains and the spectra become more and more broad. The broader spectra indicate that the segmental motion is more anisotropic with increasing crosslink density and/or is not sufficiently rapid on the nmr time scale to completely average the quadrupolar interaction. The same behavior is found for different precursor chain lengths. The longer the precursor chain in the non-crosslinked melt the broader is the line. Comparing different networks with approximately the same amount of the crosslinker DCP and microstructure, but based on various precursor chain lengths, the line broadening of the ²H spectra seems to increase a little with the chain length (Fig. 2). The line width of the elastic

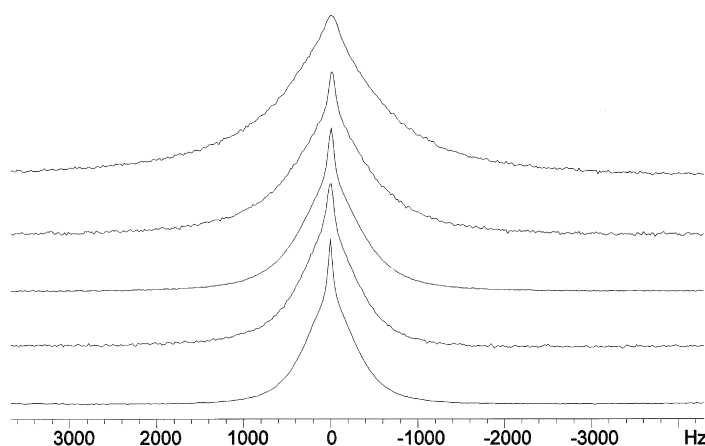


Fig. 1. ²H nmr spectra of sample series A at different amount of the crosslinker DCP, from bottom to top: 0.5, 0.8, 1.0, 2.0 and 3.0 phr DCP.

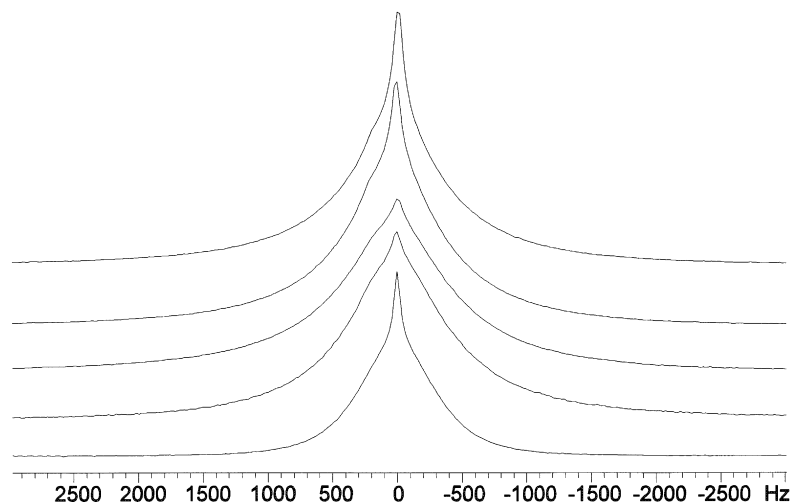


Fig. 2. ^2H nmr spectra of A-05, B-05, C-05, D-05 and E-05 (from bottom to top).

network component is about 1050 Hz for B-05 and C-05, and about 900 Hz for D-05 and E-05, respectively. But this effect is very small and influenced as well as by the mixing with the purely protonated polybutadiene (Table 1) and the small existing differences in crosslink density (Table 2). The latter is probably the most effective one. A comparison of sample A-05 with B-05 suggest that the resulting crosslink density is larger in those samples containing a 1,2-vinyl poly(butadiene) fraction.

Interpretation of ^2H nmr observations in terms of elastomer structure requires the use of theoretical models which describe motional averaging of segment orientation distributions in terms of structural parameters. Such theoretical models rely on the assumption that the motion-averaged quadrupolar interaction dominates the ^2H nmr spectra. Thus, to obtain nmr data which isolate the effect of the dipolar or quadrupolar interaction from distortions caused by field inhomogeneities, the $(90^\circ)_x - \tau - (180^\circ)_y - \tau$ sequence (Hahn echo) was used to observe the transverse magnetization as a function of the echo time.

