Macromolecules 1991, *24*, 1269–1274

Small-Angle Neutron-Scattering Investigation of a Multilinked Polybutadiene Network Cross-Linked in Solution

W. Pyckhout-Hintzen and T. Springer*

Institut für Festkörperforschung des Forschungszentrums Jülich GmbH, D-5170 Jülich, West Germany

F. Forster and W. Gronski

Institut für Makromolekulare Chemie der Universität Freiburg, D-7800 Freiburg, Germany

C. Frischkorn

Institut für Chemie 4 des Forschungszentrums Jülich GmbH, D-5170 Jülich, West Germany

Received May 4, 1990; Revised Manuscript Received August 28, 1990

ABSTRACT: Polybutadiene chemically cross-linked in solution and containing an admixture of deuterated (labeled) molecules has been investigated by small-angle neutron scattering (SANS). The chains exhibit the same dimensions (radius of gyration) in the dry network as in the melt. The structure factor was measured as a function of elongation $\alpha = L/L_0$ up to 2. The radius of gyration, R_g, obtained from Zimm plots as a function of α was compared with the theoretical predictions of the scattering theory of Ullman for a multilinked deuterium-labeled molecule. The number of cross-links per chain, neglecting loops, was determined from these results to be 4 ± 1 for a chain with M_c = 13 150 ± 3500 g/mol. From the efficiency of the cross-linking reaction, as determined from SANS, it is shown that a large fraction of small loops is present, which do not affect the radius of gyration of primary chains.

1. General Outline

The conformation of a cross-linked chain in a deformed network has been studied in terms of several macroscopic models, such as the junction–affine model by Kuhn[1] and the phantom network model as developed by James and Guth.[2,3] More recent theories by Flory[4] and Flory and Erman[5-7] try to bridge both models by allowing for restrictions or by suppression of the cross-link fluctuations in the phantom network. Apart from macroscopic tests of such networks by means of mechanical analysis (e.g., ref 8), small-angle scattering of neutrons (SANS) became a powerful tool to observe the deformation of cross-linked chains directly on a molecular scale: By replacing a fraction of the polymers by deuterium-labeled material, the static structure factor $S(Q)$ at small scattering vectors Q yields information on the chain conformation as a function of the applied strain $\alpha = L/L_0$. More recently, also the cross-link motion and its fluctuation amplitude have been investigated by means of the neutron spin–echo technique.[9] SANS investigations on deformed networks have already been carried out in the past on poly(dimethylsiloxane)[10] and polybutadiene.[11] These experiments were performed on networks consisting of independent and deuterium-labeled sections *between* the cross-links, and the mean end-to-end distance in this "end-linked" case was determined as a function of strain. On the other hand, for polystyrene,[12,13] labeled chains *multilinked* by radiation were investigated, which yields the radius of gyration of a k-fold-linked and labeled molecule. Our study is of this kind and refers to a chemically multilinked network of polybutadiene. Ten percent of the chains were perdeuterated for labeling (see section 2).

The cross-linking reaction used in this study is exhaustive and leads to four-functional cross-links. This type of reaction has first been applied to cross-linking of polybutadiene in semidilute solution[14] and later extended to cross-linking at any concentration.[15] In the latter case the cross-linking density can be determined by the amount of the cross-linking agent. Moreover, a uniform molecular weight of the chains prior to cross-linking is ensured by anionic polymerization. Both features have allowed the comparison of known structural parameters of the network to the elastic properties[16] and to the change of chain dimensions during deformation by SANS. In the present paper, however, SANS is applied to a network cross-linked in semidilute solution. This leads to a large fraction of "wasted cross-links" through formation of intramolecular loops.[17] This paper aims at a description of the chain dimensions of this type of network (isotropic and strained) by SANS. Use is made of the structure factors for multilinked phantom networks, as evaluated in detail by Ullman.[18]

2. Sample Preparation: Mechanical and Small-Angle Scattering Experiments

Preparation of the Samples. The deuterated 1,3-butadiene-d_6 monomer was prepared according to Craig and Fowler[19] by the reductive dechlorination of the hexachloro derivative using zinc dust and deuterium oxide (D_2O). Stabilization of the d_6 monomer was achieved by a reaction with sulfur dioxide, forming the sulfone.

Undeuterated and perdeuterated 1,4-polybutadiene was synthesized by anionic polymerization in cyclohexane with *sec*-butyllithium as initiator. The characterization of molecular weights (Table I) was carried out by GPC using the correction factor of 0.57 for 1,4-polybutadienes with respect to calibration with polystyrene standards.[20] The cross-linking was performed in solution by means of the dienophilic cross-linking agent 4,4-methylenebis(1,4-phenylene)bis-1,2,4-triazoline-3,5-dione (BPMTD) synthesized according to literature procedures.[21] About 3.5 g of polymer containing the appropriate weight percent of PB-h_6 and PB-d_6 polybutadiene was dissolved in 60 mL of dry THF. A predetermined amount of the cross-linking agent dissolved in the same solvent was added to the polymer solution under fast stirring. For the network investigated under strain the amount was 1 mol % of the double bonds. The polymer volume fraction during cross-linking was $v_{2c} = 0.06$. The reaction mixture was poured out into a spin-casting device where the reaction ran to completion. After evaporation of the solvent a film of ca. 1-mm thickness was obtained. The cross-linking reaction leads to four-functional cross-links.

