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ORIGINAL CONTRIBUTION

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Orientation relaxation of linear chains enclosed in a network studied by birefringence measurements

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Abstract The relaxation of linear poly(styrene sulfonate) chains in a swollen poly(acrylamide) network is investigated by birefringence measurements. After a stepwise deformation of the network relaxation occurs, because the linear chains are initially deformed as well, but diffuse into an isotropic conformation via the reptation mechanism. The course of the birefringence with time agrees essentially with what follows from the reptation model. It could be shown that the relaxation time varies approximately with the third power of the molar mass of the enclosed molecules when networks of sufficiently high network density are used. On the other hand, the dependence of the relaxation time on network density or degree of swelling, respectively, seems to be much stronger than what is expected from theory.

Key words Birefringence relaxation – orientation relaxation – linear chains in networks – reptation

Introduction

Topological constraints are of fundamental importance in concentrated polymer systems. In melts or solutions of linear or branched chains they markedly influence the dynamics of the macromolecules, whereas the static properties remain unaffected. In cross-linked systems (rubbers, gels) they also have a significant or even decisive influence on equilibrium properties.

A basic understanding of several experimental facts was achieved by the notion that entangled chains rearrange their conformations by reptation, i.e. curvilinear diffusion along their own contours. This model for polymer dynamics in concentrated solutions and melts was first proposed by de Gennes [1]. He assumed that chain motions in the direction perpendicular to the chain's contour are prevented by the other chains, which form kind of a tube around the chain under consideration. The average time necessary for complete rearrangement of conformation, τ, and the macroscopic diffusion coefficient, D, were shown to vary with chain length (or molar mass M) as

$$\tau \sim M^3 , \tag{1}$$

$$D \sim M^{-2} . \tag{2}$$

Equation (2) could be verified experimentally in a number of studies [2, 3].

Development of this concept by Doi and Edwards allowed them to predict a set of macroscopic, rheological properties of such systems [4]. However, these did not always agree quantitatively with experimental observations, and it was suggested that pure reptation is only one of several mechanisms responsible for relaxation phenomena. Another could be the renewal of the tube arising from the diffusion of the surrounding chains, a third one could be excursions of the chain from the tube [5].

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The "tube renewal" mechanism can only operate in liquids, but not in networks. The study of the dynamics of linear chains enclosed in a network is therefore conceptually somewhat simpler than to study melts or solutions. The system corresponds closer to the original model of a "polymer chain in an array of fixed obstacles" [6]. There are, however, less experimental approaches dealing with such systems.

Gent et al. reported on the diffusion of linear polyisoprene into polyisoprene networks measured by a macroscopic method [7]. They found $D \sim M^{-2}$ and only a very weak dependence on network density. Antonietti and Sillescu studied the self-diffusion of polystyrene chains in bulk polystyrene networks via a holographic grating technique [3]. They also verified the M^{-2}-dependence of the diffusion coefficient and found D in networks to be typically reduced by 25–35% compared with uncross-linked polystyrene. The stress-relaxation studies by Kramer et al. focussed solely on the molar mass dependence of the linear chains and left the network density out of consideration [8].

The influence of concentration on D seems to be less clear. In a careful investigation, Léger et al. showed that the self-diffusion coefficient of polystyrene in semi-dilute benzene solution varies with the inverse 1.7th power of concentration [9], in agreement with scaling arguments. For τ, a $c^{1.5}$ power law was predicted.

A direct measurement of τ was attempted by Lee and Wool, who used the relaxation of infrared dichroism to follow the orientation relaxation in uncross-linked polystyrene films [10]. They confirmed the M^{-3} dependence of τ when M was below 400 000 g/mol, but found a significantly different behavior with higher molar masses.

Concept of the present work

In this work we investigated the relaxation of linear probe chains enclosed in a swollen polymer network via birefringence measurements. When the network is deformed in a stepwise manner, the enclosed chains are initially deformed as well. The birefringence observed is the sum of two contributions: one due to the network polymer and one due to the enclosed linear chains. The contribution coming from the network will be essentially constant as long as the strain is kept constant while that of the enclosed chains decreases with time as the chains diffuse from the imposed anisotropic conformations towards their equilibrium (isotropic) state. It has to be ensured that the experiment is performed under conditions where the network does not show perceptible relaxation.

In terms of the tube model, the birefringence due to the linear chains should be proportional to the fraction $F(t)$ of chain lengths still trapped in their original tubes. This is given by [4]

$$F(t) = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp(-(2n+1)^2 t/\tau) , \quad (3)$$

where τ is the disengagement time (time necessary for complete rearrangement of conformations, Eq. (1)), and t is the time elapsed after the step-strain was imposed.