Fig. 3(a) and (b) shows proton and deuteron transverse magnetization decays of unfilled partially deuterated polybutadiene samples. To develop a model for transverse magnetization decays in elastomers, several authors have suggested two-component models based on two distinct motional processes averaging the segment orientation distribution [9,18,19,25–27]. This two-component model was initially proposed to describe proton transverse magnetization decays in elastomers, which is dominated by homonuclear dipolar interaction. The earliest model for elastomers simply predicted a slowly dephasing component corresponding to a fast motional process, and a second rapid one, which is attributed to a slower motional process. More recent models associate the slowly dephasing component with segments in dangling ends, whose motion is less hindered and nearly isotropic, and a fast dephasing process to intercrosslinked chains whose motion is hindered due to topological constraints by crosslinks [18,19,25]. Transverse magnetization decays are expected to be a linear superposition of contributions from these two components

Table 2

Characterization of the polymer networks from proton and deuteron nmr relaxation, mechanical stress–strain and swelling measurements. M_c is the mean molar mass between two crosslinks.

Sample	Amount of DCP (phr)	M_c (mechan.) (g/mol)	M_c (^1H nmr) (g/mol)	M_c (^2H nmr) (g/mol)	G' -modulus (MPa)
A-05	0.5	7590	8000	8200	0.6
A-08	0.8	5180	5000	4500	1.23
A-10	1	3230	4000	4260	–
A-12	1.2	2550	5300	5250	–
A-15	1.5	3310	3400	3650	1.58
A-20	2	2490	2200	1800	–
A-25	2.5	1330	1400	1150	–
A-30	3	1060	1300	930	4.2
B-05	0.506	–	10 800	7240	–
C-05	0.55	3000	3040	5100	–
D-05	0.52	7200	5300	7760	1.13
E-05	0.635	5000	4700	6270	1.09

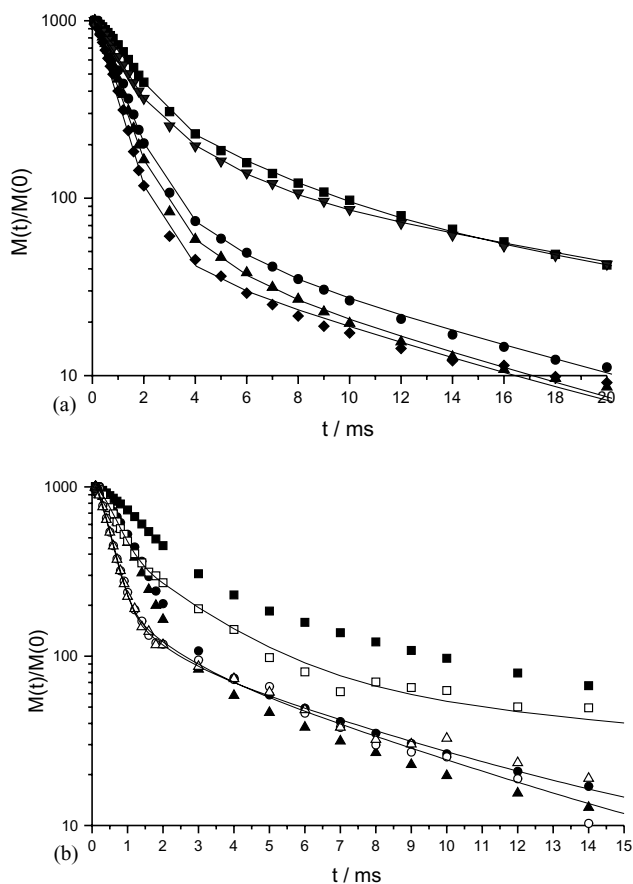


Fig. 3. (a) ^1H nmr relaxation decays vs. echo time for sample series A with different amount of crosslinker DCP: ■—0.5, ●—0.8, ▲—1.0, ▼—1.2, ◆—1.5 phr DCP. (b) ^2H nmr relaxation decays (and fitting curves) vs. echo time for sample series A with different amount of crosslinker DCP: □—0.5, ○—0.8, △—1.0 phr DCP (filled symbols for corresponding ^1H nmr relaxation curves from Fig. 3(a)).

