Macromolecules **1988**, *21*, 736–742

Solution Properties and Dynamic Bulk Behavior of Intramolecular Cross-Linked Polystyrene

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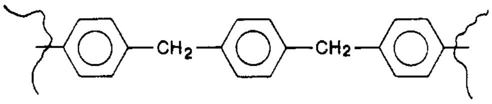
ABSTRACT: Linear Polystyrene (PS) molecules were intramolecularly cross-linked with *p*-bis(chloromethyl)benzene in dilute solution. The resulting "microgels" were characterized in solution by static and dynamic light scattering, GPC, and viscosity measurements. We find a surprisingly small reduction of the radius of gyration and the hydrodynamic radius even for highly cross-linked PS molecules having molecular weights up to 5×10^5 and an average number of $P_c = 20$ monomer units between cross-links. Dynamic mechanical measurements in samples having $P_c \geq 10$ yield no change of the plateau modulus in comparison to the linear molecules but a broadening and shift to lower frequencies of the terminal zone if compared with linear PS. Furthermore, we find that the product of the self-diffusion coefficient and the zero-shear viscosity is constant, and the diffusion of PS chains in a matrix of microgels is independent of the cross-link density. Various explanations are discussed, but no decision for a particular model (describing all experimental results) can be made.

Introduction

In attempts to relate dynamic polymer properties with molecular motion, various tube models have become very successful.[1,2] The essential idea of reptation, namely, that curvilinear motion along the contour of a polymer chain becomes predominant for entangled very long-chain systems, seems to be experimentally well established.[1,3] However, dynamic mechanical and diffusion studies in polymer systems containing short and moderately long-chain, star-branched, or ring-shaped macromolecules have led to yet unsolved problems which require modification of the reptation picture and a consideration of nonreptative modes of polymer motion.[4-10] In particular, star and ring polymers up to relatively large molecular weights have viscosities and diffusivities that differ from the reptation model.[6,7,9,10]

In order to study nonreptative models of macromolecular motion, we have investigated the diffusion of intramolecular cross-linked polystyrene (PS) molecules in various bulk PS matrices.[6] We use the short-hand notation *microgel* (μ-gel) for intramolecular cross-linked chains though we know little of their structure. The self-diffusion coefficients D of μ-gels were found to be smaller than those of ring molecules and to decrease on increasing the cross-link density. For the largest μ-gel ($M_w = 160000$, $P_c = 20$ monomers between cross-links), we found a D value smaller by a factor of 20 than that of the parent linear molecule but still larger than that of three-arm star PS of the same molecular weight in a μ-gel matrix.[6] The diffusion of μ-gels in matrices of linear PS is also similar to that of rings. In the limit of long matrix chain lengths, the μ-gel D values reach a constant value, which agrees with D in a μ-gel matrix.[6] The same behavior has also been found for the diffusion of PS rings in linear PS where the asymptotic values in μ-gel matrices have recently been measured by using the forward recoil scattering technique.[11]

The purpose of the present paper is twofold. First, we wish to gain more information on the structure of the μ-gel molecule. Friedel–Crafts cross-linking with *p*-bis(chloromethyl)benzene[12] results in a rather flexible cross-link



which should allow for sufficient segmental chain flexibility. However, we only know the average number P_c of monomers between cross-links and not their distribution. It is known from the kinetic studies of Grassie and Gilks[12] that the first step of attaching a cross-linker to the chain is slower than the second step forming the cross-link. Thus, we can assume that the slow step leads to a random distribution of cross-linkers. In the second step, however, the remaining chloromethyl group can react with any PS phenyl group along the chain. It is unknown whether nearby phenyl groups are preferred for some reason which would lead to a preference of small rings. This was suggested by Martin and Eichinger[13] who have investigated dynamic light scattering of PS μ-gels in a Θ solvent and have found only marginal size reductions. That observation was in contrast to earlier work[14] where the cross-linking reaction was only possible between precursor sites distributed randomly along the PS chain, and the resulting large reduction of the random coil size was in approximate agreement with theory.[14] Below, we report results of static and dynamic light scattering, viscosity, and GPC measurements in a good solvent. We have chosen the average cross-link density higher than in the previous measurements in order to force any initially formed small rings into further cross-linking. Furthermore, we wish to combine our diffusion results with dynamic mechanical measurements where the frequency-dependent shear moduli G' and G'' provide important information on molecular motion, and the zero-shear limit viscosity η_0 is closely related with D in the reptation and in the Stokes–Einstein model.[1] In the end, we wish to contribute to better understanding of macromolecular motion in bulk polymers by investigating model molecules where the internal structure or topology

