(28) Brandup, H.; Immergut, E. H. Eds. *Polymer Handbook*; Wiley: New York, 1974.
(29) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.
(30) Bremser, W. Diplomarbeit, Mainz, 1988.
(31) Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19.
(32) Kurata, M.; Abe, M.; Iwana, M.; Matsushima, M. *Polym. J. (Tokyo)* **1972**, *3*, 729.
(33) Zimm, B. H.; Stockmayer, W. *J. Chem. Phys.* **1949**, *17*, 1301.
(34) Roovers, J.; Toporowski, M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(35) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(36) Scherage, H. A.; Mandelkern, L. *J. Am. Chem. Soc.* **1953**, *75*, 179.
(37) Oono, Y.; Kohmoto, M. *J. Chem. Phys.* **1983**, *78*, 520; *J. Chem. Phys.* **1983**, *79*, 4629.
(38) Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1551.
(39) de Gennes, P. G. *Scaling Concepts in Polymer Science*; Cornell University Press: Ithaca, NY, 1979.
(40) Vilgis, T. A. *Phys. Rev. A* **1987**, *36*(3), 1506.
(41) Porod, G. *Kolloid Z.* **1951**, *124*, 83.
(42) Fölsch, K. J. Dissertation, Mainz, 1988.
(43) McDonnell, M. E.; Jamieson, A. M. *J. Polym. Sci.* **1980**, *18*, 1781.

Micronetworks by End-Linking of Polystyrene. 2. Dynamic Mechanical Behavior and Diffusion Experiments in the Bulk

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ABSTRACT: The frequency-dependent storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, have been determined for polystyrene μ-networks (see preceding paper). By application of the temperature–frequency shift procedure we have obtained spectra within a frequency range of ω between 10^{-3} and 10^3 s^{-1}. In all cases, power laws $G'(\omega) \sim G''(\omega) \sim \omega^\alpha$ were found to apply over 5 decades in frequency. α increases from 0.2 to 0.5 as the number of monomers between cross-links, P_c, is decreased from 141 to 23. The absolute values of $G'(\omega)$ and $G''(\omega)$ decrease with decreasing P_c, both being below the moduli values of entangled linear PS. $\tan \delta = G''/G'$ increases in the same order and approaches unity at $P_c = 23$. By a dilution experiment we can suggest a division of this behavior in two contributions: a part characterized by $G'(\omega) = G''(\omega) \sim \omega^{0.5}$ describes the internal dynamics of the μ-networks whereas the remainder is given by a P_c-dependent chain–chain interaction with a scalable lifetime distribution. The results are in harmony with similar findings in comb-shaped polymers and networks obtained by cross-linking of telechelic chains at the gel point. These data also support the description of μ-networks as "fractal" structures, which was raised during the structure examinations. Although more detailed experiments are necessary, the problems concerning this description are discussed. The tracer diffusion of labeled PS chains in μ-networks is not different from that in matrices of entangled linear PS. This result cannot be understood within a tube model having cross-links as fixed obstacles but requires consideration of the internal μ-network dynamics.

I. Introduction

In our previous paper,[1] the preceding paper in this issue, we have described the synthesis of model μ-networks and their characterization with light and neutron scattering, gel permeation chromatography, and viscosimetric measurements. We have demonstrated that we can approximate the local structure of these particles by a "fractal" distribution of the local monomer density. The scaling laws of diverse properties comply with measurements on other differently branched structures (references cited in ref 1).

The subject of this publication is the description of the dynamic behavior of these structures in the bulk state above the glass transition temperature. We present results of two different techniques: dynamic shear experiments determine the viscoelastic properties of these molecules, thus resulting in spectra of relaxation times which can be related to the molecular architecture (c.f. ref 2). In addition, diffusion experiments of linear probe chains reflect the local structure of entanglements and cross-links of the μ-network environment.[3,4] The combination of the results of these two techniques and the structure data of ref 1 should lead to a general picture for the dynamics of a whole class of cross-linked structures. Furthermore, we discuss whether the description of polymer networks as fractal structures, which was successfully used at the gel point of networks cross-linked in the bulk state,[5,6] can be extended to differently cross-linked structures, at least in a limited frequency and space regime. This should also contribute to a still open discussion that was induced by neutron-scattering results on stretched networks and could not be explained by classical structure assumptions.[7]