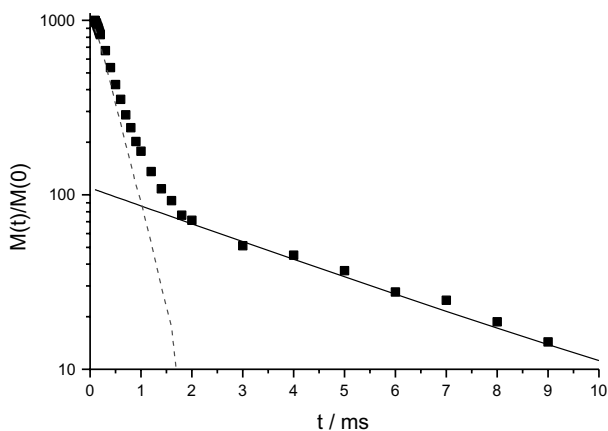


Fig. 4. Simulated ^2H nmr relaxation curve for poly(butadiene)- d_4 network B-05. The squares are the experimental data. The dashed line gives the elastic chain contribution or the transverse dephasing; the solid line gives the dangling/pendant chain contribution. The contribution of the free chains ("sol"-content) was subtracted before.

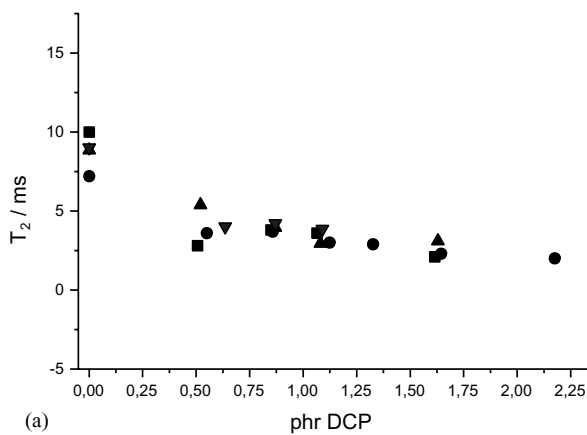
(Fig. 4): intercrosslinked chains $M_{\text{NW}}(t)$ and dangling ends $M_{\text{DE}}(t)$, which corresponds to Eq. (2):

$$\frac{M(t)}{M(0)} = AM_{\text{NW}}(t) + B M_{\text{DE}}(t) \quad (4)$$

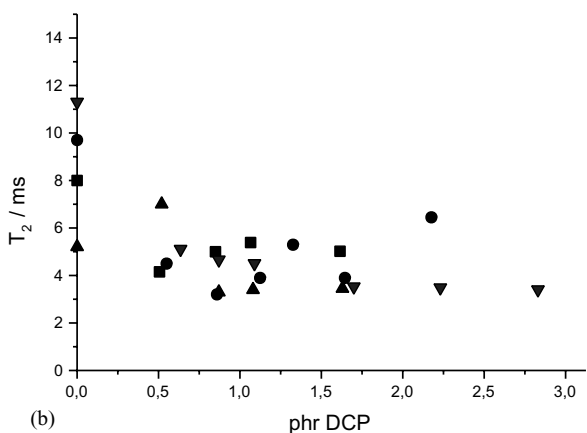
The contributions are weighted by the fractions of intercrosslink chains A and dangling ends B. The expressions $M_{\text{NW}}(t)$ and $M_{\text{DE}}(t)$ may be obtained by modeling the distinct motional processes experienced by intercrosslinked chains and free dangling ends. The expression used here are those proposed by Simon et al. [2,3,6,18] which is given by Eq. (2). Sotta et al. [8] proposed another expression for the (elastic) network component resulting in very little quantitative difference. A detailed comparison of both expressions is to be published [28].

An analysis was performed using Eq. (2) in the case of protons and with the changes mentioned above for deuterons. Eq. (3) was used to calculate the mean molecular mass between the crosslinks M_c . There are no principal differences between the proton and the deuteron relaxation curves except for faster deuteron decay due to the different strength of interaction in an order of 10. The correspondence with the theoretical curves is quite good (see Fig. 3(a) and (b)) and yields to consistent results. Within an error of $\pm 15\%$ the nmr- M_c values of both independent measurements agree very well with each other and also with the results of stress-strain, swelling and dynamical modulus measurements. Other authors [29] used the same model and found a good correlation of the nmr- M_c values with mechanical data for crosslinked samples with $M_c < 10\,000$ g/mol, while agreement between them was poor for loosely crosslinked samples ($M_c > 10\,000$ g/mol). The results are summarized in Table 2. In all cases, the larger the precursor chain length in the melts, faster is the decay of the transverse magnetization. However, there seems to be a systematic difference between the M_c values determined from ^1H and ^2H measurements in the case of a narrow distribution (low polydispersity: $U \sim 1$) of the precursor chain length: usually the $^1\text{H}-M_c$ are smaller than the $^2\text{H}-M_c$. A large discrepancy exists for sample A-12, here the nmr results disagree with mechanical testing. A possible explanation is a very inhomogeneous network due to any unknown reason. The analysis of both relaxation decays results in a large number of defects (largest portion of dangling ends, largest "sol"-fraction).