0024-9297/91/2224-1269$02.50/0

Table I
Sample Characterization by GPC

sample polymer	M_n	M_w	M_z	$U = (M_w/M_n) - 1$
PB-h_6[a]	234 000	301 900	369 700	0.29
PB-d_6	70 800	75 900	80 700	0.07

[a] PB-h_6: for the melt samples; M_w = 82 300, M_n = 76 950, M_z = 86 960, U = 0.06.

The mixtures of PB-d_6/PB-h_6 melts were first dissolved in dry THF and transferred into a Nb container. Then the solvent was evaporated off in a vacuum oven. To achieve uniformity and to reduce microbubbles, the melt was heated up to 40 °C, prior to sealing the container with inert atmosphere, having about 1-mm thickness. The experiments were carried out on samples with a volume fraction of deuterated polybutadiene ϕ_D ranging from 0.01 to 0.1. Table I summarizes the polymerization degree of the samples.

Mechanical Measurements. Stress–strain measurements were carried out with an Instron 1122 tensile testing machine on 5 × 40 mm^2 strips cut from the films; these were obtained from spin casting for the ϕ_D (0.1) sample. The strain rate was 2 mm/min. No strain rate dependence was observed in the range between 1.0 and 10.0 mm/min. The modulus in the limit of low strain was determined to be $G = 0.37 \pm 0.01$ N/mm^2. From the Mooney–Rivlin representation of the reduced stress,[22] the following values of the Mooney–Rivlin constants were obtained: $2C_1 = 0.14 \pm 0.01$ N/mm^2 and $2C_2 = 0.38 \pm 0.01$ N/mm^2.

Small-Angle Neutron-Scattering Experiment. The SANS experiments were mainly performed on the new KWS1 instrument at the FRJ-2 in the KFA Jülich. The wavelength of the incident neutrons was λ_N = 5.69 Å, and the wavelength spread was $\Delta\lambda_N/\lambda_N \simeq 18\%$. The wavevector range ($Q \cong 2\pi\theta/\lambda_N$, θ = scattering angle) obtained from detector positions at 2, 8, and 20 m from the sample varied from 0.003 to 0.14 Å^{-1}. Data, obtained from different positions and independently calibrated, agree in the overlapping regions within better than 1%. Two crossed BF$_3$ countertubes were arranged perpendicular and parallel to the imposed strain axis of the sample. The channel width was about 0.75 cm. The scattering of the molten samples before cross-linking was investigated at the twin instrument KWS2 with λ_N = 7 Å and a position-sensitive two-dimensional He-3 detector. The channel width was 0.86 cm. The data were radially averaged and processed in the same way as those for KWS1. Intensities were obtained between Q = 0.01 and 0.1 Å^{-1}. The beam apertures were 10 × 10 mm^2 for the instrument KWS1 and 8 × 8 mm^2 for KWS2. The polymer films were strained in an aluminum frame. The strain $\alpha = L/L_0$ was determined from small dots on the sample with an accuracy of 5%. For the strained samples, affinity in the macroscopic deformation was assumed. Effects of biaxial deformation and of clamping were reduced by scattering only on the center part of the strips.

3. General Scattering Theory

The scattering from deuterated chains (index D) in a nondeuterated network (index H) is given by[23]

$$\frac{1}{S(Q)} = \frac{1}{S_D(QR_{gD})} + \frac{1}{S_H(QR_{gH})} - \frac{2\chi}{\Omega_0} \tag{1}$$

S_D and S_H are the structure factors for isolated chains given by Debye where $S_{D,H}(Q) = \varphi_{D,H}V_{wD,H}g(x)$. In this function, V_w is the weight-average molar volume and $g(x) = 2(\exp(-x) - 1 + x)/x^2$ with $x = Q^2R_g^2$. R_g is the mean radius of gyration. χ is the Flory–Huggins interaction parameter for the isotopic [^{1}H]- and [^{2}H]-polybutadiene mixture to be discussed in section 4. Ω_0 is the molecular volume. For small Q the structure factors can be approximated by the so-called Zimm representation, namely

$$\frac{1}{S(Q)} = \frac{1 + V_z^{\,D}\frac{\sigma^2}{\Omega_0}\frac{Q^2}{18}}{\varphi_D V_w^{\,D}} + \frac{1 + V_z^{\,H}\frac{\sigma^2}{\Omega_0}\frac{Q^2}{18}}{(1-\varphi_D)V_w^{\,H}} - \frac{2\chi}{\Omega_0} \tag{2}$$

Here we introduced $R_{gz}^{\;2} = N_z\sigma^2/6 = (V_z/\Omega_0)\sigma^2/6$ where V_z and Ω_0 are the molar volume of the chain and of the monomer.