Table I
Characterization of Polystyrene Samples

sample	P_n[a]	M_w/M_n	P_c[b]	T_g/°C[c]	ΔT_g/°C
I	160	1.07	20	101	9
II	280	1.08	20	107	9
III	595	1.08	20	106	9
V	1290	1.07	20	107	9
VI/1	1810	1.03	lin	102	8
VI/2	1810	1.09	20	108	9
VI/3	1810	1.14	10	114	9
VI/4	1810	1.40	6	134	11
VII/1	940	1.03	lin		
VII/2	940	1.04	20		
VIII/1	4300	1.07	lin		
VIII/2	4300	1.17	20		
IX/1	1600	1.02	lin		
IX/2	1600	1.04	160		
IX/3	1600	1.06	80		
IX/4	1600	1.08	40		
IX/5	1600	1.09	20		
IX/6	1600	1.14	10		

[a] P_n is the degree of polymerization of the linear precursor polymer determined by GPC. [b] P_c is the average number of monomers between cross-links as determined by the weighed quantity of p-bis(chloromethyl)benzene. [c] T_g is the glass transition temperature determined as an average of the heating and cooling curve with the width ΔT_g.

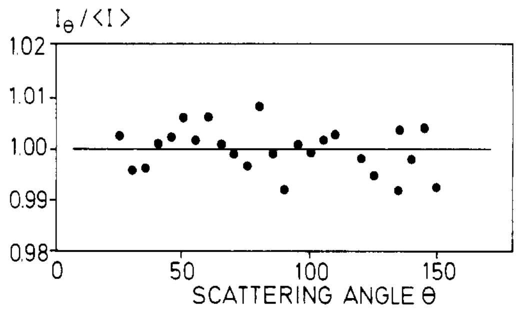


Figure 1. Angular dependence of the scattering intensities I_θ for toluene, normalized by the intensity I averaged over all angles. The intensities I_θ are volume corrected, i.e., multiplied by sin θ.

can be easily modified in a well-defined fashion. PS μ-gels have the advantage that they can easily be prepared in sufficient quantities from essentially monodisperse linear parent molecules. In addition, they are promising candidates to model network behavior with all advantages of a molecular structure avoiding the enormous handling difficulties of macroscopic model networks.

Experimental Section

1. **Synthesis of PS Microgels.** Intramolecular cross-linking of PS was performed essentially in the same fashion as described previously.[6,15] However, we avoided the presence of oxygen during the cross-linking reaction by rinsing the system with nitrogen. This way, we could reduce by a factor of about 10 the intensity of a peak at 242 nm in the UV spectrum of the μ-gels in solution, the origin of which is not yet resolved. Martin and Eichinger[13] have attributed this peak to unreacted CH_2Cl groups in contrast to the finding of Grassie and Gilks[12] that no residual CH_2Cl groups remain. We also could detect no Cl in an elementary analysis and no CH_2Cl groups by performing the dye-labeling reaction[15] which is even more sensitive. We have also confirmed that the cross-linking reaction with p-bis(chloromethyl)benzene is quantitative by determining the number of cross-links from UV spectra calibrated with poly(p-methylstyrene) standards. Most of the dimer and "multimer" μ-gels formed by intermolecular cross-linking were removed by twice-repeated fractionation with tetrahydrofurane/methanol mixtures. The alternative of cross-linking in extremely dilute solution[13] implies the danger of impurity reactions. We have kept the PS concentrations above 0.1 wt % and have checked by GPC (see Figure 2) that the amount of multimers is small after fractionation. It should be noted that the increase of the glass transition temperature T_g is less than half of the increase found for corresponding cross-linking densities in PS networks made by copolymerization of styrene and divinylbenzene.[16] This can be understood by considering the high flexibility of our cross-links (see above) as compared with the one rigid phenylene group linking two PS chains in the copolymer network. In table I, we have listed the samples studied in the present investigation as characterized by GPC and DSC.