In networks with a similar crosslink density a steeper decrease of the decay was observed in those samples prepared from a *cis/trans* microstructure rather than from those based on the high-*cis*-prepolymer although the latter has a longer chain length and a much larger polydispersity U . One reason is the larger stiffness of the vinyl and the *trans* configuration compared to the *cis* one. Another possible explanation to such a behavior was given by Sotta et al. [8]. From a theoretical point of view they expected a steeper decrease at short time for randomly crosslinked systems with a broad distribution of the intercrosslink chain length



(a)



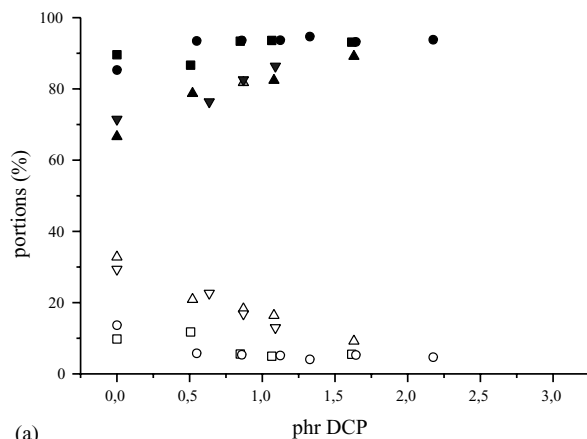
(b)

Fig. 5. (a) Proton T_2 data vs. amount of crosslinker DCP determined from the network series B (■), C (●), D (▲) and E (▼). (b) Deuteron T_2 data vs. amount of crosslinker DCP determined from the network series B (■), C (●), D (▲) and E (▼).

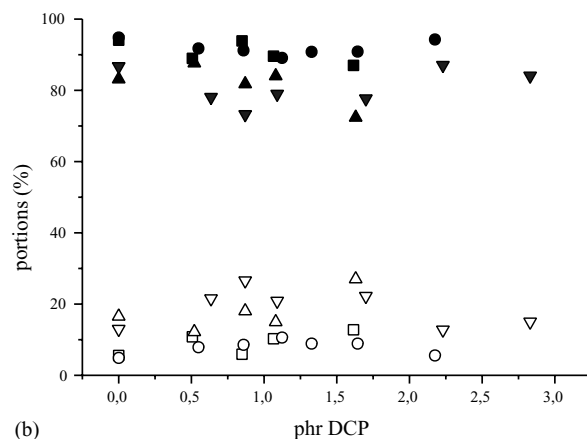
rather than in the monodisperse case. The 1,2-vinylpolybutadiene fraction in the sample series B–E is thermodynamically the most sensitive part to the crosslinking reaction used here. Therefore, the resulting distribution of the network chain length (M_c -distribution) is expected to be broader and more irregular than those of the *cis*-networks (series A).

For all samples under investigation the relaxation time T_2 decreases slightly (the corresponding “fast” correlation time τ_{fast} due to Bloembergen–Purcell–Pound (BPP) formula [11] is increasing) with increasing amounts of the crosslinking agent, whereas the changes are more pronounced at lower crosslink densities (starting from the uncrosslinked state) and in the case of proton relaxation. But the T_2 values do not differ in the dependence on precursor chain length and polydispersity (Fig. 5(a) and (b)). The correlation time τ_{slow} is in the order of 0.1 ms and does not differ very much, but it may be influenced by the polydispersity and/or a possible correlation time distribution (which is ignored here for simplicity).