Reorganizing terms leads to

$$\frac{1}{S(Q)} = \frac{1}{\varphi_D V_w^{\,D}} + \frac{1}{(1-\varphi_D)V_w^{\,H}} + \frac{1}{18}\frac{\sigma^2}{\Omega_0}\left[\frac{V_z^{\,D}}{\varphi_D V_w^{\,D}} + \frac{V_z^{\,H}}{(1-\varphi_D)V_w^{\,H}}\right]Q^2 - \frac{2\chi}{\Omega_0} \tag{3}$$

The difference in molecular weights for the deuterated and nondeuterated species is introduced by

$$V_w^{\,H} = V_w^{\,D}(1 + w) \quad \text{and} \quad V_z^{\,H} = V_z^{\,D}(1 + z) \tag{4}$$

This yields

$$\frac{1}{S(Q)} = \frac{1 - (\varphi_D w/1 + w)}{V_w^{\,D}\varphi_D(1-\varphi_D)}\left(1 + \frac{1}{18}\frac{\sigma^2}{\Omega_0}Q^2[1 + \varphi_D\, z/1 + w]\right) - \frac{2\chi}{\Omega_0} \tag{5}$$

The term in the square brackets is near unity. The interaction parameter χ/Ω_0 is only known for un-cross-linked blends[24-27] but not for a cross-linked system, and the choice of χ influences the resulting molecular weight (see section 4).

Absolute values for the cross sections per unit volume can be calculated from

$$\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega = (\Delta\rho^2/N_L)S(Q) \tag{6}$$

where $\Delta\rho^2$ is the contrast factor per unit volume

$$\Delta\rho^2 = n^2N_L^2(b_H - b_D)^2/\Omega_0^{\,2} \tag{7}$$

b_H and b_D are the nuclear coherent scattering lengths for hydrogen and deuterium and n is the number of exchanged hydrogen atoms per monomer. The absolute values for the cross sections per unit volume are experimentally derived from the measured neutron scattering intensity I^S by calibration to the incoherent scattering from a secondary Lupolen standard.[28]

$$\mathrm{d}\Sigma^S(Q)/\mathrm{d}\Omega = [T^LD^L(\mathrm{d}\Sigma^L/\mathrm{d}\Omega)A^L(R^S)^2/T^SD^SI^LA^S(R^L)^2](I^S - T^SB^S) \tag{8}$$

L and S refer to Lupolen standard and sample, D and T stand for thickness and transmission, respectively. A is the illuminated sample area, and R is the sample-to-detector distance. I are the intensities and B is the experimental background. The value of $T^LD^L(\mathrm{d}\Sigma^L/\mathrm{d}\Omega)$ for the Lupolen standard has been calibrated with vanadium to be $(7.34 \pm 0.03) \times 10^{-2}$.

The incoherent cross sections per solid angle and per unit volume for the two protonated samples ($\varphi_D = 0$) were independently obtained, again following the Lupolen calibration as in eq 8. An eventual error due to a different multiple scattering of the deuterated and blank sample is small since the contribution I(single)/I(single + total multiple) = $\Sigma_{inc}D\exp(-\Sigma_{inc}D)/[1 - \exp(-\Sigma_{inc}D)]$ is 15%, such that the resulting error is only a few percent.

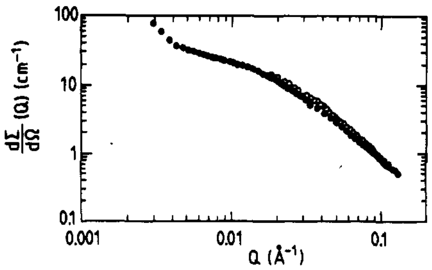

Figure 1. Neutron-scattering intensity (absolute units) for polybutadiene in double-logarithmic scale for the $\phi(0.093)$ melt (open symbols ○) and the $\phi(0.1)$ network (closed symbols ●).

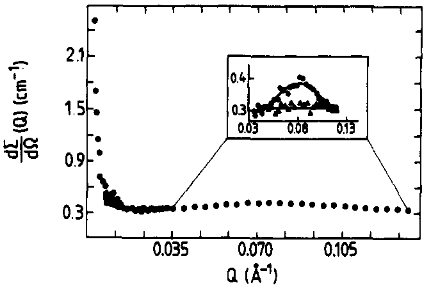

Figure 2. Neutron-scattering intensity for unlabeled samples as a function of Q: cross-linked (●), molten and un-cross-linked sample (▲) (insert). The large forward scattering may arise from inhomogeneities included during preparation.

The coherent part of the intensity scattered by the labeled sample is given by

$$d\Sigma^{\mathrm{coh,D}}(Q)/d\Omega = d\Sigma^{\mathrm{S}}(Q)/d\Omega - (1-\varphi_{\mathrm{D}})d\Sigma^{\mathrm{H}}(Q)/d\Omega \quad (9)$$

and plotted in a double-logarithmic scale in Figure 1 for a melt showing Gaussian statistics for the chains, whereas for the network excluded-volume effects affect the scattering on larger Q.

The Zimm approximation reads in a simplified form for $\chi = 0$

$$S(Q)^{-1} = S(0)^{-1}\,[1 + Q^2 R_{az}{}^2/3] \quad (10)$$

From the intercept at $Q = 0$, one extracts the molecular weight of the molecule. The slope of $d\Sigma/d\Omega(Q)^{-1}$ or $S(Q)^{-1}$ vs Q^2 yields the apparent radius of gyration R_{az}, which is converted to R_{gz} by the square bracket in eq 5. For deformed coils, the radii of gyration are determined in the same way from the anisotropic intensities in parallel and perpendicular direction to the strain axis. In the Zimm approximations, this leads to $R_a{}^{\parallel}$ or $R_a{}^{\perp}$ instead of R_g.[29,30]

4. Experimental Results

The cross sections $d\Sigma(Q)/d\Omega$ have to be corrected for the incoherent cross section $d\Sigma^{\mathrm{H}}(Q)/d\Omega$. The scattering from a cross-linked matrix sample (Figure 2), consisting of only unlabeled chains, shows, however, a weak peak that may result from nonhomogeneous cross-linking. On the other hand, the signal of a molten sample in the un-cross-linked state is perfectly flat. Consequently, the incoherent contribution in the networks under investigation was calculated from the molten sample, properly weighted by the fraction of the nondeuterated chains.