As known for many diffusion problems, some useful approximations exist for Eq. (3) [10, 11]. For short times, $t < \tau/2$, we have

$$F(t) = 1 - 4\pi^{-3/2}\sqrt{t/\tau} , \quad (3a)$$

whereas a long-time approximation is

$$F(t) = \frac{8}{\pi^2} \exp(-t/\tau) . \quad (3b)$$

It is advantageous to use a network polymer showing a small anisotropy of polarizability and to enclose linear chains having a strong anisotropy of polarizability. This enhances the sensitivity of the experiment significantly and one can keep the amount of enclosed linear material small. We incorporated linear poly(sodium styrene sulfonate) (PSS) in poly(acrylamide) networks (PAAm) in the gel state.

The aim of the study is to find out:

- whether the transient of birefringence is of the form of Eq. (3);
- how the disengagement time τ varies with the molar mass of the enclosed chains;
- how the network properties (network density, degree of swelling) affect the disengagement time.

Studying the orientation relaxation in gels has some advantages, but also poses additional problems. The structure in a gel is more open than in a dense system, hence motions are faster. The dependence of relaxation rate on concentration can be investigated over a wide concentration range. This is important because as the system becomes more dilute a crossover from reptation to Rouse-like behavior can be expected. The network density of the gel can – at least in principle – be varied independently of the degree of swelling. Thus, the influences of the concentration of the network polymer and of the concentration of cross-linkages could be separated.

Experimental

Materials

Polystyrene: Polystyrene was prepared by anionic polymerization in tetrahydrofurane using butyl-lithium as

initiator. The reaction was terminated with methanol, the polymer was precipitated by adding methanol, subsequently dried and characterized by GPC. Table 1 contains the molar mass averages thus determined of the polymer samples used.

Poly(sodium styrene sulfonate) [12]: 1.5 g of polystyrene was dissolved in 75 ml cyclohexane at 40 °C. 11 g P_4O_{10} was suspended in 50 ml sulfuric acid (98%) and this mixture was added dropwise to the cyclohexane solution. The sulfonation reaction was performed for 4 h at 40 °C. Poly(styrene sulfonic acid) was then precipitated by addition of ice, dissolved in water and separated from the organic phase. After neutralization with 0.5 M NaOH, the solution was dialyzed against doubly distilled water for 2 weeks, and then freeze-dried. Elementary analysis yielded a degree of sulfonation of $(85 \pm 3)\%$. Table 1 also contains the weight-average molar mass of the poly(sodium styrene sulfonate), calculated from the corresponding data of the polystyrene.

Poly(acrylamide) networks [13, 14]: 15 g acrylamide, 60 mg $(NH_4)_2S_2O_8$ and 230–770 mg (variable) N',N'-methylene-bis-acrylamide were dissolved in 50 ml water. 72 mg of N,N,N',N'-tetramethyl ethylene diamine was dissolved in 20 ml water. The two solutions were mixed, water was added to yield a volume of 100 ml, and the solution thus obtained was poured into cylindrical glass tubes (inner diameter 14.5 mm) which were finally covered with Teflon plugs on both sides. The glass tubes were stored in an oven at 55 °C for 24 h. During this time the cross-linking polymerization occurred.

When gels containing poly(sodium styrene sulfonate) were prepared, the procedure was as above except that 0.5 g of PSS was dissolved in the starting solution. Hence, the concentration of PSS is 3.3% with respect to poly(acrylamide).

The transparency of the gels containing PSS was inspected by light-scattering experiments. No notable difference to the pure polyacrylamide gels was observed, and we take that as evidence that microphase separation did not occur.

Gel cylinders cut to a height of 15 mm were stored in doubly distilled water until the equilibrium degree of swelling was attained. This was checked by weighing the gels from time to time. If a small sol fraction was present, it was extracted during this time. The ratio of the weight of the gel after attaining swelling equilibrium and the weight after preparation is termed the relative degree of swelling, q_{rel}. As the weight fraction of polymer at the gel synthesis is 0.15, the weight fraction of polyacrylamide in the gel at swelling equilibrium, ϕ_2, is $0.15/q_{rel}$, usually in the range 0.06–0.12.

To characterize the networks further, the shear modulus, G, was measured. From G, the effective network density can be calculated according to rubber elasticity theory (see below).

Five sets of networks were thus prepared, each of them covering five different network densities. One of the sets did not contain PSS and was used just for comparison. The others contained one of the four PSS samples listed in Table 1. The network parameters of the reference set and of the networks containing PSS are listed in Table 2.