II. Experimental Section

1. **Dynamic Mechanical Experiments.** The μ-network samples were precipitated from solution and carefully dried overnight in vacuo at 80 °C. By compression molding at 150 °C optically clear disks with 13-mm diameter were prepared, fitting the geometry of a plate/plate rheometer. A Rheometrics RMS 800 apparatus was used in an oscillating low-amplitude mode in a frequency range between 10^{-2} and 10^2 rad·s^{-1} with an amplitude of 2%. For one chosen sample it was checked that our measurements are within the linear regime, which typically goes up to 20% strain. The measurements were controlled by a FRT2000 frequency response analyzer, which also records the complex torque. A stream of dry nitrogen was blown over the sample in order to avoid thermal oxidative damage during the measurements performed at 130–210 °C. After the sample was heated to the maximum temperature, the measurements at 150 °C were repeated in order to check for alteration. The changes remain within

Table I
Sample Designations and Apparent Degrees of Polymerization As Obtained by GPC

	linear precursor		μ-network		
sample	P_N	M_w/M_N	P_N(app)	M_w/M_N(app)	T_g/K[b]
N1600/23	23	1.11	1600	1.62	
N1100/24	24	1.10	1140	1.33	383
N5900/59	59	1.07	5910	1.66	378
N(e.v.)/71	71	1.05	>10000[a]		
N2000/71	71	1.05	2910	1.51	
N(e.v.)/75	75	1.04	>10000[a]		
N2800/141	141	1.05	2820	1.33	380
N4100/141	141	1.05	4140	1.86	

[a] The real degrees of polymerization are beyond the excluded volume of the GPC combination used. [b] T_g has been measured just in a few selected cases.

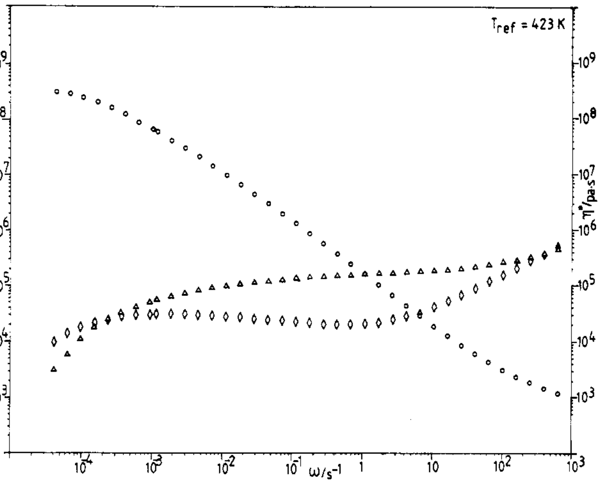

Figure 1. Storage modulus G' (△), loss modulus G'' (◇), and dynamic viscosity η^* (○) of a linear reference polystyrene with $M_w \approx 800\,000$ g/mol. The data are shifted to a reference temperature T_{ref} = 423 K.

5%, especially in the non-Newtonian regimes of our measurements.

2. Diffusion Measurements. Diffusion coefficients of labeled linear polystyrene molecules we measured using the holographic grating technique and the o-nitrostilbene dye label, as described in our previous publications.[8,9]

3. DSC Measurements. DSC measurements were performed with a Perkin-Elmer Model DSC 2C instrument. Pellets of 10–20 mg have been used which were heated in aluminium pans with a heating or cooling rate of 10 K/min, giving a small hysteresis. The samples were measured 2–4 times, the first run was only used for equilibration.

III. Results and Discussion

Table I recapitulates the data for the μ-networks which have been examined in the present set of experiments. The polymer analysis has been extensively described in our previous publication.[1] Some T_g values obtained from the DSC measurements are also included. For dynamic mechanical experiments, we selected four fractions with a moderately high molecular weight and chain lengths between the cross-links varying from 20 to 150 monomer units. For comparison, a linear polystyrene of narrow molecular weight distribution (M_w = 800 000 g/mol, $M_w/M_N \geq 1.10$) has also been examined.

The mechanical spectra are presented in the form of master curves obtained from frequency dependencies measured at various temperatures. Only horizontal shifts to the reference temperature of 423 K have been made. The shift parameters a_T are in good agreement with values for linear and ring-shaped polystyrene.[10] Figure 1 shows the frequency dependence of the storage modulus G', the loss modulus G'', and the dynamic viscosity η^* of the linear reference polymer in a double-logarithmic plot. With our experimental conditions chosen, the complete range from the transition to the terminal zone (7 decades in frequency) can be observed reflecting the important part of the mode spectrum of this polymer melt. The absolute values of the plateau modulus (2×10^5 Pa) and the extrapolated zero-shear viscosity ($\eta_0 \approx 4 \times 10^8$ (Pa·s)) are in good agreement with other experiments.[2,10] This confirms the compatibility of our experimental setup and procedure of the measurements with techniques used by other authors. One should note that the curve of the dynamic viscosity cannot be described with a scaling law in the non-Newtonian regime.