In Figures 3 and 4, Zimm plots for both orientations are shown as a function of strain α, imposed on the network with $\varphi_{\mathrm{D}} = 0.1$. From the slope we derive the apparent radii of gyration $R_a{}^{\parallel}$ and $R_a{}^{\perp}$ (see eqs 5 and 10). The sharp downturn of the inverse scattered intensity at the lowest Q may be caused by "parasitic scattering", e.g., from frozen-in density fluctuations with a long range of the order of 500–1000 Å, probably formed during solvent evaporation after cross-linking. This effect was also found for the cross-linked protonated sample. We do not know conclusively the origin of this scattering. The scattering by the D-labeled polymers at larger Q corresponds to a length scale of the gyration radius being a factor 10 smaller. Consequently, the fluctuations and the labeled-molecule contribution are well separated, and the slope of the Zimm plot is not influenced.

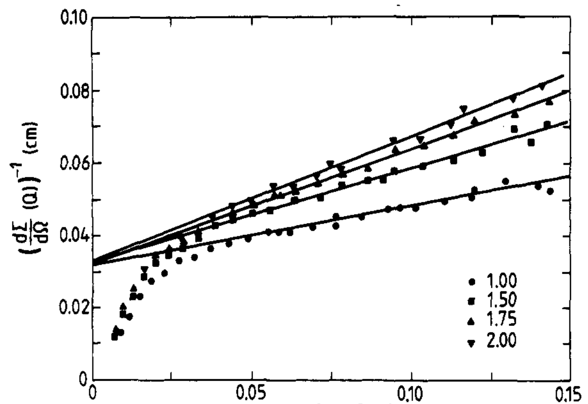

Figure 3. Inverse neutron-scattering cross sections $(d\Sigma(Q)/d\Omega)^{-1}$ as a Zimm plot for the scattering vector Q parallel to the drawing axis of the samples, for different elongations $\alpha = L/L_0$. The extrapolated value for $Q = 0$ yields the molecular weight. The strong decrease for small Q is probably caused by frozen-in and long-range density fluctuations.

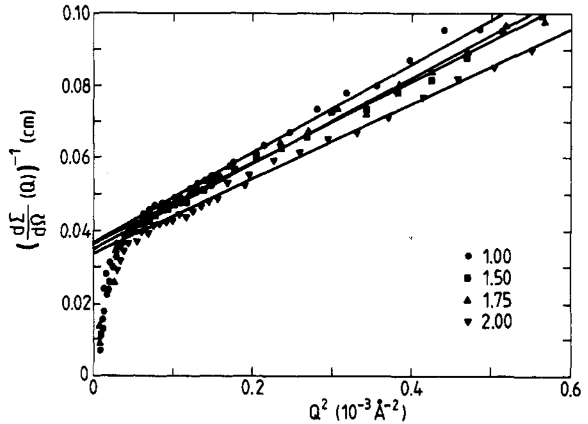

Figure 4. Zimm plot $d\Sigma(Q)/d\Omega^{-1}$ with Q perpendicular to the drawing direction, for different values of α.

The intercepts from the linearly extrapolated fitted curves for various α at $Q = 0$ all coincide within statistical error. This is also an indication of the consistency of the data. The resulting molecular weight was derived from eq 5 to be 68 000 ± 7000 g/mol, putting $\chi = 0$. The values differ slightly from the GPC values (see Table I). The discrepancies may mainly result from systematic errors in the absolute calibration (~5%) and from the calibration of GPC on polystyrene standards (~10%).[20] All data are summarized in Table II. A nonzero value of the unknown interaction parameter χ would lower the resulting molecular weight M_w. For an order of magnitude judgement we take the experimental value of Bates et al.[24-26] for the PB–dPB system at $\varphi_{\mathrm{D}} = 0.3$–$0.65$, being $\chi/\Omega_0 = 0.130 \times 10^{-4}$ mol/cm³. With half of this value we stay still in the quoted errors of M_w. The values of M_w (Table II) for four different φ_{D} values from 0.8 to 10% do not indicate any trend that could be attributed to a concentration-dependent χ.[27]

In addition, the scatterings from an isotropic network with $\varphi_{\mathrm{D}} = 0.05$ and of melts with $\varphi_{\mathrm{D}} \simeq 0.01$ and 0.093 were

Table II
Root-Mean-Square Radii of Gyration by SANS for the Investigated Samples[a]

sample	R_{ga}	R_{gz}	R_{gw}	M_w(Zimm)
0.8‰D	114 ± 7	114 ± 7	110 ± 7	67 000 ± 11000
9.3%D	112 ± 6	112 ± 6	109 ± 6	68 300 ± 8000
5.0%D	112 ± 10	110 ± 10	107 ± 9	79 000 ± 6000
10.0%D	108 ± 4	104 ± 4	101 ± 4	66 800 ± 7000
$\langle R_{ga}\rangle = 111 \pm 3$ Å				$\bar{M}_w = 70\,300 \pm 7000$
$\langle R_{gz}\rangle = 110 \pm 5$ Å				$\bar{M}_n = 65\,700 \pm 7000$
$\langle R_{gw}\rangle = 107 \pm 5$ Å				

[a] R_{ga} are obtained from the Zimm plots, R_{gw} and R_{gz} are calculated by using eqs 5 and 11. The molecular weight is M_w as obtained from SANS by independent calibration, setting $\chi = 0$.

