Macromolecules **2003,** *36,* 7155−7157

Self-Diffusion Anisotropy of Small Penetrants in Compressed Elastomers

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Received May 13, 2003

ABSTRACT: The anisotropy of self-diffusion of toluene in uniaxially compressed natural rubber samples with different cross-link densities was detected using the pulsed-gradient stimulated spin-echo NMR method. The effective diffusion coefficients and the displacement probabilities of toluene were measured along and perpendicular to the direction of the compression force. The diffusion anisotropy increases with increasing compression and cross-link density. The anisotropy of diffusion can be used for NMR investigations of the deformation of the polymer networks by the changes in the shape of the free volume.

Introduction

Investigations of molecular self-diffusion provide important information on molecular organization and interactions with the environment in many systems.[1−3] In the past few years the study of anomalous diffusion in complex systems has become a most attractive subject to both fundamental and applied research.[1−3] The deviation from ordinary diffusion due to the presence of internal boundaries in polymer solutions, melts, and solid samples which leads in many cases to anomalous diffusion has been investigated using the pulsed gradient spin-echo (PGSE) method.[4,5]

A well-known consequence of the theory of rubber elasticity is bond orientation.[6,7] Deformation of an elastomer induces anisotropy of the backbone bonds of the polymer coil. In recent NMR studies of rubber elasticity, the mechanism of deformation and the orientation of network chains have received increasing attention. One- and two-dimensional NMR spectroscopy of ^{2}H and ^{1}H has been used intensively in the past decade to measure the dipolar correlation effect, homonuclear and heteronuclear residual dipolar couplings, and the corresponding dynamic order parameters.[8−20] Moreover, a study of diffusion of penetrant molecules in highly stretched *cis*-polyisoprene has shown that the self-diffusion coefficients (D) are essentially isotropic and elongation-independent.[21] The aim of this work is to report the existence of diffusion anisotropy of a small penetrant molecule in a compressed polymer network.

Experimental Section

Materials. A series of differently cross-linked samples from commercially available natural rubber (NR) SMR10 (Malaysia) were investigated. The additives were 3 phr (*p*arts per *h*undred *r*ubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents of the samples are given in Table 1. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-*tert*-butylsulfenamide). After mixing the compounds in a laboratory mixer at 50 °C, the samples were vulcanized at 160 °C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low-frequency shear modulus (G) or torque at a temperature of 160 °C in the vulcameter directly after vulcanization. The disk-shaped samples of natural rubber were swollen in toluene for several hours until the equilibrium value was reached.

Table 1. Properties of the Series of Cross-Linked NR Samples

sample	sulfur−accelerator content (phr)	shear modulus[a] G (dNm)	equilib toluene concn[b] c_S (%)
NR1	1−1	5.2	0.652
NR2	2−2	8.5	0.671
NR3	3−3	11.2	0.678
NR4	4−4	13.2	0.692
NR5	5−5	14.5	0.712
NR6	6−6	15.4	0.750
NR7	7−7	16.2	0.800

[a] The uncertainties are less than 10%. [b] The uncertainties are less than 1%.

NMR Measurements. The NMR experiments were performed at a ^{1}H frequency of 200.025 MHz on a Bruker DSX-200 spectrometer. The diffusivity of toluene swollen in NR samples was measured with the pulse gradient stimulated echo (PGSE) method at the temperature of 293 K.[2,3] The 90° pulse length was 13.5 μs and the recycle delays 1 s. The maximum strength and duration of the gradient pulses were 0.474 T/m and 1 ms, respectively. The gradient strength was changed in 64 equidistant steps. Diffusivities of toluene molecules were measured for two gradient orientations parallel (z direction) and perpendicular (x direction) to the static magnetic field. The proton signal from elastomer will give a constant contribution the amplitude of the stimulated echo that was taken into account in the data processing. The uniaxial compression was applied parallel to the z direction.