From the effective network densities it is readily calculated that the average spatial distance between cross links is about 4–6 nm and that the number-average molar

Table 1 Molar masses of polystyrenes and poly(sodium styrene sulfonates) made thereof

Polystyrene			Poly(sodium styrene sulfonate)	
M_n [g/mol]	M_w [g/mol]	M_w/M_n	M_w [g/mol]	Sample code
154000	194000	1.26	360000	PSS 360
390000	410000	1.05	750000	PSS 750
545000	556000	1.02	1020000	PSS 1020
991000	1050000	1.06	1930000	PSS 1930

Table 2 Characteristic parameters of the networks studied

ν_{nom} [mol/m^3]	ν_{eff}[mol/m^3]	q_{rel}	G [kPa]	q_{rel}	G [kPa]
		Without PSS		With PSS	
30	15.6	1.89	14.1	2.46	15.3
40	20.3	1.79	19.1	2.16	20.4
50	23.2	1.55	22.8	1.92	24.4
70	35.7	1.34	37.3	1.59	38.8
100	50.8	1.21	55.4	1.40	57.2

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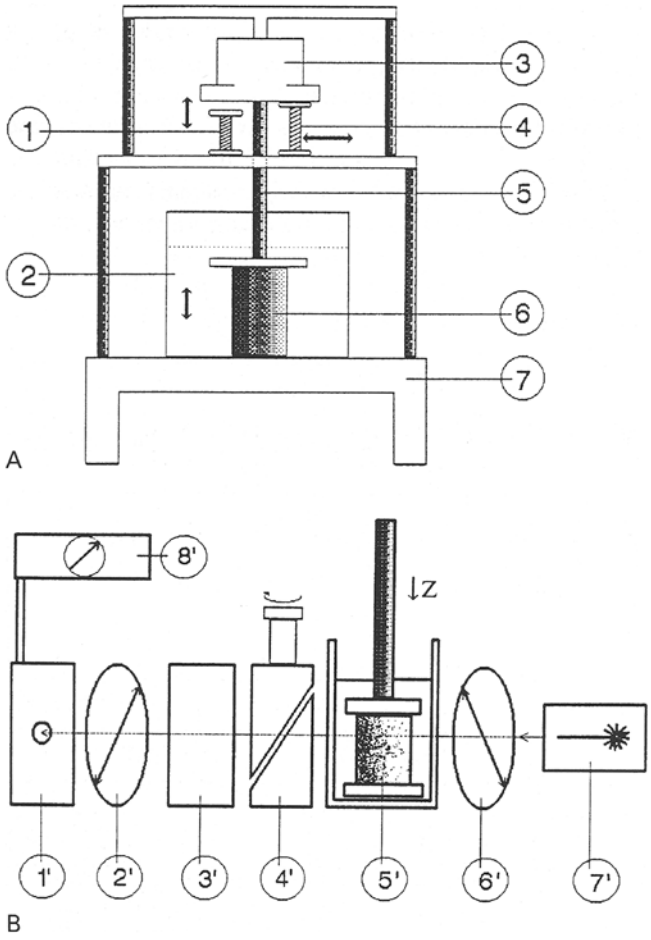
mass of the network chains ranges from 3000 to 10000 g/mol. These figures illustrate how the mesh size of the network compares to the dimensions of the PSS chains.

Mechanical set-up

A sketch of the apparatus used for the measurements is given in Fig. 1A. The cylindrical sample (6) is placed in a quartz cuvette (2) filled with water. Uniaxial compression can be achieved by means of a piston (5) whose vertical position is controlled by two stops (1 and 4). The height of stop (4) is adjusted such that the piston just touches the undeformed sample, while the height of stop (1) determines the deformation λ. The piston can be moved manually in a stepwise manner between the two stops and fixed in either position. The time span necessary to apply or reverse the deformation is short ($\approx$0.1 s) with respect to the time span of the experiment.

The force f exerted on the sample is measured via a load cell (3), while the deformation λ is determined by means of a cathetometer.

Fig. 1A Mechanical set-up used for the measurements, **B** optical system used to measure birefringence (cf. explanations in the text)



Optics

A He–Ne laser (7′) is used as a light source. It is adjusted so that the laser beam passes the sample (5′) perpendicular to the direction of deformation and that the plane of polarization forms an angle of $\pi/4$ with the axis of deformation. To improve the degree of polarization, a film polarizer (6′) is employed. The quarter-wave-plate (3′) behind the sample is arranged with its slow axis parallel to the plane of polarization of the incident light, and the analyzer (2′) is rotated a certain angle (typically 10°) from the crossed position. The light intensity is measured by means of a photo diode (1′) whose output voltage is fed to a strip-chart recorder (8′) (cf. Fig. 1B).