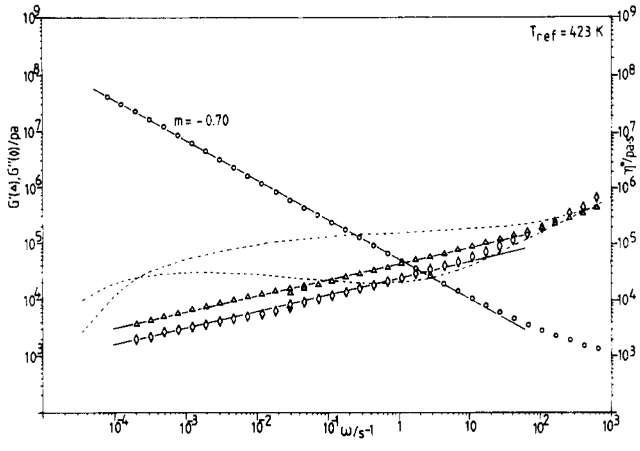

Figure 2. G' (△), G'' (◇), and η^* (○) of N2000/71 at T_{ref} = 423 K. The dashed line indicates the behavior of the linear reference polymer.

The quite unusual behavior, typical for the μ-networks, is shown in Figure 2, where the data of sample N2000/71 with a molecular weight of the chain between two cross-links of M_N = 7400 g/mol are plotted. In this double-logarithmic plot, the frequency dependences of G', G'', and η^* are strictly linear over more than 5 decades of frequency. Deviations of such dependences are observed only close to the transition to the glassy state, which is known to depend slightly on polymer topology. The extension of spectra in the low-frequency range is limited by the thermal stability of the samples. G' and G'' are parallel and have a scaling of $G' \sim G'' \sim \omega^{0.3}$. This results in a scaling of the dynamic viscosity:

$$\eta^* = \frac{(G'^2 + G''^2)^{0.5}}{\omega} \tag{1}$$

$$\Rightarrow \eta^* \sim \omega^{-0.7} \tag{2}$$

A bending of the curves at low frequencies to the behavior expected for a Newtonian liquid is not observed in the accessible temperature range, which is simply due to the fact that we have chosen a sufficiently large size for our molecular μ-networks in order to observe only the internal modes of mobility.

This can be proven by measuring a different fraction of the same condensation reaction with much higher molecular weight (N(e.v.)/71, $M_w \geq 50 \times 10^6$ g/mol) thus having a μ-network with comparable topological parameters. Within the experimental errors, no change of the mechanical properties was observable. This comparison shows also that the behavior observed is not influenced by the molecular nature of the network particles, which, in principle, can lead to clearly molecular weight dependent properties. Although the molecular weight is very high compared to $M_c' \approx 150\,000$ g/mol of linear polystyrene, we

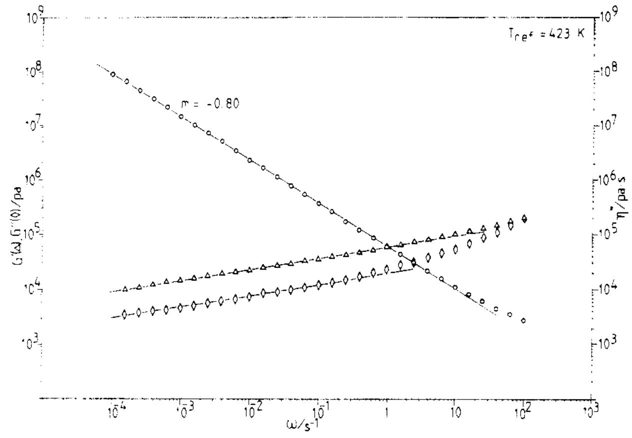

Figure 3. G'(△), G''(◇), and η^* (○) of N2800/141 at T_{ref} = 423 K.

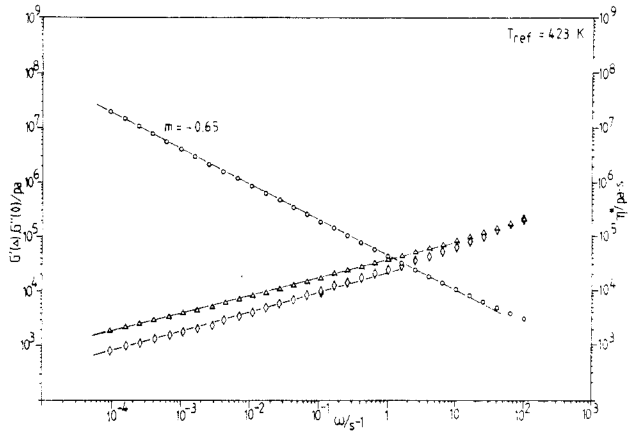

Figure 4. G'(△), G''(◇), and η^* (○) of N(e.v.)/75 at T_{ref} = 423 K.