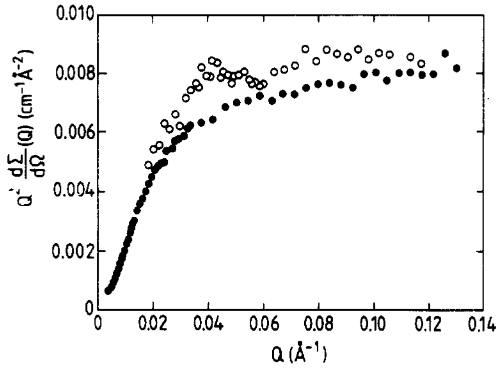

Figure 5. Kratky plot for the $\phi(0.1)$ network (●) and the uncross-linked $\phi(0.093)$ melt (○).

investigated. These lead independently to the same average molecular weight ($M_w = 70\,300$ g/mol, $M_n = 65\,700$ g/mol). The Zimm values for the radii of gyration vary only slightly with D-content and were averaged to give a mean apparent value $\langle R_a\rangle = 111 \pm 3$ Å, corresponding to $\langle R_{gz}\rangle = 110 \pm 5$ Å for the labeled chains only. The average R_{gz} is converted to the weight-average R_{gw} using the polydispersity correction[31]

$$R_{gw}^{\ 2} = \left(\frac{U+1}{2U+1}\right)R_{gz}^{\ 2} \tag{11}$$

for which we find (with $U = 0.07$) $R_{gw} = 107 \pm 5$ Å. Very good agreement is obtained with the relationship as proposed for polybutadiene by Fernandez;[32] namely $R_{gw} = 0.39 \pm 0.02\ (M_w)^{1/2}$ with M_w taken from GPC or SANS. The square-root dependence on M should only be valid for the melt sample with Gaussian statistics (Figure 1). However, no striking difference between the melt dimension with $R_g = 109 \pm 6$ Å and the dimension of the chain in the dry network with $R_g = 104 \pm 6$ Å has been found within a few percent.

From its ratio being 0.95 ± 0.05, the so-called memory term $\langle r^2\rangle/\langle r^2\rangle_0$ is estimated to be 0.92 ± 0.07. In order to check the consistency of our results, we have also evaluated the Kuhn segment length σ for both states. This is found from the second moment of the intensity (Figure 5), in the limit for high Q,

$$[\mathrm{d}\Sigma(Q)/\mathrm{d}\Omega]Q^2N_L/\Delta\rho^2 = 12\varphi_D(1-\varphi_D)\Omega_0/\sigma^2 \tag{12}$$

Ω_0 is the monomer volume (centimeters cubed per mole). For the networks with $\varphi_D = 0.05$ and 0.1, we determined $\sigma = 7.1 \pm 0.2$ and 6.9 ± 0.2 Å despite a slight nonideal Gaussian chain on the monomer level, whereas the $\varphi(0.1)$ melt gave $\sigma = 6.8 \pm 0.3$ Å with the expected Q^{-2} behavior. Again, this agrees well with small-angle scattering data by Wignall et al.[24] and Hasegawa.[33] The result is further confirmed by recent Monte Carlo calculations with $\sigma = 6.6$ Å.[34]

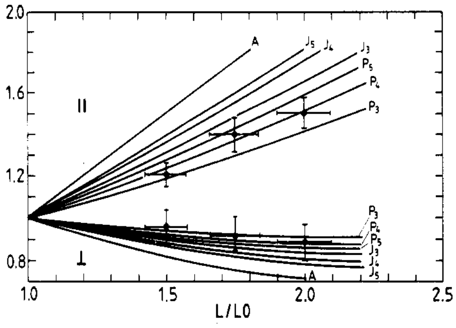

Figure 6. Radius of gyration as a function of elongation $\alpha = L/L_0$ for the scattering vector parallel and perpendicular to the drawing direction. The curves correspond to the affine model (A), the Kuhn model (J), and the phantom network theory (P). The subscript is the number of cross-links per deuterated molecule. The best fit is obtained for $k = 4 \pm 1$.

In Figure 6 we present $R_g^{\parallel}/R_g^0$ and $R_g^{\perp}/R_g^0$ as a function of strain α, taken from the data in Figures 3 and 4. Chain dimensions are given in Table III. The measurements are compared with Ullman's calculations for networks,[18] containing k cross-links per primary labeled chain.