To provide the calibration curve for the correlation of retardation or phase shift δ between the light components polarized parallel and perpendicular to the strain direction and the output voltage of the photo diode, a babinet compensator (4′) is put in the beam between sample-cell and quarter-wave plate.

Data treatment

The relative deformation λ is the height of the deformed sample divided by the height of the undeformed sample:

$$\lambda = L/L_0 \,. \tag{4}$$

Upon deformation, the cross-sectional area of the cylindrical sample A changes by a factor λ^{-1}: $A = A_0\lambda^{-1}$, and the diameter, which is the path-length d of light in the sample, changes by $\lambda^{-1/2}$: $d = d_0\lambda^{-1/2}$.

In order to calculate the shear modulus, the force per unit cross-sectional area of the deformed sample is divided by the strain function $\lambda^2 - \lambda^{-1}$:

$$G = \frac{f}{A(\lambda^2 - \lambda^{-1})} = \frac{f}{A_0(\lambda - \lambda^{-2})} \,. \tag{5}$$

The effective network density (expressed with respect to the state of formation) is obtained from G according to

$$\nu_{\text{eff}} = \frac{2G}{RT} q_{\text{rel}}^{1/3} \,. \tag{6}$$

The birefringence of the sample is calculated from the retardation δ via:

$$\Delta n = \frac{\lambda_0 \delta}{2\pi d} = \frac{\lambda_0 \lambda^{1/2} \delta}{2\pi d_0}, \tag{7}$$

where λ_0 is the wavelength of the light in vacuum (632 nm). For the analysis of the final data, the absolute value of the birefringence is not of much importance; we rather focus on its time dependence after a strain transient. A normalization was made therefore according to

$$\Delta n_{rel} = \frac{\Delta n(t) - \Delta n(t = \infty)}{\Delta n(t = 0) - \Delta n(t = \infty)}. \tag{8}$$

To base the discussion on these relative values Δn_{rel} has the advantage that different samples which may, for example, differ slightly in their content of PSS, are now comparable.

Results

Preliminary considerations

An important prerequisite for a solid discussion is that the presence of poly(sodium styrene sulfonate) does not significantly influence network formation and hence the network topology. The data in Table 2 show that the modulus of gels containing PSS is slightly larger than that of gels without PSS. However, the difference is raher small (<10%), and this may serve as an argument that the condition mentioned above is essentially fulfilled.

The relative degrees of swelling q_{rel} differ more markedly. Figure 2 shows q_{rel} as a function of ν_{eff}, and it is seen that gels containing PSS swell more strongly. This is due to the fact that because of the ionic nature of PSS, the swelling pressure of the PSS trapped in the network is quite appreciable although its weight fraction is rather small. The different degrees of swelling do not imply that the network structures are different.

An important condition to get meaningful data is that the concentration of PSS in the network does not change during the measurement. When the gels are immersed in an aqueous solution, PSS will of course diffuse out of the gel, but this is a long-term process. This kind of extraction was monitored for 10 days using networks with network density 23.2 and 50.8 mol/m^3 and the PSS with molar mass 360.000 g/mol. The concentration of PSS in the surrounding solution was measured by UV-absorption at 262 nm. Figure 3 shows the dependence of the PSS concentration in the gel. The duration of a relaxation experiment is usually less than 10 min, the change of concentration of PSS in this time span is far below 0.1%.

A second basic condition necessary to allow for an unambiguous interpretation of the data is that the time dependence of the birefringence is solely due to the PSS in the gel. To prove this point, networks which do not contain PSS were investigated in a similar manner, Figure 4 gives an example of the course of birefringence with time when a strain is applied in a stepwise manner at $t = 0$ and removed at $t = 600$ s. Figure 4A showing the response of the gel without PSS demonstrates that the birefringence is constant while the strain is maintained, and that no birefringence is present after removal of the strain.

Figure 4B shows data for a sample with the same network density containing 3.3% PSS (with respect to

Fig. 2 Relative degree of swelling as a function of the effective network density for gels containing PSS (▼) and not containing PSS (●)