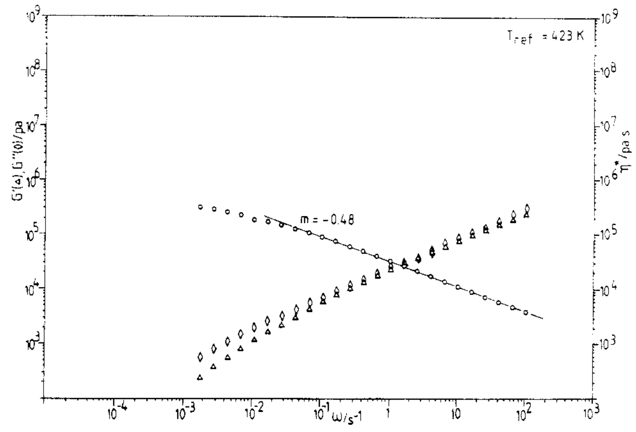

Figure 5. G'(△), G''(◇), and η^* (○) of N1600/23 at T_{ref} = 423 K.

Table II
Frequency Exponents α of Dynamic Quantities

sample	η^{*a}	G'^{b}	G''^{c}
N1600/23	-0.45	0.55	0.55
N2000/71	-0.70	0.30	0.30
N(e.v.)/75	-0.65	0.32	0.36
N2800/141	-0.80	0.20	0.20
N2800/141 30% dil	-0.48	0.52	0.52

[a] $\eta^* \sim \omega^\alpha$. [b] $G' \sim \omega^\alpha$. [c] $G'' \sim \omega^\alpha$.

do not observe any elastic plateau corresponding to a "tube" or a conventional transient network between different molecules. Therefore, we have to conclude that the lifetime of entanglements is not given by a constant time τ_R (in analogy to the tube model of a linear chain in the melt) but by a broad continuous spectrum of relaxation times. This is similar to the well-described case of comb-shaped polymers (see, for instance, ref 11), although one major difference must be mentioned. Combs seem to have power law frequency dependences at some intermediate frequencies only, whereas μ-networks exhibit these dependences in the terminal zone. The dashed line in Figure 2 indicates the behavior of the linear polymer shifted according to the difference in glass transition temperature. This comparison demonstrates the continuous reduction of the moduli with decreasing frequency.

Figure 3–5 represent, in analogy to Figure 2, G', G'', and η^* of the μ-networks N2800/141, N(e.v.)/75, and N1600/23, thus covering our complete range of cross-linking densities. In all plots, we observe strictly linear scalings where G' parallels G'' in the low-frequency part of the spectra. In Figure 5, the absolute molecular weight of the μ-network (sample N1600/23) was too low to ensure a larger linear scaling. It should be noted that we can detect a small difference between the spectra of samples N2000/71 and N(e.v.)/75, even though the primary chain lengths are comparable. This is due to the still existing imperfections of our μ-network synthesis and should be taken as a measure of the reproducibility. Table II summarizes the frequency-dependent data. In contrast to simple expectations, the moduli curves *decrease* with increasing cross-linking densities, in other words, the shorter the primary chain lengths, the lower the moduli at a certain frequency. In addition, tan δ defined as the ratio of G'' over G' becomes larger and reaches a value near unity for the smallest primary chains.

The linearities shown in Figures 2–5 have no counterpart in the behavior of linear polymers. However, restricted to certain domains of frequency and temperature, a scalable behavior is known for more complex polymer topologies. Graessley and Roovers[11] found in comb-shaped polymers in an intermediate-frequency window a region extending over 2.5 decades where G' parallels G'' and was proportional to $\omega^{0.5}$. A similar regime with the same width has been observed in randomly branched polystyrenes.[12] Finally, Winter has shown in a set of papers that networks yield universally $G' = G'' \sim \omega^{0.5}$ in the terminal zone when the cross-linking reaction is stopped at the gel point (see, for instance, ref 5 and 13). The similarity of all these systems seems to be that there is a region in time still shorter than the longest Rouse relaxation time where the influence of entanglements has vanished, thus leading to the typical $\omega^{0.5}$ behavior of Rouse dynamics.[14] However, the μ-networks examined in the present study show a still different behavior, because it seems that they reach the limiting Rouse behavior only for very small primary chains. Above this limit, we observe decreasing scaling exponents of G' and G'' and an increasing tan δ value. The same is observed in the publication of Havranec et al.,[15] who have investigated the sol fraction of model networks and have found a domain extending over 4.5 decades where J' and J'' are proportional to $\omega^{-0.37}$.