Results and Discussion

The normalized intensity $E(q)/E(0)$ of the stimulated echo is a decay function of the reciprocal space vector $q = \gamma G\delta/2\pi$, where γ is the magnetogyric ratio, G is the gradient strength, and δ is the duration of the pulsed gradient. These decays shown in Figure 1 were measured for toluene swollen at equilibrium in uniaxially compressed NR4 (cf. Table 1) for a compression ratio $\lambda \approx 0.43$, a diffusion time $\Delta = 1$ s, and two orientations of the magnetic field gradient. A diffusion anisotropy is observed. The stimulated echo decays for the x and z gradient orientations depend on the cross-link density, as shown in Figure 2. The measurements made on a cross-linked natural rubber sample as a function of the toluene concentrations show that for a fixed λ the

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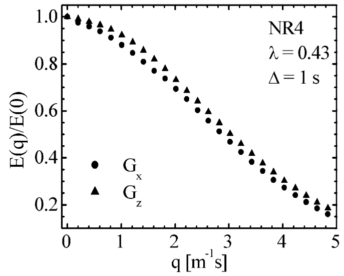

Figure 1. Normalized amplitude of stimulated echo decays of toluene in NR4 for a diffusion time of $\Delta = 1$ s and uniaxial compression by $\lambda \approx 0.43$. The diffusion measurements were made with G_x and G_z gradients of the same strength.

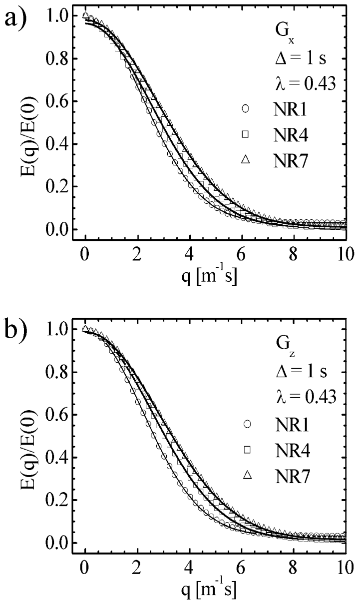

Figure 2. Normalized amplitudes of stimulated echo decays measured for the natural rubber samples NR1, NR4, and NR7 (cf. Table 1) for a diffusion time of $\Delta = 1$ s. The diffusion measurements were made on the samples swollen in toluene using G_x (a) and G_z (b) gradients under uniaxial compression along the z direction and $\lambda \approx 0.43$. The data points were fitted with a Stejskal–Tanner decay function plus a constant.

diffusion anisotropy is at its maximum for the equilibrium concentration. Therefore, we shall compare the samples with different values of cross-link densities for the equilibrium concentration of toluene.

The effective diffusion tensor components, i.e., D_{ii} ($i = x, z$), can be obtained from the fits of the stimulated echo data shown in Figures 1 and 2. These data were fitted with an exponential function in q^2 plus a constant (cf. solid lines in Figure 2).[1–3] This constant takes into account the presence of elastomer protons and has a small value of the order of few percentages from the maximum amplitude of stimulated echo. The dependence of the diffusivities D_{xx} and D_{zz} on the equilibrium concentrations c_s of toluene in the NR samples of a cross-link series is shown in Figure 3a. It is evident that the anisotropy of the effective diffusivity defined by $a_D = (D_{xx} - D_{zz})/D_{\mathrm{iso}}$, where the isotropic value is $D_{\mathrm{iso}} = (2D_{xx} + D_{zz})/3$, increases with the cross-link density (see Figure 3b). The dependence of diffusion anisotropy a_D on the compression ratio λ is shown in Figure 3c for the sample NR4. The anisotropy increases about 6 times when the compression ratio is changed by 50%.

The dependence of D_{ii} ($i = x, z$) on the diffusion time Δ measured for the sample NR4 shows an anomalous dependence in the range from 0.1 to 0.5 s. The time dependence of the effective diffusion coefficients is given by $D_{xx} \propto \Delta^{k_{xx}-1}$ and $D_{zz} \propto \Delta^{k_{zz}-1}$, where $k_{xx} \cong 0.95 \pm 0.02$ and $k_{zz} \cong 0.94 \pm 0.01$. Therefore, within the accuracy of our experiment the fractal structure of the polymer network is not detected to become essentially anisotropic under deformation. Moreover, the diffusion coefficients show a weak dependence on Δ in the range from 0.5 to 1.5 s. A more detailed investigation of this matter will be conducted in the future.