For the case of affine deformation of the individual segments, the ratio of the radius of gyration in the strained network $R_g^{\parallel}$ to that in the undeformed network is then given by model "A" with

$$(R_g^{\parallel}/R_g^{0})^2 = \alpha^2 \tag{13}$$

If only cross-links are allowed to deform in an affine way, neglecting entanglements, Ullman ended up with the expression for cross-link–affine deformation (Kuhn model "J")

$$(R_g^{\parallel}/R_g^{0})^2 = 1 + [(\alpha^2-1)/2(k+1)^3][(k-1)(2k^2+6k+1)] \tag{14}$$

For a phantom network, which allows for fluctuating motion of cross-links and which deforms affinely in the mean position of the cross-links, one gets (phantom model "P")

$$(R_g^{\parallel}/R_g^{0})^2 = 1 + (\alpha^2-1)F(k,f) \tag{15}$$

$F(k,f)$ is a function of the network functionality f and the number of cross-links k and is quoted in ref 18. The perpendicular component is obtained by replacing α by its counterpart $1/\sqrt{\alpha}$. The theoretical curves in Figure 6 refer to these three models for different values of k. The experimental results can be readily explained by the phantom network model with $k = 4 \pm 1$. Table III also quotes the product $\alpha_{\parallel}\alpha_{\perp}^2$. In a purely affine deformation and volume conservation, one would expect 1. The tendency to have preferential elongational strain, as calculated from Ullman, is also found experimentally ($\alpha^{\parallel} > 1/\alpha^{\perp 2}$). From the estimated number of k and the molecular weight of the labeled chains prior to cross-linking, the average molecular weight M_c of the sections between cross-links is calculated from the relation $M_c = M_n/(k+1)$, yielding 13 200 ± 3500 g/mol.

5. Discussion

The results of the SANS measurements are to be discussed in light of the chemistry of cross-linking in solution, the resulting topology of the network, and its relation to the stress–strain behavior. Using the scattering theory of Ullman, our results can be interpreted by $k = 4$, this means 4 cross-links/chain on the average. This number can now be compared with the value that is expected from the concentration of the cross-link agent.

Table III
Results Obtained at Low Q Compared to the Phantom Model by Ullman for a Tetrafunctional Network and 4 Cross-Links/Chain[a]

α	$R_{ga}^{\parallel}$	$R_{ga}^{\perp}$	$R_g^{\parallel}/R_g$ exptl	$R_g^{\perp}/R_g$ exptl	$R_g^{\parallel}/R_g$ theor	$R_g^{\perp}/R_g$ theor	$\alpha^{\parallel}\alpha^{\perp 2}$ exptl	$\alpha^{\parallel}\alpha^{\perp 2}$ theor
1.00	110 ± 3	106 ± 6						
1.50 ± 0.07	133 ± 5	102 ± 6	1.21 ± 0.06	0.96 ± 0.08	1.24	0.93	1.11 ± 0.10	1.07
1.75 ± 0.09	154 ± 6	97 ± 5	1.40 ± 0.07	0.92 ± 0.07	1.37	0.90	1.18 ± 0.10	1.11
2.00 ± 0.10	165 ± 7	94 ± 7	1.50 ± 0.07	0.89 ± 0.08	1.51	0.89	1.19 ± 0.11	1.19

[a] The radii of gyration are of the R_{ga} type.

Taking the experimental concentration of 10^{-2} molecules of the bifunctional cross-linking agent per number of monomer units, the effectivity of the cross-linking reaction is calculated as $\eta = k/(2 \times 10^{-2}M_n/M_0)$ where M_0 is the molecular weight of the monomer. With the average value of M_n from SANS or GPC and $k = 4$, one gets only $\eta = 0.18 \pm 0.02$ or 0.16 ± 0.02, respectively, indicating that the number of cross-links, calculated from the cross-linker concentration is considerably larger than 4. Assuming that each agent creates one cross-link, we conclude that loops are formed by self-linking. Diffusion experiments by means of quasi-elastic light scattering and photon correlation spectroscopy[35] have shown that even for a high degree of cross-linking the radius of gyration R_g is very close to its unperturbed value. This means that loops are being formed and that these loops are rather small. Recent unpublished Monte Carlo simulations[34] of the cross-linking process over a broad range of polymer concentration (from semidilute solution to the bulk) corroborate the observed high fraction of "inactive" cross-links (ca. 70% for $v_2 = 0.06$ and $M_n = 10^5$ g/mol). An even smaller efficiency of about 10% is obtained if mutually cross-linked loops and entangled loops would not contribute to the active cross-linking. The calculations also show that the weight fraction of loops is only ca. 25%. This confirms that small loops were formed preferentially. The number-average weight of the loops is ca. 1100, and a loop consists of ca. 20 monomer units on average.

The observation of the practically unperturbed dimension of R_g in the dry network has also another aspect. It concerns the change of chain dimensions during the removal of the solvent from the solution in which cross-linking took place. In the theory of rubber elasticity, the change of the dimensions of network chains between cross-links, occurring when passing from the state of cross-linking to the dry state, is generally described by the memory factor[36]

$$h^{2/3} = \langle r^2 \rangle / \langle r_0^{\,2} \rangle \tag{16}$$

where $\langle r^2 \rangle$ is the mean-square end-to-end distance of the network chains in the dry state, and $\langle r_0^2 \rangle$ is the mean-square end-to-end distance of the free chains in the unperturbed state considered as reference state. Usually, it is assumed that the mean-square dimensions change affinely, corresponding to the volume change during the removal of solvent.[37] In this case, h is equal to the volume fraction of the polymer, v_{2c}, during cross-linking. In the present case of cross-linking in semidilute solution, $v_{2c}^{2/3} = 0.16$; i.e., the assumption of affine deformation would imply a large degree of "supercoiling" of the network chains in the dry state. The SANS result, however, shows that the labeled primary chains consisting of 5 elementary chains on average have approximately unperturbed dimensions. This result cannot be explained if the network chains would exhibit strong deviations from Gaussian statistics as in the affine model. The SANS result rather indicates that the network chains are in the unperturbed state; i.e., the memory term in eq 16 is close to 1.0.