A possible explanation for the different scaling behavior of our μ-networks is that they can be partly entangled as the elementary chains become larger and approach the entanglement molecular weight M_e ($M_e \approx 18000$ g/mol for polystyrene). (In that context one should note that a μ-network contains longer linear substructures than the elementary chain. If we look for some average contour length of a mesh, we certainly find a multiple of the primary chain length.) Thus, we have no real vanishing of the influence of entanglements within the accessible tem-

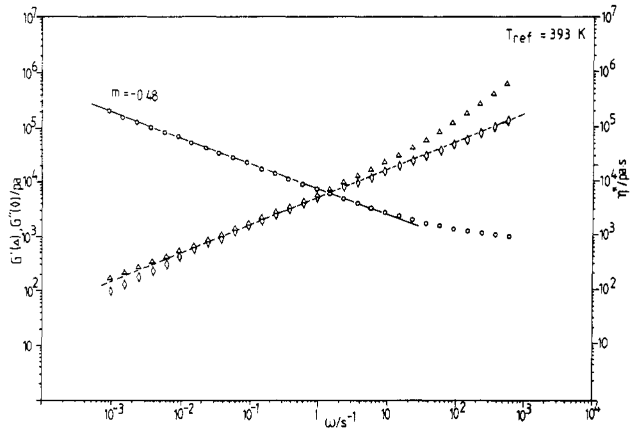

Figure 6. G' (△), G'' (◊), and η^* (○) of N2800/141 diluted with oligostyrene ($M_w \approx 2000$ g/mol) to Φ (μN) = 0.3. The reference temperature was chosen as 393 K.

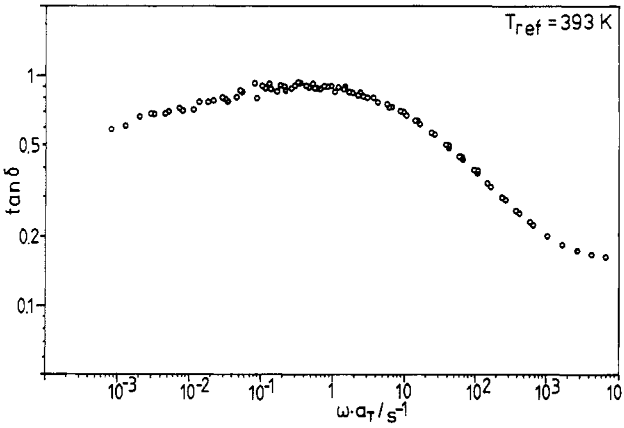

Figure 7. tan δ = G''/G' for the data plotted in Figure 6.

perature range but a continuous disappearance. This results in a systematic increase of the moduli in comparison with the "unperturbed" Rouse behavior, and the plateau modulus (Figure 1) provides the limit of a fully entangled system.

We can check this assumption by diluting the μ-networks with styrene oligomers, thus leading to a decrease of the entanglement density.[2] Figure 6 shows the behavior of the μ-network N2800/141, the sample with the largest primary chains, in a mixture with an oligostyrene ($M_w \approx$ 2000 g/mol) where the volume fraction of the μ-network in the mixture is 0.3. According to the different T_g of 349 K, the reference temperature was chosen as T_{ref} = 393 K. Compared with the results of the corresponding pure μ-network (Figure 3), we observe a complete change of the spectrum. Now our system scales approximately as $G' \approx G'' \sim \omega^{0.5}$, which is indicated by the dashed line. Therefore we conclude that the decrease of the frequency dependence is really due to an intercatenary phenomenon, as discussed above, which can be suppressed by dilution.

The still-existing deviations from an "ideal" Rouse behavior are shown in Figure 7, where tan δ of the same set of measurements is plotted versus frequency. Starting from the transition zone with smaller tan δ values, we observe systematic deviations from the expected tan δ = 1. In view of the fact that we have to deal with real systems containing different kinds of defects, the agreement is nevertheless satisfactory. In the first part of this study,[1] we have determined from SANS results the exponent of the spatial monomer–monomer pair correlation function, d_f. It is obvious that we also compare our dynamical scaling exponents with calculated values coming from a fractal theory of networks.[16,17] Taking the complex viscosity η^* as the characterisitc property influenced by the spectral dimension of a fractal d_s, these treatments predict for the screened regime

$$\eta^*(\omega) \sim \omega^{-2/(2+d_f)} \tag{3}$$

With our SANS values $d_f \approx 3$ in a pure μ-network melt or $d_f \approx 2.5$ in the Θ state, we should obtain values for the frequency always larger than −0.5, which is our limiting exponent without any entanglement influence.

Although we have both a scaling of structure *and* internal dynamics, these two properties are apparently not related by eq 3. This may be due to the fact that the radial density function and the spatial connectivity of a network are rather different properties: the first is measured by SANS; the second is relevant for all transport properties. Therefore, an examination of the validy of the fractal description of networks is becoming more complicated. We cannot even exclude that the whole treatment is unappropriate to be applied to our system and possibly to all systems beyond the gel point. At this state of the art, a simple Rouse treatment leads to a better correspondence. The theory of Martin and Eichinger,[18] which also includes transport properties of cyclic structures, cannot be tested because the pronounced deviations from Rouse behavior are within our experimental uncertainty.

