Macromolecules **2002,** *35,* 9253−9255 **9253**

Influence of Cross-Link Density and Deformation on the NMR Relaxation Dispersion of Natural Rubber

Sobiroh Kariyo and Siegfried Stapf*

Lehrstuhl für Makromolekulare Chemie and Magnetic Resonance Center MARC, ITMC, RWTH Aachen, Germany

Received August 26, 2002
Revised Manuscript Received September 17, 2002

Introduction. Nuclear magnetic resonance (NMR) provides versatile tools for the investigation of different aspects of the molecular dynamics in polymers and elastomers. The use of line-narrowing methods,[1] multiple quantum spectroscopy,[2] dipolar correlation effects,[3] and transverse and longitudinal relaxation parameters[4−6] are among the most frequently employed techniques to characterize the mobility and order in soft matter such as polymer melts and rubbers. Each of them gives insight into processes on characteristic time scales, usually given by the Larmor frequency or encoding and evolution times, of the sequences used. One particularly favorable experimental NMR approach that allows the determination of dynamic parameters over several orders of magnitude in time without changing the sample temperature is given by field-cycling NMR relaxometry.[7] From measuring the spin−lattice relaxation time as a function of Larmor frequency, $T_1(\nu)$, it provides access to the spectral density function of motion in the kilohertz to megahertz region which cannot be obtained by conventional NMR techniques over a similarly broad range. Relaxometry is sensitive to the reorientation of spin-bearing nuclei and therefore to the chain dynamics in polymers at the corresponding frequencies. It has predominantly been used to test the different models that describe the dynamics of polymer solutions and melts.[8−10] More recently, the influence of rigid confinements on the segmental mobility and the reorientation spectrum has been under study.[11] The effect of fluctuating cross-links in a thermoreversible polybutadiene network was discussed by Kimmich et al.,[12] while only a minor influence on T_1 at high cross-link densities was found for the very flexible polymer PDMS.[9] A systematic study of permanently cross-linked elastomers using this method has not been presented in the literature.

As an elastomer of high technical importance, natural rubber (i.e., cross-linked polyisoprene), was studied extensively by NMR. In particular, the influence of cross-link density on the relaxation parameters has been investigated for example by relaxometry in the rotating frame[13] which, however, stretches only over one decade in frequency. NMR deuteron spectroscopy has clearly revealed the microscopic ordering effects induced by macroscopic deformation,[14−17] but the influence of these processes on the spin−lattice relaxation have not yet been described in the literature.

In this paper, we discuss relaxometry results of natural rubber as a function of cross-link density and temperature in comparison to un-cross-linked, high-molecular-weight polyisoprene. Moreover, we present experimental evidence for the effect of uniaxial deformation on the relaxational dynamics of the segments.

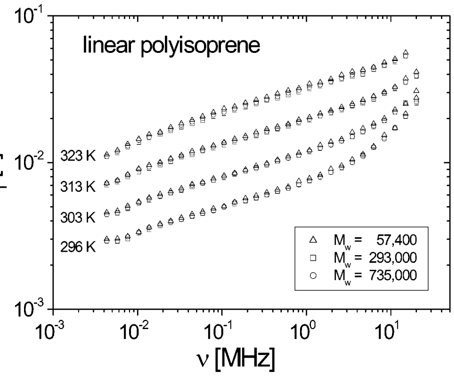

Figure 1. Relaxation dispersion for linear polyisoprene of three molecular weights M_w at different temperatures.

Experimental Section. The rubber samples were provided from Dunlop GmbH, Hanau, Germany. Natural rubber SMR-10 was vulcanized into sheets of 2 mm thickness at 160 °C with 3 phr ZnO, 2 phr stearic acid, and between 1 and 7 phr sulfur and TBBS as accelerator each (in the following designated as NR 1/1...7/7). Linear polyisoprene was purchased from Polymer Standards Service, Mainz, Germany, and was characterized as 95% 1,4-linked and 5% 3,4-linked. The polydispersity M_w/M_n was better than 1.10. All samples were evacuated at room temperature and were stored at 277 K between experiments. A single band of rubber was used for the deformation experiments and was either stretched in a U-shape about a plate or wound tightly around a rod, with spacer materials not contributing to the NMR signal. Small cubes of rubber were placed between Teflon disks fitting inside a glass tube and were squeezed with a plastic screw.

Relaxometry data were obtained on a commercial Stelar fast field cycling relaxometer (Stelar s.r.l., Mede, Italy), which allowed the determination of proton longitudinal relaxation times at Larmor frequencies between 5 kHz and 20 MHz which were determined by high-frequency magnetometers and test samples of known relaxation dispersion. The lowest detectable values of T_1 of approximately 0.7 ms were limited by the shortest possible switching time between polarization/relaxation field and relaxation/detection field of 1.3 ms each.[18] The signal was acquired with a filter bandwidth of typically 90 kHz following a dead time of 25 μs. Decays were found to be monoexponential over more than one decade. The relaxation times were reproducible within 2%; the temperature control was better than ±1 K.

