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Quasielastic light scattering on swollen silicon networks

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Summary

We have measured cooperative diffusion coefficients D_c of different polymer networks (PDMS, PDMSM) at equilibrium swelling by using the quasielastic light scattering technique. The model networks have been prepared by tetrafunctional endlinking of linear chains having different molecular masses. D_c is a function of the molecular mass of the network chains and the swelling degree at equilibrium, which can be described by scaling laws. The existence of a slow mode motion, similar to that in concentrated polymer solution, could be shown.

Introduction

In the past few years the reptation model has been proposed by de Gennes (1) to describe the chains rearrangements. Its consequences on the viscoelastic properties of a polymer melt have been worked out by Doi and Edwards (2). In the case of polymer solutions the polymer concentration c has to be taken into account. This has been done, theoretically, by the scaling approach developed by de Gennes (3) and des Cloizeaux (4).

In the dynamics of polymer solutions the diffusion of a polymer chain is of interest. We can distinguish the cooperative diffusion coefficient D_c, which describes cooperative, wavelike motions of the gel-like state, and the self diffusion coefficient D_s, which describes the macroscopic translation of the polymer chain.

For cooperative diffusion, the equation $D_c = kT(6\pi \eta_0 \xi)^{-1}$ applies. Since $\xi \propto (c/c^+)^{-3/4}$ (ξ = screening length, c^+ = overlap concentration), the following equation holds for the concentration dependence:

$$D_c(c) = D_c(c=0)(c/c^+)^{3/4} \tag{1}$$

The self diffusion coefficient scales as

$$D_s \propto M^{-2}\ c^{-1.75} \tag{2}$$

for the semidilute region, and

$$D_s \propto M^{-2}\ c^{-3} \tag{3}$$

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for the concentrated region, with the concentration c and the molecular mass M (5).
In polymer solutions, both types of motion have been proven (6,7,8).
According to the arguments of the scaling concept, swollen polymer networks should show the behaviour of the pseudo gels formed by entanglement. The theory of the dynamics of an isotropic elastic body does not predict the slow mode which is observed in transient networks of entangled chains (9).
Measurements with real gels appear to indicate that slow mode disappears when the gel point has been passed (10).
Slow mode motion is retained in thermoreversible networks ($D_s \propto c^{-4.8}$) (9).
Recently, (11), neutron-spin echo results concerning the dynamics of crosslinks in a model network of PDMS have been published. A report on the effects of the motion of crosslinks on the structural factor of QELS and a theoretical description of the Brownian motion of chains and crosslinks in a permanently linked network has been given in (12).
With the help of QELS, the dynamic behaviour of polymer molecules in solution can be studied. D_c of swollen polymer networks (13) can be calculated from the measured autocorrelation function (14).
In the present work, D_c of polymer networks with different network densities are measured in the state of equilibrium swelling. Slow mode motion can be found in the polymer network. The dependence of the cooperative diffusion coefficient and the diffusion coefficient of slow mode motion on the concentration and molar mass is discussed.

Experimental

The QELS-measurements were performed with the light scattering apparatus described in (15) in heterodyne regime. The reference beam was produced by means of the flare from a needle introduced into the incident beam inside the scattering cell. The measured autocorrelation function in this case has the form:

$$C(t) = A \cdot g^{(1)}(t) + B \qquad (4)$$

where A and B are constants dependent on the experimental conditions, $g^{(1)}(t)$ is the first order, normalized field autocorrelation function, t is the delay time, here $t = \Delta t$, $2\Delta t, .. 64\Delta t$, Δt being the sampling time of the autocorrelator. Hydrodynamic theories (3,12) predict that the time-dependent term of the autocorrelation function of light scattered of a swollen polymer network is a single exponential function:

$$g^{(1)}(t) = \exp(-q^2 Dt) \qquad (5)$$

The magnitude of the scattering vector q is given by $q = (4\pi \tilde{n}/\lambda_0) \sin \vartheta/2$, where λ_0 is the wavelength of the incident light in a vacuum (633 nm), ϑ is the scattering angle ($\vartheta = 90°$), and $\tilde{n}$ is the index of refraction of the scattering medium.
The diffusion coefficient is determined by fitting the

measured autocorrelation function to eq. (5). Since

$$\sigma = \left(\frac{1}{61} \sum_{i=1}^{64} \left[\frac{C_i - C_i^{fit}}{C_i} \right]^2 \right)^{1/2} \lesssim 0.02 ,$$

the one-exponent fitting is justified.
The best fitted D and A/B values are shown in the Table 1 for all investigated samples.