Table III
Diffusion Coefficients D (in 10^{-11} cm^2•s^{-1}) of Labeled PS Chains in μ-Network

	P_N of labeled chain			
	79	291[a]	322	725
linear PS[b]	17.7	1.7	2.3	0.45
N2800/141	16.0	1.9	2.3	0.41
N5900/59	16.8	1.6	1.9	0.33
N1100/24	15.0	1.7	2.1	0.37

[a] Labeled at both ends. [b] Reference matrix with $M_w \approx 110\,000$ g/mol, $M_w/M_N < 1.05$.

As already mentioned, diffusion measurements are a second tool for studying the entangled nature of a polymer melt. With these experiments we have already obtained sensitive information about the topology of the environment which surrounds the observed probe chains in different networks[3,4] or even linear chains.[9] By assuming the validity of the tube model, the diffusion coefficient D of a chain is given by

$$D = D_0 \frac{M_0 M_e}{M^2} \tag{4}$$

(see ref 19) where M_0 is the molecular weight of a monomer unit, M_e that of the chain segment between two entanglements (M_e) or cross-links (M_n in analogy), and M that of the probe chain. Therefore, the diffusion coefficient should be directly proportional to the primary chain length of the μ-networks. Table III summarizes the diffusion coefficients achieved for four different probe chains with molecular weights between 8200 and 75 000 g/mol at 185 °C in three different networks and a linear reference matrix with $M_w \approx 110\,000$ g/mol. We have not corrected for the difference in T_g, which is 7 K maximum compared to the linear reference (T_g (lin) $\approx$ 376 K). Three samples are carrying one terminal dye molecule, one sample is labeled on both ends. We observe that the values of the diffusion coefficients agree within the experimental error.

This fact clearly excludes the above treatment if M_n is taken as the molecular weight of the chain between two cross-links: in that case we should expect a slowing down of the diffusion by a factor of 8. However, we have already noted above that any average contour length between two cross-links is some multiple of the primary chain length since loops and larger cyclic structures are formed in the μ-network synthesis. These cyclic structures having sizes below the entanglement spacing cause the decrease of $G'(\omega)$ below that of the plateau modulus G_N^0, as demonstrated in Figure 2–5. If we try to apply the Doi–Edwards model[20] to linear probe chain diffusion in μ-network matrices, we have to realize that the tube size is no longer given by a constant entanglement spacing as defined through M_e and G_N^0 in entangled linear chain systems. In particular, the tube disengagement time τ_d is affected by the characteristic time dependence of the environment. Thus, the expression

$$\tau_d^0 = \frac{15}{\pi^2}\frac{\eta_0(M)}{G_N^0} \tag{5}$$

for entangled linear chain systems, eq 2, should be modified by replacing G_N^0 and η_0 through frequency-dependent quantities, the first being related with the mobility of the cyclic network structures (matrix) and the second describing the dynamics of the probe (tracer). Since D is proportional to R_G^2/τ_d, chain diffusion explores the frequency dependence of the matrix on the time scale of the probe chain mobiltiy. For an estimation of the frequency regime probed by our labeled chains (Table III), we have calculated τ_d^0 using literature values of $\eta_0(M)$ and G_N^0[10,11] at 423 K. The resultant range $0.05 \leq \tau_d^0/\mathrm{s} \leq 0.5$ corresponds to shear frequencies between 12 and 125 rad·s^{-1}. Here, G' differs relatively little from G_N^0 (see Figures 2–5), which is consistent with the determined diffusion coefficients. Thus, D values for much longer probe chains should be determined in order to investigate the frequency dependence of the μ-network moduli. This is out of range of our present experimental setup and procedure but will be examined in the future.

It should be noted that slowed down diffusion of probe chains is observed in cross-linked systems obtained by copolymerization of styrene with *m*-diisopropenylbenzene in suspension. Here, the mesh size of the network can be sufficiently reduced, resulting in increased moduli and decreased diffusion coefficients.[21] These results will be discussed in a future publication.

IV. Conclusions

The dynamic behavior of polystyrene μ-networks has been examined by dynamic mechanical shear experiments. The storage modulus G', the loss modulus G'', and the dynamic shear viscosity η^* are determined in a frequency range of ω between 10^{-3} and 10^3 s^{-1} at a reference temperature of 150 °C, using the time–temperature superposition principle. The obtained mechanical responses are independent of the molecular weight of the μ-networks, which gives clear evidence that we are observing intramolecular relaxation mechanisms.