Results and Discussion. The relaxation dispersion curves for linear polyisoprene of three different molecular weights are shown in Figure 1. The constant slope found in the lower range of frequencies corresponds to a power-law relation of $T_1 \propto \nu^\gamma$ with $\gamma = 0.16 \pm 0.01$ for all M_w and temperatures. Power-law dependences of T_1 on the frequency have been predicted by theory for polymer melts above a critical molecular weight, $M_w > M_c$, and have been divided into at least three distinct regimes for which $\gamma \approx 0.5$ (high frequencies, “regime I”), $\gamma \approx 0.2−0.25$ (intermediate frequencies, “regime II”),

---

* Corresponding author: Tel +49-241-8026971; Fax +49-241-8022185; e-mail sstapf@mc.rwth-aachen.de.

10.1021/ma025632f CCC: $22.00

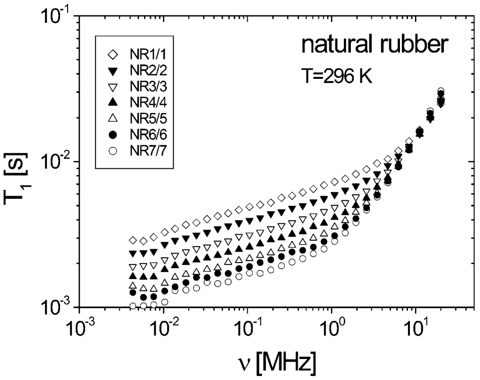

Figure 2. Relaxation dispersion at $T = 296$ K for natural rubber with sulfur/accelerator contents from 1/1 phr to 7/7 phr.

and $\gamma \approx 0.45-0.5$ (low frequencies, "regime III").[8,10] Exponents found experimentally for polymer melts were in the same range, but a value as low as the one found in this study has not been described before. Still, the observed behavior must be attributed to regime II, which is characterized by displacements being influenced by the tube constraint but not dominated by coherent chain motions. The absence of a molecular weight dependence is consistent with this assumption. We merely mention the deviation of the particular value of γ for polyisoprene as a reference for the following presentation of relaxation data of cross-linked rubber. A full analysis has to take into account intrasegmental correlations and intermolecular contributions to the dipole−dipole interactions and will be discussed in a forthcoming paper.

The dispersion curves for natural rubber at room temperature are presented in Figure 2. The most prominent feature is the unchanged power-law relation in the lower frequency regime, which indicates that the segmental reorientation spectrum is not altered by cross-linking. The absolute values of T_1 at low frequencies, however, decrease. The same behavior was found for $T_{1,\rho}$ in a narrower frequency range.[13] At high fields, on the other hand, the curves overlap and high cross-link densities correspond to longer T_1. This shift of the whole dispersion profile toward the "lower left" corner would be expected from an Arrhenius-type slowing down of all reorientation processes with the shape of the autocorrelation function remaining unchanged. The same observation is indeed made if the temperature is varied. In Figure 3a, the dispersion of NR 1/1 as a function of temperature is presented. Again, the slope remains unchanged in the low-frequency regime, but a high-frequency branch is found with an approximate dependence of $T_1 \propto \nu^{1.2}$. This exponent does not agree with the mentioned predictions for chain-mode motion in regime I but can be attributed to an overlap of the time scales of reorientations within the Kuhn segment and translations of the Kuhn segments themselves. This behavior is frequently found if regime I falls in the vicinity of the temperature minimum of T_1.[9] In Figure 3b, the temperature minima are observable for the upper range of frequencies, and their shift toward higher temperatures for increasing cross-link density becomes obvious. At the minima, $2\pi\nu\tau_s \approx 0.62$, and one obtains the temperature dependence of the segmental reorientation time, $\tau_s = \tau_{s,0}(\mathrm{cl}) \exp[E/RT]$ with $E = 58$ kJ/mol. The cross-link density dependent prefactor $\tau_{s,0}(\mathrm{cl})$ is shifted corresponding to a temperature difference of 15 K between NR 1/1 and NR 7/7. By fitting a phenomenological function $T_1 = a_1\nu^{0.16} + a_2\nu^{1.2}$, the crossover times between the two regimes were determined and found to obey the same Arrhenius-type behavior as τ_s. The shape of the reorientation spectrum is thus not affected by the presence of cross-links, but the dynamics are slowed down as a whole due to the chemical links. We note that, of course, long-range motions which are governed by coherent chain motions must be affected by the network, as the center-of-mass diffusion coefficient is constrained to zero, but these motions are below the frequency range accessible in this study.