Table 1

Sample	$D_1/10^{-7}cm^2s^{-1}$	A/B	$D_2/10^{-7}cm^2s^{-1}$	A/B	D_1/D_2
A 1	9.00	0.088			
A 2	8.04	0.106	0.114	0.009	70.5
A 3	6.92	0.089	0.046	0.010	150
A 4/1	6.59	0.093	0.047	0.007	142
A 4/2	6.60	0.105	0.046	0.012	143.5
A 5	5.31	0.102	0.064	0.011	83
M 1	6.51	0.103	0.087	0.009	75
M 2	7.71	0.110	0.076	0.009	101
M 3	7.75	0.096	0.066	0.010	117
B 1	5.61	0.088			
B 2	4.71	0.095			
B 3	4.31	0.069	0.031	0.010	139
B 4	4.10	0.091			
B 5	2.80	0.065			
PB-γ	10.9	0.111	0.080	0.007	136

The cubic or cylindrical samples (diameter of the dry sample ≈ 5 mm, thickness ≈ 2 mm) were placed into the swelling liquid. They were allowed to stand for at least 2 days to attain thermodynamic stability. The samples were fixed at a defines position in the light scattering cell. All measurements were performed at room temperature (20°C).
In some cases, problems arose during sample positioning. They were caused by folded sample surface or fragility. For these reasons we were not able to perform measurements in such cases.
We investigated 1,4-cis-polybutadiene crosslinked by γ-irradiation (dosis of irradiation 0.3 MGy) and poly(dimethylsiloxane) and poly(dimethylsilmethylene) with crosslinked end groups.
The poly(dimethylsiloxane) networks (series A) were synthesized by end-linking α,ω-dihydroxy poly(dimethylsiloxane) with tetra ortho silicate as a crosslinking agent and one weight percent of tin 2-ethyl hexanoate as a catalyst. The bifunctional siloxanes were prepared by anionic ring opening polymerization of octamethyl cyclo tetrasiloxane. The ratio of functional groups was near 1, $r=n(OC_2H_5)/n(OH)$, and in some cases (series M) extremly different from 1.
The poly(dimethylsilmethylene) precursors were prepared as described in (16). They were crosslinked in the same manner

(series B). All precursor chains were characterized by water content, end group analysis of hydroxy groups, number average and weight average molecular masses by gel permeation chromatography. The values are summarized in Table 2.

Table 2

Sample	M^{eg}/gmol^{-1}	r	w_w/%	M_c/gmol^{-1}	φ_B	w_s/wt%
A 1	10,600	1.000	0.055	12,100	0.213	4.5
A 2	16,200	1.007	0.060	15,700	0.172	5.1
A 3	18,700	1.012	0.048	17,800	0.167	3.0
A 4	24,000	1.008	0.060	21,000	0.149	1.7
A 5	27,500	1.004	0.050	27,500	0.100	1.4
M 1	12,900	1.060	0.140	13,300	0.164	1.8
M 2	12,900	1.942	0.140	11,000	0.208	0.9
M 3	12,900	3.901	0.140	4,000	0.370	0.3
B 1	7,100	0.999	0.062	7,800	0.278	5.8
B 2	10,800	1.004	0.065	11,300	0.217	4.8
B 3	16,200	1.003	0.051	18,300	0.187	4.0
B 4	20,700	1.003	0.043	22,900	0.156	3.0
B 5	22,500	1.005	0.032	24,600	0.130	2.8
PB-γ				9,600	0.168	

The networks prepared from each polymer were extracted in toluene at room temperature for 3 days in order to remove unreacted materials. In most cases the soluble fraction w_s was smaller than 3 wt%.