The moduli are below those of linear chains with high molecular weight and depend on the number of monomers between cross-links, which was varied between 23 and 141 monomer units. Opposite to usual networks, where we expect an increase of the storage modulus with increasing cross-linking density, G' is decreasing in the case of the μ-networks. In all cases, G' parallels G'' over 5 decades in frequency, just limited at the low-frequency side by the measuring range of the instrument. The moduli can be described by power laws $G' \sim G'' \sim \omega^\alpha$, where α increases from 0.2 to 0.5 with decreasing chain length between cross-links.

These findings support the description of μ-networks as "fractals", which was discussed during the structure examinations; however, a couple of new questions arise. From the fact that the structure is independent of cross-linking density, we would expect also an independent scaling of the internal dynamics, which is not observed in the bulk state. The results of a dilution experiment indicate that the mechanical behavior can be divided into two components. One part approximately characterized by $G' \approx G'' \sim \omega^{0.5}$ describes the internal dynamics and should be independent of molecular weight *and* cross-linking density. The second contribution is due to intracatenary interactions, "entanglements" with a scalable lifetime distribution. The weight of this entanglement contribution increases with the length of the primary chains and should predominate in the limit of very long chains. Our suggestion should be checked in more detailed dilution experiments, where the length of the solvent chains is also varied.

$\tan\delta$ is increasing with decreasing chain length between cross-links and approaches unity in the limit of short chains. Again this supports the interpretation of the μ-network dynamics in the way discussed above: the decrease of $\tan\delta$ from 1, the typical value for Rouse chains, to lower values is due to the existence of entanglements. Because of the entanglement problem, the accuracy of our experiments is not high enough to relate structure properties and internal dynamics via eq 3. We cannot decide whether the observed small deviation is due to experimental errors or—more severe—caused by a failure of fractal theory for our systems. The tracer diffusion of labeled linear PS chains is not influenced by the different matrix structure and dynamics. This is possibly due to the fact that the chains used in this examination are too short in order to reflect the relaxation of the environment. However, we find considerably slowed diffusion of chains in μ-networks prepared by suspension copolymerization, which are currently being investigated. Thus, dynamic mechanical *and* diffusion experiments in μ-network systems are suited for studying relations between internal dynamics and network topology.

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References and Notes

(1) Antonietti, M.; Ehlich, D.; Fölsch, K. J.; Sillescu, H.; Schmidt, M.; Lindner, P. *Macromolecules*, preceding paper in this issue.
(2) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(3) Antonietti, M.; Sillescu, H. *Macromolecules* **1985**, *18*, 162.
(4) Antonietti, M.; Sillescu, H.; Schmidt, M.; Schuch, H. *Macromolecules* **1988**, *21*, 736.
(5) Muthukamar, M.; Winter, H. H. *Macromolecules* **1986**, *19*, 1284.
(6) Vilgis, T. A.; Winter, H. H. *Colloid Polym. Sci.* **1988**, *266*, 494.
(7) Boue, F.; Bastide, J.; Buzier, M.; Collette, C.; Lapp, A.; Herz, J. *Prog. Colloid Polym. Sci.* **1987**, *75*, 152.
(8) Antonietti, M.; Coutandin, J.; Grütter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798.
(9) Antonietti, M.; Coutandin, J. H.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(10) McKenna, G. B.; Hadziioannou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 498.
(11) Roovers, J.; Graessley, W. W. *Macromolecules* **1981**, *14*, 766.
(12) Masuda, T.; Ohta, Y.; Onagi, S. *Macromolecules* **1986**, *19*, 2524.
(13) Chambon, F.; Winter, H. H. *J. Rheol.* **1986**, *30*(2), 367.
(14) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(15) Havranec, A.; Ilavski, M.; Nedbal, J.; Böhm, M.; v. Soden, W.; Stoll, B. *Colloid Polym. Sci.* **1987**, *265*, 8.

Macromolecules **1989**, *22*, 2817–2824 **2817**

(16) Muthukumar, M. *J. Chem. Phys.* **1985**, *83*, 3161.
(17) Vilgis, T. A. *Phys. Rev. A* **1987**, *36*(3), 1506.
(18) Eichinger, B. E.; Martin, J. *Macromolecules* **1980**, *13*, 626.
(19) de Gennes, P. G. *Scaling Concepts in Polymer Science*; Cornell University Press: Ithaca, NY, 1979.
(20) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(21) Fölsch, K. J. Dissertation, Mainz, 1988.