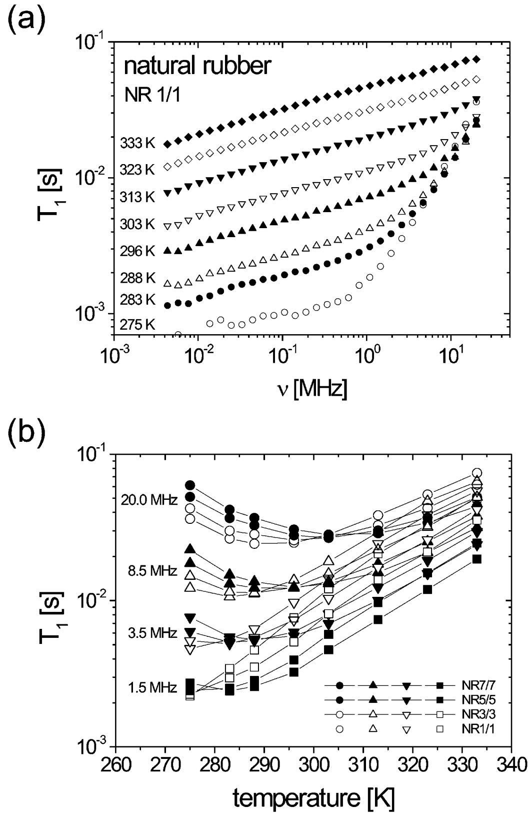

Figure 3. (a) Relaxation dispersion for natural rubber (NR 1/1) as a function of temperature. (b) Temperature dependence of T_1 at selected Larmor frequencies for rubber with different cross-link densities.

Deformation of the polymer network introduces local order, but it also affects the degrees of freedom for chain segment reorientations. In Figure 4 we present dispersion curves for NR 1/1 under uniaxial deformation of elongation ratios $\lambda > 1$ (stretching) and $\lambda < 1$ (compression). While the compression axis was parallel to the direction of the magnetic field, B_0, stretching occurred both parallel and perpendicular to B_0. Irrespective of the direction of deformation, relaxation at low frequencies was always found to be reduced, with larger effects found not only for larger deformations but also at higher temperatures. High-field relaxation times remained essentially unaffected, and the slope of the dispersion was found to change gradually up to a maximum observed value of $\gamma = 0.24 \pm 0.01$. We tentatively suggest two possible interpretations for this finding: first, deformation can change the reorientation spectrum itself; i.e., the time dependence of the motional modes is affected. Second, the relative contribution of the intermolecular interaction is changed with chain deformation. This contribution might also be one of the reasons for the deviation of the power-law exponent

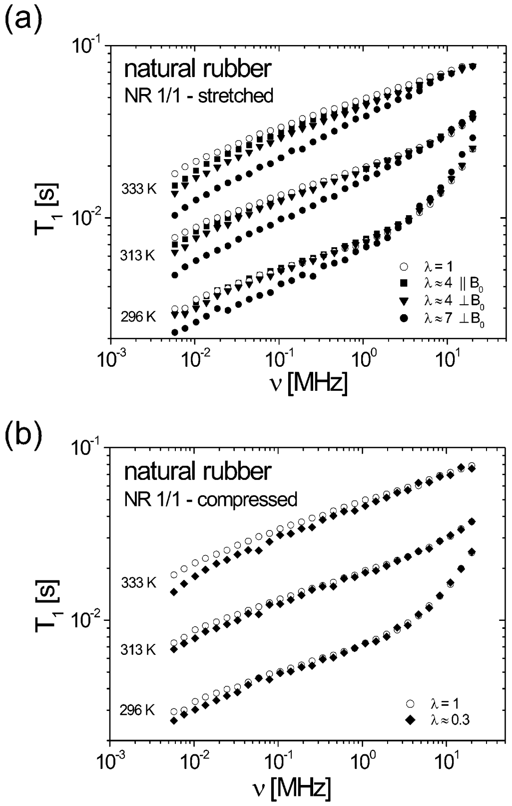

Figure 4. (a) Relaxation dispersion for natural rubber (NR 1/1) under uniaxial strain at different strain ratios λ in directions parallel (∥ B_0) or perpendicular (⊥ B_0) to the magnetic field. (b) As in (a) but for compression.