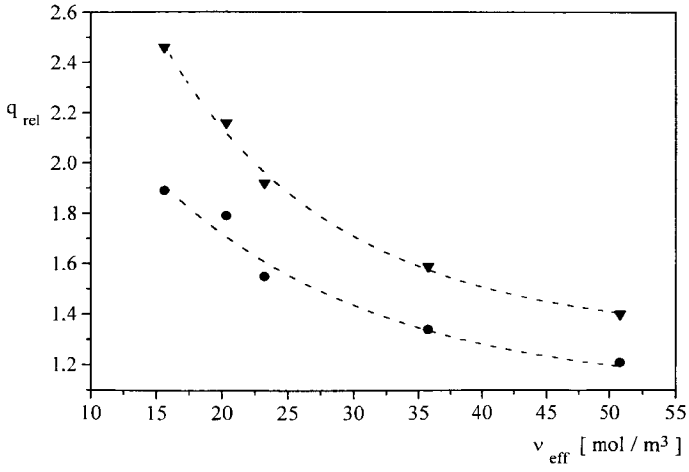
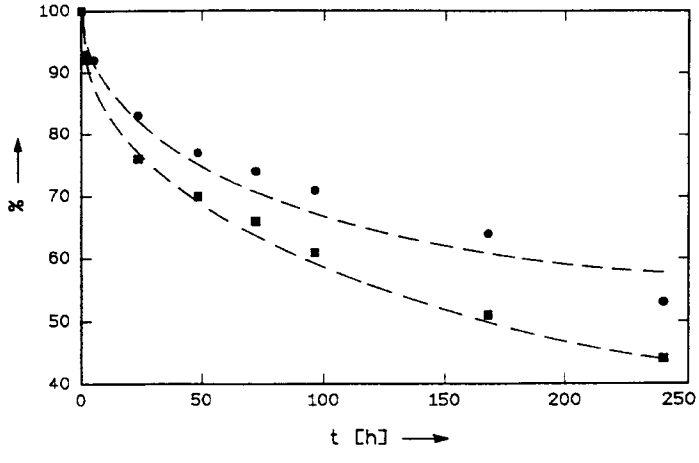


Fig. 3 Relative change of concentration of PSS 360 with time in a gel immersed in water: (■) ν_{eff} = 23.2 mol/m^3, (●) ν_{eff} = 50.8 mol/m^3



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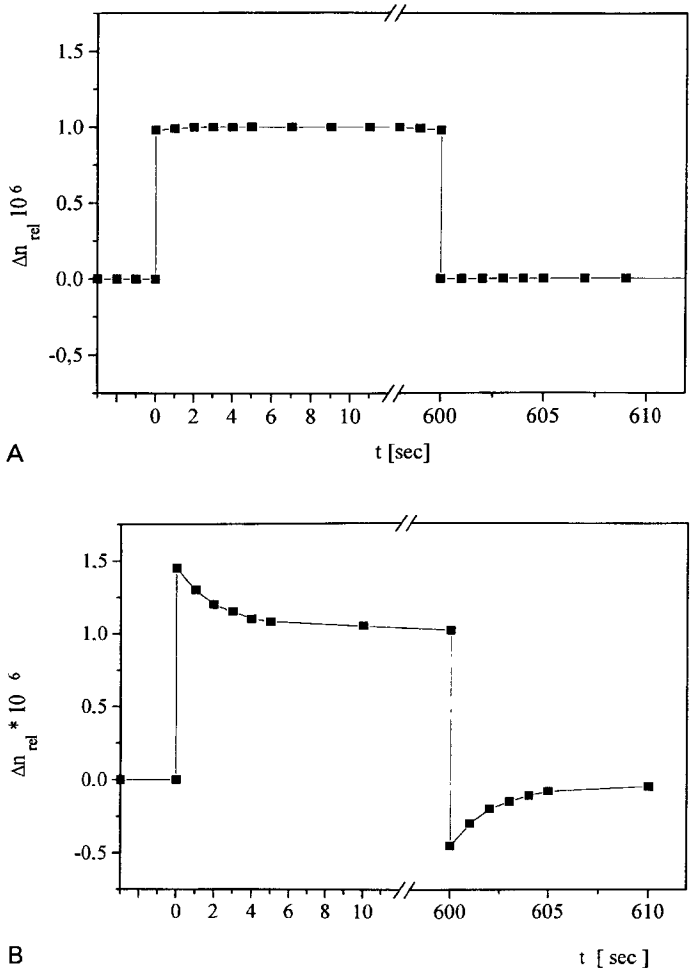


Fig. 4 Course of birefringence with time in a step-strain experiment. **A** gel not containing PSS, **B** gel containing PSS

PAAm). It is seen that now a significant time dependence of the birefringence occurs: the birefringence relaxes from 1.36 to 0.88 during the time span when the sample is compressed. After removal of the strain, an instantaneous birefringence of -0.48 is observed, which then relaxes to zero. The relaxation strengths after application and after removal of the strain are comparable. This fact supports the notion that the birefringence due to the network and that due to the incorporated linear macromolecules are additive and separable.