As one additional result from Eq. (3) the different



(a)



(b)

Fig. 6. (a) Fractions of intercrosslinked chains (filled symbols) and pendant chains (open symbols), respectively, vs amount of crosslinker DCP determined from proton nmr relaxation measurements on the network series B (■), C (●), D (▲) and E (▼). (b) Fractions of intercrosslinked chains (filled symbols) and pendant chains (open symbols), respectively, vs amount of crosslinker DCP determined from deuteron nmr relaxation measurements on the network series B (■), C (●), D (▲) and E (▼).

portions of network chains, dangling ends and additional free chains (“sol”-content) are available. These components are distinguished by shape, due to differences in segment mobility. Segments of dangling ends and free chains reorient isotropically on the nmr time scale. As a result, the dangling ends and free chains can be represented by exponential decays, corresponding to rapid, isotropic motional averaging of the quadrupolar or dipolar interaction, respectively. The segments of intercrosslinked chains, however, reorient anisotropically, due to topological constraints, which results in a solid-like behavior. With increasing amount of the crosslinker DCP an increase of intercrosslink chains and a decrease of dangling ends and free chains were observed. At high concentrations of the crosslinking agent (about 3 phr DCP) an opposite trend is found: the portion of dangling ends increases again due to chain scission. The networks prepared from polymers D and E are also characterized by larger fractions of dangling ends compared to those from B and C as already shown in Fig. 2.

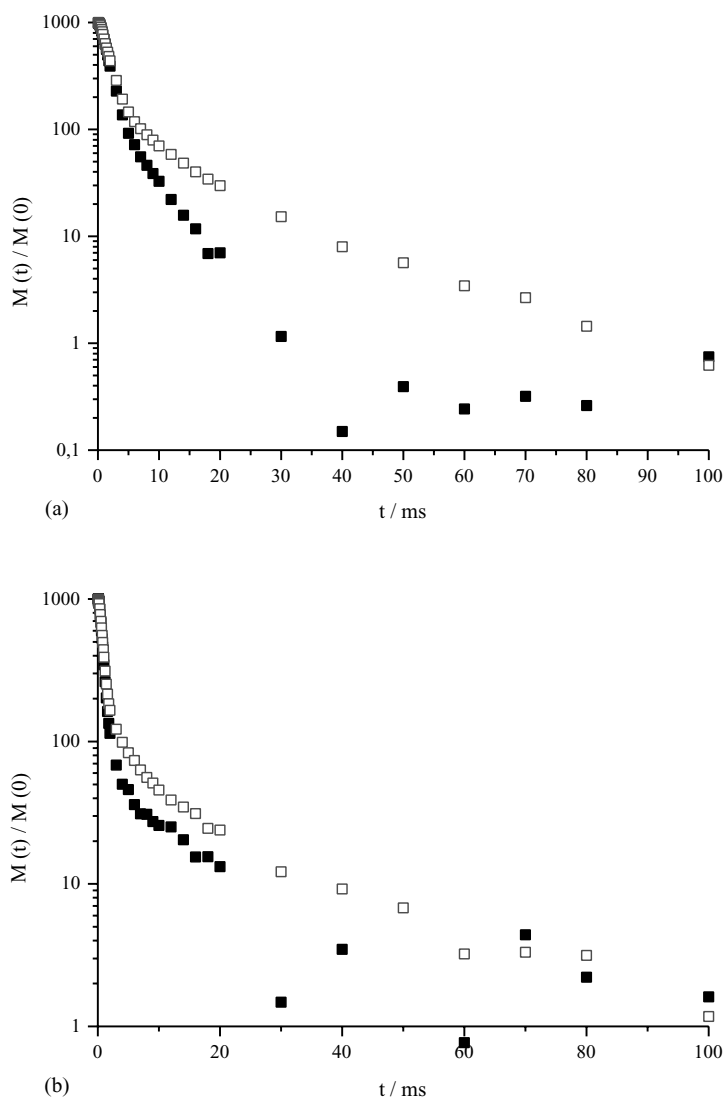


Fig. 7. (a) ^1H nmr relaxation decays vs. echo time for network A-05-2 (20% PB- d_4) before (□) and after (■) the extraction in toluene. (b) ^2H nmr relaxation decays vs. echo time for network A-05-2 (20% PB- d_4) before (□) and after (■) the extraction in toluene.

These changes are more pronounced in the case of proton measurements and for the samples D and E with the shorter precursor chain length. This is caused by the mixing ratio of partially deuterated and protonated chains (1:9): due to the relatively small amount of free chains (the “sol”-content is usually less than 2%) the portion of free polymer chains could not be distinguished from the dangling ends in the case of deuterium measurements (Fig. 6(a) and (b)).