found for polyisoprene from those of other polymers. When considering these possibilities, the phenomenon of strain-induced crystallization has to be taken into account. It is known that for natural rubber above $\lambda \approx 2$ chain ordering leads to the formation of crystal domains,[19] which remain stable up to about 85 K above their theoretical melting point of ≈303 K.[20] Both mentioned effects can be induced by the presence of such crystals. A direct contribution of the crystals themselves to the NMR signal can be excluded due to their broad spectral lines which are filtered out by the dead time of the spectrometer; no indication of a second component was found in the signals obtained from deformed rubber. Moreover, the change of relaxation dispersion becomes more obvious at higher temperatures, where the degree of crystallinity must be equal or smaller. The contribution of spin diffusion, leading to a mixing of the relaxation times of crystalline and amorphous parts of the deformed rubber, is expected to generate two distinctly different dispersion regimes which is not suitable to explain the observed behavior. Further experiments will be performed on grown samples of uncross-linked polyisoprene with a well-defined degree of crystallinity and will include measurements of the relaxation anisotropy.

Conclusions. Molecular dynamics in cross-linked natural rubber, as obtained from the analysis of proton NMR relaxometry data, was shown to possess the same phenomenological reorientational spectrum as in uncross-linked polyisoprene within the accessible frequency range of upward from 5 kHz. The presence of cross-links merely leads to a slowing down of the whole time scale of motions which can be correlated with the cross-link density and thus can serve for a characterization of the state of technical elastomer samples. Uniaxial deformation affects the dipole−dipole spin interactions in such a way as to enhance the frequency dependence of $T_1(\nu)$. More thorough investigations of the amorphous/crystalline spin interactions and modeling of the deformed network are currently pursued with the goal of discriminating the processes which lead to this change in relaxation dynamics.

Acknowledgment. The authors are grateful to V. Herrmann, Dunlop GmbH, for kindly providing the rubber samples, and to B. Blümich, M. Adams, K. Kupferschläger, and G. Schroeder for continuous support throughout this study. Funding from Deutsche Forschungsgemeinschaft (Sta 511/3-1) is gratefully acknowledged.

References and Notes

(1) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers;* Academic Press: London, 1994.
(2) Graf, R.; Demco, D. E.; Hafner, S.; Spiess, H. W. *Solid State Nucl. Magn. Reson.* **1998**, *12*, 139.
(3) Grinberg, F.; Garbarczyk, M.; Kuhn, W. *J. Chem. Phys.* **1999**, *111*, 11222.
(4) Brereton, M. G. *Macromolecules* **1990**, *23*, 1119.
(5) Cohen-Addad, J. P. *Prog. NMR Spectrosc.* **1993**, *25*, 1.
(6) Menge, H.; Hotopf, S.; Heuert, U.; Schneider, H. *Polymer* **2000**, *41*, 3019.
(7) Noack, F. *Prog. NMR Spectrosc.* **1986**, *18*, 171.
(8) Kimmich, R.; Weber, H. W. *J. Chem. Phys.* **1993**, *98*, 5847.
(9) Weber, H. W.; Kimmich, R. *Macromolecules* **1993**, *26*, 2597.
(10) Fatkullin, N.; Kimmich, R. *J. Chem. Phys.* **1994**, *101*, 822.
(11) Kimmich, R.; Seitter, R.-O.; Beginn, U.; Möller, M.; Fatkullin, N. *Chem. Phys. Lett.* **1999**, *307*, 147.
(12) Kimmich, R.; Gille, K.; Fatkullin, N.; Seitter, R.; Hafner, S.; Müller, M. *J. Chem. Phys.* **1997**, *107*, 5973.
(13) Chaumette, H.; Grandclaude, D.; Tekely, P.; Canet, D.; Cardinet, C.; Verschave, E. *J. Phys. Chem. A* **2001**, *105*, 8850.
(14) Sotta, P.; Deloche, B.; Herz, J.; Lapp, A.; Durand, D.; Rabadeux, J.-C. *Macromolecules* **1987**, *20*, 2769.
(15) Callaghan, P. T.; Samulski, E. T. *Macromolecules* **1997**, *30*, 113.
(16) Menge, H.; Hotopf, S.; Schneider, H. *Polymer* **2000**, *41*, 4189.
(17) Schneider, M.; Demco, D. E.; Blümich, B. *Macromolecules* **2001**, *34*, 4019.
(18) Kimmich, R. *NMR: Tomography−Diffusometry−Relaxometry*; Springer-Verlag: Berlin, 1997.
(19) Toki, S.; Sics, I.; Ran, S.; Liu, L.; Hsiao, B. S.; Murakami, S.; Senoo, K.; Kohjiya, S. *Macromolecules* **2002**, *35*, 6578.
(20) Schnetger, J. *Lexikon der Kautschuk-Technik;* Hüthig: Heidelberg, 1991 and references therein.

MA025632F