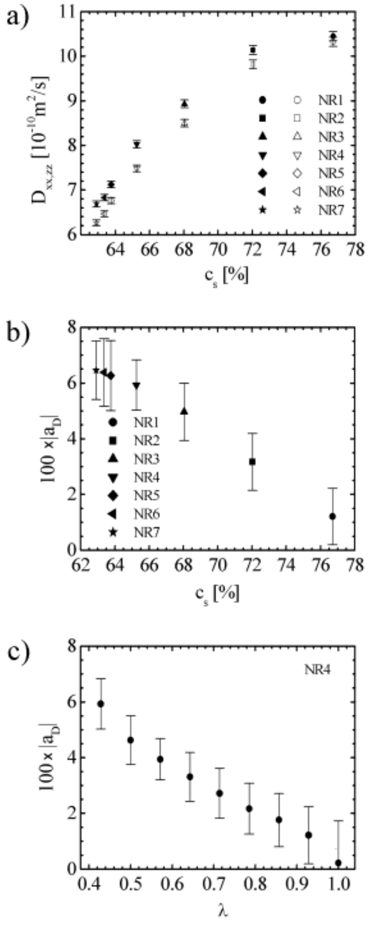

Figure 3. (a) Effective diffusivities D_{xx} (closed symbols) and D_{zz} (open symbols) of toluene vs the solvent equilibrium concentration c_s for the NR samples of Table 1. (b) The diffusion tensor anisotropy $|a_D|$ as a function of c_s. The compression force was applied along the z direction parallel to the static magnetic field, and the compression ratio was $\lambda \approx 0.43$. (c) The anisotropy $|a_D|$ as a function of λ.

The displacement probabilities or propagators[1–3] of toluene molecules diffusing in the uniaxially compressed samples NR1, NR4, and NR7 were obtained for $\Delta = 1$ s and $\lambda \approx 0.43$ after Fourier transformation of the Gaussian decays shown by the fitted lines in Figure 2a (Figure 4a). The anisotropy of the propagators is investigated by the data shown in Figure 4b for sample NR4 and compared with the propagator measured for the sample at rest. For all the cases the shape of the propagators is given by a Gaussian function as a consequence of the Gaussian stimulated echo decays (cf. Figure 2). This is consistent with other cases of self-diffusion.[4]

Conclusions

A small diffusion anisotropy of the order of 10% was detected for toluene molecules in cross-linked natural

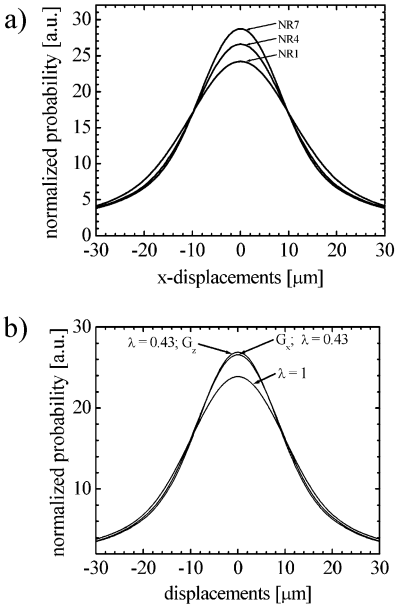

Figure 4. (a) Displacement probabilities of toluene in the natural rubber samples of Table 1 under uniaxial compression for $\lambda \approx 0.43$ measured in the x direction, orthogonal to the direction of compression. (b) Displacement probabilities of toluene in NR4 for uniaxial compression ($\lambda \approx 0.43$) and $\lambda = 1$.

rubber samples. This mainly reflects the deformation of the free volume under the compression. The anisotropy increases with the cross-link density and compression ratio. This quantity remains approximately constant for the range of diffusion times investigated. The diffusivity is isotropic for the solvent concentration much lower than the equilibrium value in agreement with previously reported data (ref 21). A quantitative interpretation of the diffusivities is complicated by a complex strain distribution in the sample. Rodlike solvent molecules in the polymer network are likely to enhance the diffusion anisotropy. Work along this line is in progress.

Acknowledgment. This work was supported by a grant from Deutsche Forschungsgemeinschaft (DE 780/1-1). The authors are also grateful to Dr. B. Jagadeesh, Dr. V. M. Litvinov, DSM, and H. Kühn for helpful discussions and to Dr. K. Unseld and Dr. V. Hermann, Dunlop GmbH, Hanau, for providing the samples.

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