Assuming isotropic swelling, the degree of swelling Q ($Q=1/\varphi_B$, φ_B= volume fraction polymer) can be calculated from the ratio of thickness of the swollen and unswollen test specimen. The thickness was measured with a cathetometer. The molecular masses M_c of the network chains were determined by measurements of compression and stress-strain, assuming the structure factor A=1.

Results and Discussion

QEIS experiments with short delay time (sampling time $\Delta t=5\mu s$) give the diffusion coefficient D_1. They show the behaviour expected in cooperative diffusion. When QEIS measurements are performed at a long delay time ($\Delta t=1ms$), a slow mode motion can be found (D_2).

The cooperative diffusion coefficient is concentration-dependent. For a series of networks of the same functionality but different crosslinking densities and swollen to equilibrium by a pure good solvent, the concentration dependence of D_c can be expressed as (18)

$$D_c \propto \varphi_B^{(9/4-\alpha)}$$

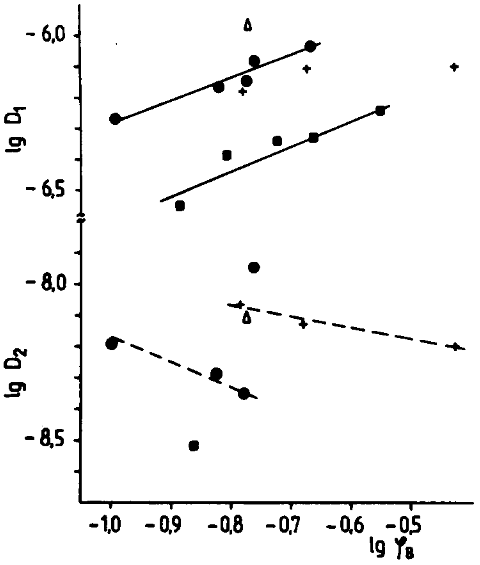

Fig. 1: Concentration dependence of diffusion coefficients

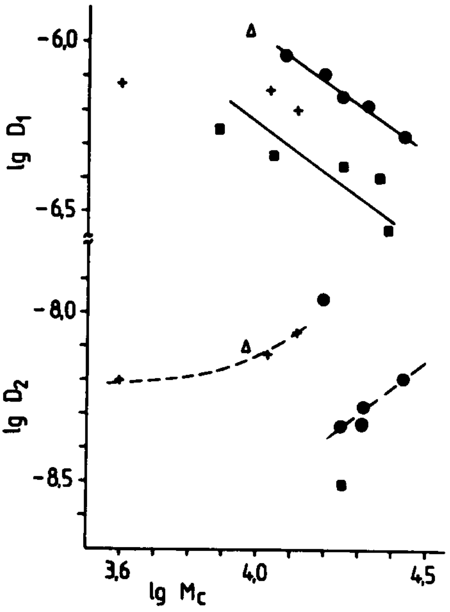

Fig. 2: Dependence of diffusion coefficients on M_c

(series A: ●; series B: ■ ; series M: + ; PB-γ : Δ ; solvent: toluene)

where α is the exponent of the concentration dependence of the friction factor (experimental studies showed that ≥ 1.5). Hence an exponent ≤ 0.75 is to be expected for the concentration dependence of D_c. For the samples of series A and B,

$$D_1 \propto \varphi_B^{0.8}$$

applies (Fig. 1).

The exponent agrees well with a value of 0.77 ± 0.02 measured in ref. (17) for PDMS networks in toluene. The samples of series M, which was synthesized with an excess of crosslinking agent, deviate from the straight line.

For D_2, no unequivocal relationship with φ_B can be found. As compared with D_1, D_2 becomes smaller with increasing polymer concentration,

$$D_2 \propto \varphi_B^{-a} \text{ , } a = 0.4 \ldots 0.7 .$$

Fig. 2 represents the dependence of the D_1 and D_2 on M_c. For PDMS networks, $D_1 \propto M_c^{-0.7}$, for PDMSM networks, $D_1 \propto M_c^{-1}$. The exponent can be explained by the M_c-Q dependence derived from the Flory-Rehner equation. For good swelling agents,

$$\varphi_B \propto M_c^{-3/5}$$

applies.