The mechanical stress, on the other hand, does not show any appreciable relaxation. Its course with time is the same as in the case of the network not containing PSS. Although the network polymer, PAAm, accounts for 97% of the total amount of polymer, the birefringence of the network is only twice as large as the instantaneous birefringence of the PSS. This is due to the fact that the optical anisotropy of the PSS chain is markedly higher than that of PAAm, and this is a significant requirement enabling the measurements to be conducted with reasonable sensitivity and reliability.

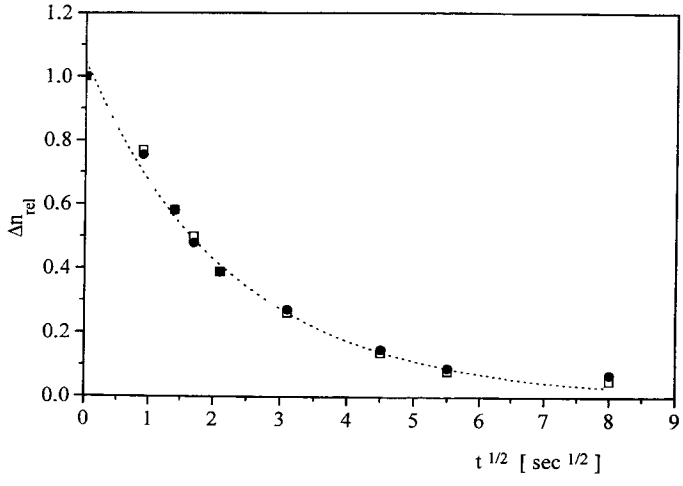
Figure 5 shows a comparison of the relative birefringence as a function of the square root of time for transient application and removal of strain. It is for a network with $\nu_{eff} = 23.2\ mol/m^3$ and PSS 750. The plot vs. $\sqrt{t}$ was chosen because the beginning of the curve is then linear (cf. Eq. (3a)). It is obvious that the two curves coincide within the limits of experimental error. The use of the data obtained after removal of the strain has the advantage that the final birefringence is zero, hence $\Delta n_{rel} = \Delta n(t)/\Delta n(t=0)$, whereas with the application of strain, $\Delta n(t=\infty)$ has to be determined with sufficient accuracy to calculate Δn_{rel}. Therefore, in the following only data derived from strain-removal experiments will be used.

The influence of strain magnitude on the relaxation of birefringence is shown in Fig. 6. Results obtained with $\lambda = 0.95, 0.93, 0.88$, and 0.82 are depicted covering a factor of ≈ 4 of initial birefringence. The curves for the three smallest strains coincide while the data for $\lambda = 0.82$ evidently deviate from the others. The strain applied in the following experiments was therefore limited to $\lambda = 0.93$, hence the system is studied at small strains close to the isotropic state.

Dependence of the relaxation on the molar mass of the linear chains

Several series of identical networks which contained PSS of different molar masses were studied. As an example,

Fig. 5 Relaxation of relative birefringence, plotted versus square root of time, for a gel ($\nu_{eff} = 23.2\ mol/m^3$) containing PSS 750: (□) after uniaxial compression, (●) after removal of strain



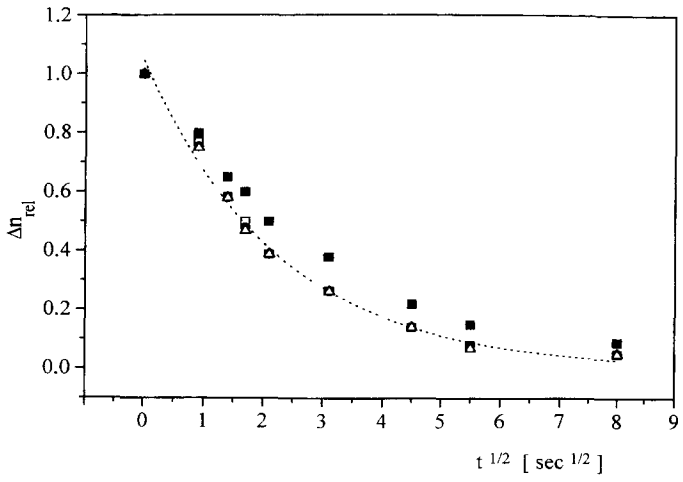


Fig. 6 Relaxation of relative birefringence for a gel (ν_{eff} = 23.2 mol/m^3) containing PSS 750 at different step-wise deformations: (●) λ = 0.95, (□) λ = 0.93, (△) λ = 0.88, (■) λ = 0.82