In the case of uniaxial stretching of the deuterated elastomer sample a line splitting is observed in the ^2H nmr spectra. In a lot of previous papers the splitting was simply obtained from peak maxima [10,13–15,19,23,24,30]. Compared with our data these peak maxima are mainly determined by dangling ends and free chains and correspond to an order parameter of those chains. This is in agreement with an explanation of Kornfield and co-workers [19] suggesting that the central portions of ^2H

nmr spectra of elastomers are dominated by deuterons in pendant chains.

This argument may also be supported by the interpretation and comparison of the samples A-05 and A-05-2. Both samples were prepared on the basis of exactly the same precursor polymer A and the same amount of crosslinker DCP (0.5 phr DCP). The preparation and vulcanization process was identical with the exception of a higher portion of partially deuterated chains (the mixing ratios were 1:9 or 2:8, respectively). So the ^2H nmr spectra of the two samples were expected to be identical, but they differed in shape and splitting at approximately the same deformation ratio. The spectra of sample A-05-2 was much narrower and the obtained splitting was much smaller compared to those of sample A-05. These spectra will be published elsewhere (part II). Performing the relaxation measurements for protons as well as for deuterons, larger portions of dangling ends and free chains (“sol”-content)

Table 3

Results from proton and deuterium nmr relaxation measurements of sample A-05-2 before and after extraction. M_c is the mean molar mass between two crosslinks. A, B and C are the fractions of intercrosslinked chain, dangling ends and free chains, respectively

Transversal magnetization from		M_c (kg/mol)	A (%)	B (%)	C (%)
^1H measurement	Before extraction	7.5	77	17	6
	After extraction	7.3	88	12	–
^2H measurement	Before extraction	9.6	82	14	4
	After extraction	7.2	93	7	–

were obtained in the sample A-05-2 compared to A-05 (Fig. 7(a) and (b)).

The extraction procedure of the network sample A-05-2 in toluene ended with a mass loss of about 40%. The ^2H nmr spectra after extraction with and without deformation were similar to those of the sample A-05. The investigation of the extracted solution by infra-red spectroscopy and GPC indicates a mixture of deuterated and protonated polymer corresponding to the initial mixing ratio and a number average molar mass M_n of 49 000 g/mol and a weight average M_w of 213 000 g/mol. The width of molecular mass distribution was found to be similar to that of the precursor mass distribution, but shifted towards shorter chains. These removable short deuterated chains are responsible for the observed small splitting. This peak-to-peak splitting corresponds to dangling ends and free pendant chains. A “sol”-contribution of more than 10% could strongly influence the shape and the splitting of the ^2H nmr spectra and is non-negligible. The reduction of free chains and dangling ends was checked by relaxation measurements using Eq. (2). The M_c -values of both samples determined from transversal relaxation remains nearly unchanged due to the extraction procedure (Table 3).

4. Conclusion

Deuterated elastomers were prepared with a systematic variation of crosslink density, microstructure, precursor chain length and precursor molecular weight distribution. The networks have been characterized by analyzing their elasticity and by transversal relaxation measurements of two different nuclei (protons and deuterons) in terms of well-established models. Transverse ^2H nmr relaxation data obtained for the networks are well represented by a sum of two components: one was attributed to dangling ends, the other to intercrosslink chains. The nmr measurements (^1H -, ^2H -relaxation, ^2H nmr spectra) differentiate between intercrosslink chains and dangling ends on the basis of their mobility. The relaxation decay at nearly fixed microstructure was observed to be faster the larger the precursor chain length. The faster decay in the initial part of the relaxation curve for networks prepared from a polymer precursor with *cis/trans*/vinyl-microstructure compared to those from a high-*cis* one is probable mainly due to a broader distribution of the chain length between

crosslinks and the higher stiffness of the vinyl and the *trans* configuration. Best fits of the model to the relaxation decays obtained from partially deuterated polybutadiene- d_4 networks give parameters, which are correlated with structural parameters mechanically observed. These relaxation parameters could explain the ^2H nmr observations (line broadening with increasing amount of crosslinker, line shape) and support the suggestion that the central part of the ^2H nmr spectra is dominated by free and pendant chains. A fraction of free short deuterated chains in the order of more than 10% is non-negligible. It produces a ^2H nmr spectra with narrow lines and a small peak-to-peak splitting in the case of deformation.

The investigation of the deformation behavior of these samples will be published in a forthcoming paper (part II).

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