This would give $D_1 \propto M_c^b$, $b \geq -0.45$; the experimental values are smaller than expected. By contrast with D_1, the D_2 values become greater with increasing molecular mass of the network chains.

Ref. (19) gives coefficients of the self diffusion of PDMS chains in PDMS model networks. In this work it has been found that for a diffusant with M_n = 4,700 gmol-1, D_s has a value of 0.7 $10^{-7}cm^2s^{-1}$ in the melt (matrix = diffusant) and 0.34 $10^{-7}cm^2s^{-1}$ in a network (M_c = 3,700 $gmol^{-1}$).

The diffusion coefficient of the slow mode motion found by us is smaller by a factor of 5...10. This means that D_2 cannot be related with non-crosslinked chains and free ends of chains, but has to be attributed to dynamic processes in the network, i.e. to the motion of the crosslinks.

A motion based on a reptation mechanism has to exhibit the characteristic M^{-2} dependence (Equations 2,3). In the case of reptation, a plot lg $D_2 M_c^2$ - lg φ_B give a straight line with a slope of -1.75...-3. Actually, for $\varphi_B \leq 0.25$,

$$D_2 \propto M_c^{-2} \varphi_B^{-1.7} .$$

When we include the value at φ_B = 0.37 into the calculation, the exponent is -2.8 (Fig. 3).

Fig. 4 represents the ratio of the cooperative diffusion coefficient D_1 to D_2. D_1/D_2 decreases with increasing molecular mass M_c. Sample M_3, which has been synthesized with equal molecular mass M_n of the initial chains, but with an increased amount of crosslinking agent, must have a functionality f >4

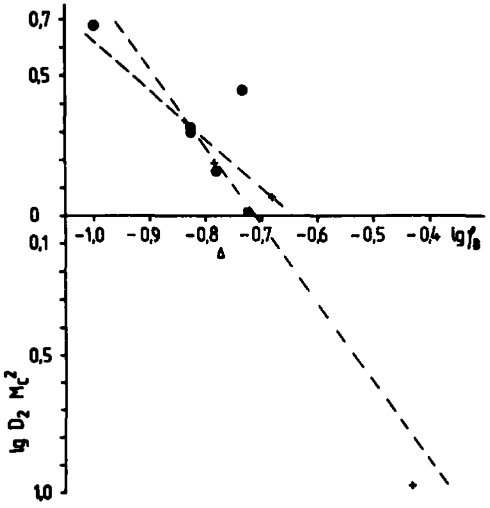

Fig. 3: Concentration dependence of the product $D_2M_c^2$ (Equation 2,3)

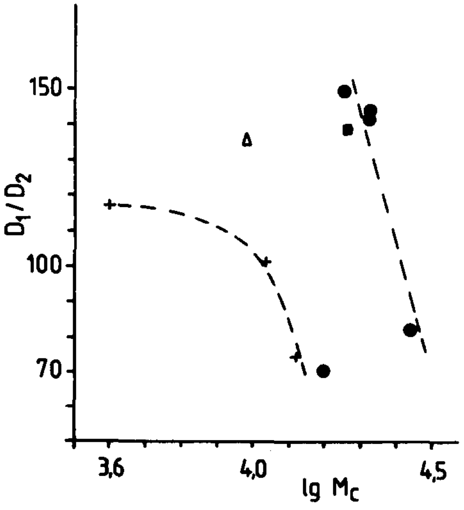

Fig. 4: Dependence of the ratio of cooperative diffusion coefficient to diffusion coefficient of the slow mode motion

(the crosslinking agent reacts with itself). The D_1/D_2 ratio is clearly lower than would have been expected from the M_c dependence. Hence the functionality has an effect on the motion of the crosslinks. Thus, the following applies: The smaller the molecular mass of the network chains M_c, and the greater the functionality, the smaller is D_2, and the greater is the hindrance of the motion of the crosslinks. This should give the possibility of obtaining information on the functionality of the crosslinks by comparing the slow mode motion and the cooperative diffusion.

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