In section 4 Ullman's theory for multilinked linear chains was used to interpret the topology of the strained network. This may be criticized because of the presence of loops. The basic assumption in evaluating the structure factor is the validity of the Gaussian chain statistics. At the given cross-link concentration of 1% and the estimated effectiveness of 18%, 20 cross-link molecules are wasted during network generation. Each of the 5 subchains contain then 20/5 = 4 loops on average. Considering that the majority of loops are of small size, the assumption of Gaussian statistics for the "backbone chain" carrying the loops remains approximately correct in the present case. A significant deviation from the Gaussian behavior of linear chains would appear by a considerable deviation of the radius of gyration from the free chain in the dry network. As already stated, this is not the case.

The SANS data were explained for a phantom network. This is characterized by fluctuating cross-links and an underaffine deformation of the sections. From the M_c value of these active network chains, excluding loops, the shear modulus can be calculated and compared with the experimental value. According to the classical theories of rubber elasticity, the modulus in the limit of small strains is

$$G = \mathcal{F}\rho RT/M_c \tag{17}$$

where $\mathcal{F}$ is 1.0 for the "affine network" and 0.5 for the tetrafunctional "phantom network".[8,37] According to the junction–constraint model of Flory–Erman theory, these two cases are the upper and lower limits for different degrees of suppressing the cross-link motion. By virtue of the high molecular weight of the majority of chains, the correction due to chain ends[38,39] can be neglected in eq 17. With the M_c value from SANS one finds then $G = 0.19$ N/mm^2 for the affine network and $G = 0.095$ N/mm^2 for the phantom network. Our experimental value of 0.37 N/mm^2 is considerably greater.

It is often argued that the mechanical modulus is overestimated because of nonequilibrium. At least in the time scale of our measurements with different strain velocities, no differences were observed. This does not exclude the presence of very long relaxation times, however. The larger experimental modulus can also be explained by entanglements that do not contribute explicitly to the modulus calculated from the Flory–Erman theory. In fact, due to the low entanglement molecular weight in 1,4-polybutadiene (ca. 2000[40]), the contribution of entanglements will be particularly pronounced. This has been shown for polybutadiene networks randomly cross-linked in bulk[6] and in solution.[17] In the former work, it was also shown that the entanglement contribution to the phantom modulus increases with the molecular weight of the primary chains. For the molecular weight of the primary (undeuterated and deuterated) chains in the network studied in ref 16 (M_n = 180 000), the contribution of entanglements is estimated to be ca. 0.15 N/mm^2;[16] this probably overestimates the entanglement contribution in a network cross-linked in semidilute solution. On the other hand, for a network cross-linked at the same polymer concentration, and with similar molecular weight of primary chains, the entanglement contribution to the Mooney–Rivlin constant $2C_1$ was 0.05 N/mm^2. This must be considered as a lower limit, because the phantom modulus is always larger than $2C_1$ according to the Flory–Erman theory. Therefore, the large difference between the experimental modulus and the value determined from SANS can only partly be explained by entanglements. A better agreement with the phantom modulus calculated on the basis of the SANS measurements can be achieved if the Mooney–Rivlin constant is corrected as follows: One extrapolates $2C_1$ to zero cross-link density,[17] and the finite value may be interpreted as the entanglement contribution to $2C_1$. This can then be subtracted from the experimental value.

In our evaluation, the SANS data were interpreted in the phantom model where underaffinity is due to cross-link fluctuations. This model describes satisfactorily the deformation of elementary network chains by measuring anisotropic small-angle neutron scattering as a function of deformation[10] or the junction fluctuations as observed by spin–echo spectroscopy in end-linked PDMS networks.[9] Despite its success to account for many experimental observations, we are aware that the phantom model does not describe all features of molecular deformation in networks, e.g., the loss of affineness of very long chains in deswollen gels and deformed melts[41] and the negligible change of the radius of gyration of medium-size chains in deswollen networks as observed by other authors[6] and in our work. A qualitative explanation of the latter effect by a nonaffine-network unfolding or cross-link rearrangement was suggested by Bastide et al.[42] from measurements with very large molecules (outside the Zimm region). However, it has not led to quantitative predictions that could be applied here.

6. Summary

The main results of this work can be summarized as follows: The SANS experiments give the anisotropy of the radius of gyration as a function of sample elongation α, which leads to a number of $k = 4 \pm 1$ cross-links/molecular chain, corresponding to a molecular weight of $M_c = 13\,200 \pm 3500$ g/mol. This result is based on the validity of the phantom model. Furthermore, the experiments have shown that the radius of gyration before and after cross-linking is nearly the same; the memory factor $\langle r^2 \rangle / \langle r_0^2 \rangle$ is close to unity.