Order–Disorder Transition of Star Block Copolymers. 2. Effect of Arm Number

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ABSTRACT: Ordered structure, order–disorder transition, and the thermal concentration fluctuations in the disordered state were investigated by the small-angle X-ray scattering (SAXS) method, for a series of poly(styrene–isoprene) star block copolymers having a fixed molecular weight and composition for the arm diblock copolymer but a different number of arms (n = 1–18). The characteristic length $D_{\mathrm{ord}}(n,T)$ of the order parameter $\psi(\mathbf{r};T)$ in the ordered state was found to obey $D_{\mathrm{ord}}(n,T) = D_{\mathrm{dis}}(n)(T/T_{\mathrm{b}})^{-1/3}$ where D_{dis} is the characteristic length of $\psi(\mathbf{r};T)$ in the disordered state, which was found to obey $D_{\mathrm{dis}}(n,T) = f(n)T^0$, $f(n)$ being a weak function of n as seen in $q_{\mathrm{max}}(n)$ in the paper. The order–disorder temperature T_{b} and spinodal temperature T_{s} were found to be almost independent of n for $n > 2$. The SAXS profiles from the disordered state were found to be fitted quite well with the theoretical profiles given by a mean-field random-phase approximation. The analyses yielded a remarkable n-dependence of the Flory–Huggins interaction parameter χ, χ decreasing with increasing n. The analyses yielded also the values D_{dis} (defined as $D_{\mathrm{dis,exp}}$) and χ at the spinodal point (defined as $\chi_{\mathrm{s,exp}}$). These values were compared with the corresponding theoretical values $D_{\mathrm{dis,theor}}$ and $\chi_{\mathrm{s,theor}}$; $\chi_{\mathrm{s,theor}} \simeq \chi_{\mathrm{s,exp}}$ and $D_{\mathrm{dis,exp}} \simeq 1.1\ D_{\mathrm{dis,theor}}$, irrespective of the value n.

I. Introduction

Experimental and theoretical investigations of the thermal concentration fluctuations of the constituent components for the two-component polymer systems, polymer A and polymer B, are one of the important subjects in condensed-state polymer physics.[1-18] The main interests involve the exploration of the effects of chemical connectivity on the fluctuation spectra or, in more general sense, on the physics of cooperative phenomena.

Here in this paper we deal with two kinds of *connectivity*, (i) the connectivity of monomers A and B in polymers A and B (the "first-kind connectivity") and (ii) the connectivity of different polymers A and B (the "second-kind connectivity"), giving rise to A–B type linear block polymers,[2-4,7-9] grafted polymers,[6,8] and star block copolymers.[6,8] It has been found that the latter connectivity generates the dominant mode of the concentration fluctuations with a wavenumber $q = q_{\mathrm{max}}$ other than zero in both the ordered and disordered state. The connectivity induces the thermodynamic instability[3] also at $q \neq 0$. The growth of the dominant mode of the fluctuations with $q_{\mathrm{max}} \neq 0$ is known traditionally as "microphase separation" or recently "microphase-separation transition"[3] or "order-disorder transition",[11] in contrast to the ordinary liquid-liquid phase transition for the mixtures of polymers A and B, which causes the growth of the fluctuations with $q_{\mathrm{max}} = 0$. Thus, this kind of the order–disorder transition is a unique cooperative phenomenon inherent to polymer systems.

In this paper we further focus our interests on the effects of the second-kind connectivity on the spectra of the spatial concentration fluctuations of A and B monomers at thermal equilibrium by selecting a series of star block copolymers as a model system. The starblock copolymers were prepared by chemically connecting a poly(styrene–isoprene) diblock polymer with a given total polymerization index and a given fraction of styrene and isoprene where the polystyrene block was the outer segments. We studied a series of copolymers having different arm numbers n by small-angle X-ray scattering (SAXS) and analyzed the order parameter ψ (the concentration fluctuations of the constituent monomeric units) both in the ordered and disordered states as well as the order–disorder transition as a function of n. The fluctuation spectra in the disordered state will be compared with those predicted by a current theory of a mean-field random-phase approximation, first presented by de la Cruz and Sanchez[6] and later by others.[8,18]

Our analyses are restricted to the mean-field approach. A more general analysis including nonclassical effects (Brazovskii effect) as suggested first by Leibler[3] and calculated by Fredrickson and Helfand[19] for diblock copolymers will be very important. However, that kind of a generalized analysis is beyond the scope of this paper. This work is an extension of earlier work by Fetters, Richards, and Thomas[20] on the composition dependence of the fluctuations of the star block copolymers in the disordered state and by Hashimoto, Ijichi, and Fetters[18] on star block copolymers with n = 1 and 6.

This paper is constructed as follows. We first describe experimental methods (section II), theoretical background (section III), and some selected typical experimental results (section IV). We then present some theoretical interpretations on the fluctuations in the ordered state (section V-A), the fluctuation spectra in the disordered state (section V-B), the estimated Flory–Huggins thermody-

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