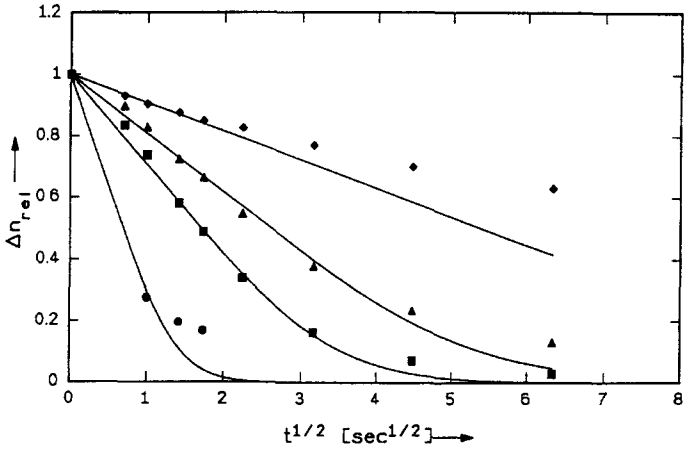


Fig. 7 Relaxation of relative birefringence for a gel with ν_{eff} = 23.2 mol/m^3 containing: (●) PSS 360, (■) PSS 750, (▲) PSS 1020, (◆) PSS 1930

Fig. 7 shows the course of Δn_{rel} vs. $\sqrt{t}$ obtained with a network density of 23.2 mol/m^3. The curves depicted correspond to the theoretical relationship given in Eq. (3) with $\Delta n_{rel}(t)$ being equated to $F(t)$. τ was chosen to get a reasonable agreement with the data points, in particular, at short times. It is obvious that only for PSS 750 and PSS 1020, the curves are a good representation of the experimental findings. With PSS 360, relaxation is so fast that the limits of our time resolution were reached and only few data points could be collected. At the other extreme, with PSS 1930 the plot of the experimental data exhibits a marked curvature which cannot be accounted for on the basis of Eq. (3).

Despite these limitations it is obvious that the relaxation time depends severely on the molar mass of the PSS. Figure 8 represents the dependence of the relaxation time τ on the molar mass of the PSS in a log–log plot. Data obtained when networks with different network densities were used as the matrix are included in this graph. Straight lines are drawn through each set of points implying that a power law $\tau \sim M^a$ is a valid approximation of the actual dependence.

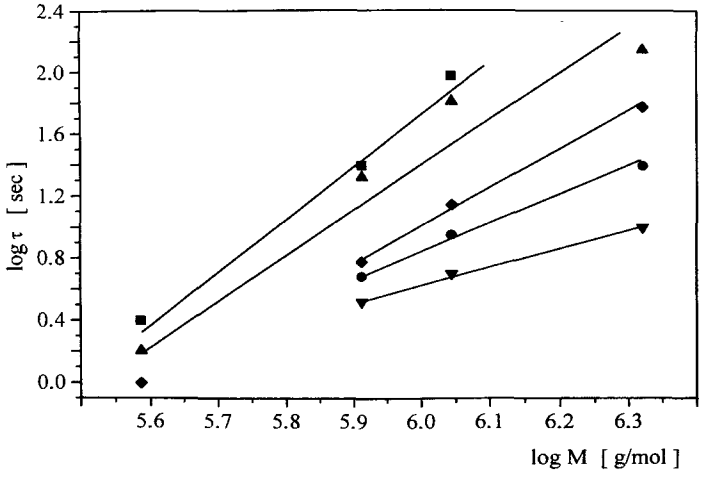
The lines obtained for the networks having the three highest network densities have slopes around 3 (a = 3.4, 2.7 and 2.5), while those for the other two networks are appreciably lower (a = 1.8 and 1.2). However, the precision of these exponents should not be overestimated (standard deviation is 0.4), as the linear regression is based on 3–4 points only. Some of the lines drawn in Fig. 8 tend to intersect at fairly high molar masses, which is of course unreasonable. Careful interpretation of the data just permits to state that the relaxation time varies roughly as the third power of the molar mass when the network density is sufficiently high. With lower network densities, deviations occur which seem to correspond to smaller exponents.

It should also be kept in mind that a lower network density corresponds to a higher degree of swelling and *vice versa*.