Assuming a 100% efficiency η of the cross-linking agent, the number of cross-links expected per chain is about 5 times larger than the value obtained from the SANS experiments. This leads to the conclusion that "self-linking" occurs, forming rather small loops, distributed randomly over the chains. The observation that a great number of cross-links form only small loops is supported by measurements of the self-diffusion constant of similar networks by means of light scattering.

The extrapolated shear modulus has been found to be considerably greater than the value as calculated from the number of "active" cross-links (not forming the small loops). This may only be partially due to entanglements. The presence of very long relaxation times associated with the motions of cross-links during deformation and the resulting measurement of the modulus in a nonequilibrium state may be a further reason. SANS measurements are currently being carried out on polybutadiene networks randomly cross-linked in the bulk, which presumably lead to simpler network structures.

Acknowledgment. We are grateful to D. Schwahn for his help and critical discussions and G. Pohl for his valuable technical assistance.

References and Notes

(1) Kuhn, W. *Kolloid-Z.* **1936**, *76*, 258.
(2) James, H. M. *J. Chem. Phys.* **1947**, *15*, 651.
(3) James, H. M.; Guth, E. *J. Chem. Phys.* **1947**, *15*, 669; **1953**, *21*, 1039.
(4) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(5) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363.
(6) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(7) Erman, B.; Flory, P. J. *Macromolecules* **1982**, *15*, 806.
(8) Queslel, J. P.; Mark, J. E. *Adv. Polym. Sci.* **1984**, *65*, 135.
(9) Richter, D.; Ewen, B.; Oeser, R. In *Polymer Motions in Dense Systems*; Richter, D., Springer, T., Eds.; Springer-Verlag: Berlin, 1988.
(10) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1984**, *17*, 663.
(11) Hinkley, J. A.; Han, C. C.; Mozer, B.; Yu, H. *Macromolecules* **1978**, *11*, 836.
(12) Clough, S. B.; Maconnachie, A.; Allen, G. *Macromolecules* **1980**, *13*, 774.
(13) Davidson, N. S.; Richards, R. W. *Macromolecules* **1986**, *19*, 2576.
(14) Stadler, R.; Maldaner Jacobi, M.; Gronski, W. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 129.
(15) Jacobi, M. M.; Stadler, R. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 709.
(16) Maldaner Jacobi, M.; Abetz, N.; Stadler, R.; Gronski, W., submitted for publication in *Macromolecules*.
(17) Stadler, R.; Bühler, F.; Gronski, W. *Makromol. Chem.* **1986**, *187*, 1301.
(18) Ullman, R. *Macromolecules* **1982**, *15*, 1395.
(19) Craig, D.; Fowler, R. B. *J. Org. Chem.* **1961**, *26*, 713.
(20) Tung, L. H. *J. Appl. Polym. Sci.* **1979**, *24*, 953.
(21) Cookson, R. S.; Gupte, S. S.; Stevens, J. P. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121.
(22) Mooney, M. *J. Appl. Phys.* **1940**, *11*, 582.
(23) de Gennes, P.-G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(24) Bates, F. S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev. Lett.* **1985**, *55*, 2425.
(25) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
(26) Bates, F. S.; Dierker, S. B.; Wignall, G. D. *Macromolecules* **1986**, *19*, 1938.
(27) Schwahn, D.; Hahn, K.; Streib, J.; Springer, T. *J. Chem. Phys.* **1990**, *93*, 8383.
(28) Wignall, G. D.; Bates, F. S. *J. Appl. Cryst.* **1987**, *20*, 28.
(29) Benoit, H.; Duplessix, R.; Ober, R.; Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G. *Macromolecules* **1975**, *8*, 45.
(30) Ullman, R. *J. Chem. Phys.* **1979**, *71*, 436.
(31) Brandup, J.; Immergut, E. H. In *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; p IV-310.
(32) Fernandez, A. M.; Sperling, L. H.; Wignall, G. D. *Macromolecules* **1986**, *19*, 2572.
(33) Hasegawa, H.; Tanaka, T.; Hashimoto, T.; Han, C. C. *Macromolecules* **1987**, *20*, 2120. Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Han, C. C. *Polym. Commun.* **1990**, *31*, 99.
(34) Gronski, W.; Forster, F.; Pyckhout-Hintzen, W.; Springer, T. 10th International Symposium on Polymer Networks. *Makromol Chem., Macromol. Symp.*, in press.
(35) Antonietti, M.; Sillescu, H.; Schmidt, M.; Schuch, H. *Macromolecules* **1988**, *21*, 736. See also: Martin, J. E.; Eichinger, B. E. *Macromolecules* **1983**, *16*, 1350.
(36) Candau, S.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 27.
(37) Mark, J. E.; Erman, B. In *Rubberlike Elasticity, A Molecular Primer*; John Wiley & Sons: New York, 1988.
(38) Flory, P. J. *Macromolecules* **1982**, *15*, 99.
(39) Queslel, J. P.; Mark, J. E. *J. Chem. Phys.* **1985**, *82*, 3449.
(40) Ferry, J. D. In *Viscoelastic Properties of Polymers*; John Wiley & Sons: New York, 1980.
(41) Bastide, J.; Herz, J.; Boué, F. *J. Phys. (Paris)* **1985**, *46*, 1967.
(42) Bastide, J.; Picot, C.; Candau, S. *J. Macromol. Sci., Phys. B* **1980**, *19*, 13.

Registry No. (BPMTD)(butadiene) (copolymer), 131761-22-3.