Influence of network parameters on relaxation

To study the influence of the network density or the degree of swelling of the network which contains the PSS more

Fig. 8 Plot of disengagement time versus molar mass of PSS. ν_{eff} = 15.6 mol/m^3 (▼), 20.3 mol/m^3 (●), 23.2 mol/m^3 (◆), 35.7 mol/m^3 (▲), 50.8 mol/m^3 (■)



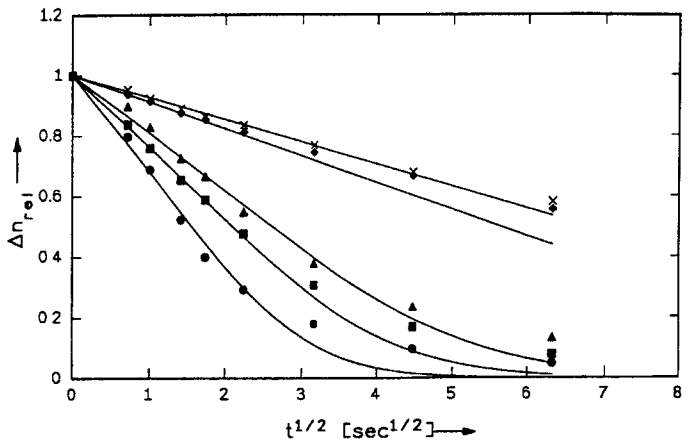


Fig. 9 Relaxation of relative birefringence for gels containing PSS 1020: (●) $v_{eff} = 15.6$ mol/m^3, $\phi_2 = 0.0609$, (■) $v_{eff} = 20.3$ mol/m^3, $\phi_2 = 0.0693$, (▲) $v_{eff} = 23.2$ mol/m^3, $\phi_2 = 0.0780$, (◆) $v_{eff} = 35.7$ mol/m^3, $\phi_2 = 0.0942$, (x) $v_{eff} = 50.8$ mol/m^3, $\phi_2 = 0.1075$

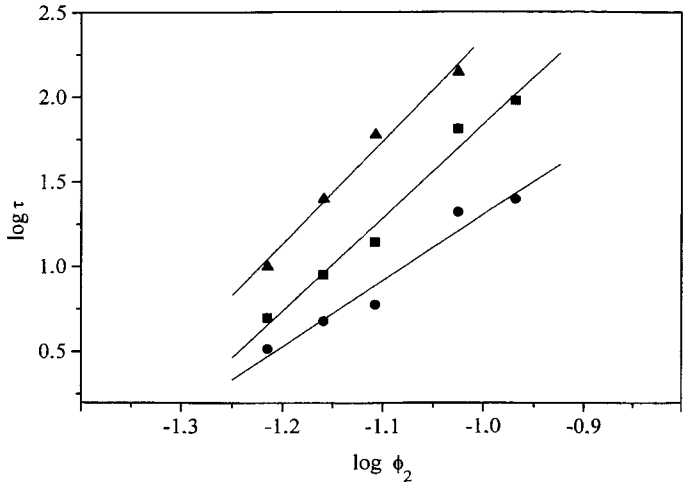


Fig. 10 Plot of disengagement time versus the weight fraction of the PAAm in the gel: (●) PSS 750, (■) PSS 1020, (▲) PSS 1930

systematically, relaxation curves for PSS 1020 are compared in Fig. 9. The relaxation rate increases strongly with increasing degree of swelling or decreasing network density, respectively. τ varies for about a factor of 20 in Fig. 9. Whether this is due to the variable density of polymer material (i.e., the degree of swelling), or to the network density (namely how tightly the polymer chains are interconnected), or to a combination of the two causes cannot be answered so far. As all experiments were performed at swelling equilibrium, the network density determines the degree of swelling. The two parameters were not changed independently (such work is presently in progress). We have deliberately decided to use the weight fraction ϕ_2 of the PAAm as the parameter vs. which the relaxation times are plotted in Fig. 10. Only data obtained with PSS 1930, 1020, and 750 are shown, because with PSS 360 the relaxation is so fast that the experimental error is too large. τ seems to increase with ϕ_2 according to a power law, $\tau \sim \phi_2^b$, with b ranging from 3.9 to 6.1 (standard deviation is 0.5), as the molar mass of the PSS rises from 750.000 to 1.9 million g/mol. This exponent is far above what is predicted at least for uncross-linked systems [9].

Conclusions

Our experiments have shown that birefringence measurements conducted under proper conditions are well suited to study the orientation relaxation of linear chains enclosed in swollen networks. When the cross-link density of the network is sufficiently high, the relaxation time varies approximately with the third power of the molar mass of the enclosed molecules, in agreement with the prediction of reptation theory. However, the number of data points has been too small to allow for a precise determination of the exponent. What can be said without doubt is that the exponent assumes markedly smaller values when the network density is lowered.

When the relaxation behavior of a linear polymer in networks of different cross-link density or different degree of swelling, respectively, are considered, it turns out that τ depends on a fairly high power of the concentration of the network polymer with an exponent in the range 4–6. Such steep dependences are beyond any theoretical prediction and need further investigation.

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