2. **Viscosity Measurements in Solution.** The viscosity measurements were performed in toluene at 20.0 °C with an automatic Schott AVS300 instrument which allows the determination of the flow time with the accuracy of ±0.01 s. The flow times were determined in an Ubbelohde viscosimeter for six to nine concentrations ranging from 2 to 10 mg/mL.

3. **Light Scattering.** Simultaneous static and dynamic light scattering measurements were performed with a commercially available spectrometer consisting of an ALV-SP81 goniometer and an ALV-3000 correlator. A krypton ion laser (Spectra Physics, Model 2025) operating at 647.1-nm wavelength was used as the light source. The samples were dissolved in freshly distilled, sodium-dried toluene at concentrations from 1 to 8 mg/mL. The solutions were clarified from dust particles by ultracentrifugation in a Beckman L8-55M ultracentrifuge equipped with a SW28 swinging bucket rotor, applying a special floating technique with cesium chloride as the density agent.[17] The centrifugation time varied from 1.5 to 2 h at 15 000 rpm corresponding to 20 000 g.

In dynamic light scattering, the time correlation function of the scattering intensity $g_2(t)$ is measured which usually is converted to the electric field correlation function $g_1(t)$ via the Siegert relation

$$g_1(t) = [(g_2(t) - A)/A]^{1/2}$$

with A the experimentally determined base line. The correlation function $g_1(t)$ was analyzed according to the method of cumulants[18]

$$\ln g_1(t) = -\Gamma t + \tfrac{1}{2}\mu_2\Gamma^2 t^2 - \tfrac{1}{3}\mu_3\Gamma^3 t^3 + \ldots$$

with $\Gamma = -(\mathrm{d} \ln g_1(t)/\mathrm{d}t)_{t\to 0}$. Γ is called the first cumulant; μ_2 and μ_3 measure the deviation from a single exponential decay. Extrapolated to zero angle, the reduced first cumulant Γ/q^2 yields the z-average translational diffusion coefficient D_z where $q = 4\pi/\lambda \sin(\theta/2)$ is the scattering vector with λ the wavelength in the medium and θ the scattering angle. To all correlation functions, a second-order cumulant fit was applied, since the deviation from a single exponential decay was generally small.

The reduced scattering intensities Kc/R_θ were derived according to standard procedures, using toluene as the reference with known absolute scattering intensity. Moreover, the angular dependent scattering intensities of toluene were determined in order to check the calibration of the instrument. Figure 1 shows a typical example of the volume-corrected scattering intensities for angles from 20° to 150°. No angular dependence of the scattering intensity of toluene is observed, as expected.

The reduced scattering intensities were plotted and evaluated as proposed by Berry[19] (i.e., $(Kc/R_\theta)^{1/2}$ versus c). The refractive index increment was taken from the literature[20] as $\mathrm{d}n/\mathrm{d}c = 0.106$ mL/g.

4. **Dynamic Mechanical Measurements.** The PS samples, obtained by preciptatation from solution, were carefully dried overnight in vacuo at 80 °C. By compression molding at 150 °C, samples were prepared fitting the geometry of a cone and plate rheometer with a 7.5° cone angle and 20-mm radius. An Instron 3250 apparatus was used in an oscillating low-amplitude mode operating in a frequency range between 0.001 and 200 s^{-1} with an amplitude of 1.5%. A Solartron 1172 frequency response analyzer was used for controlling the measurement and recording the complex torque. During the measurements, performed at 150 and 170 °C, a stream of dry nitrogen was blown over the sample for protection. In order to avoid misinterpretations caused by thermal oxidative damage, one of the controls was to repeat the high-frequency range after long time experiments. The maximum increase remains within the range of 20%.

5. **Diffusion Measurements.** Diffusion coefficients of labeled PS molecules were measured by using the holographic grating technique and the o-nitrostilbene dye label as described in our previous publications.[15,21]

Table II
Characterization of Polystyrene Samples by Static and Dynamic Light Scattering

sample	$M_w/10^3$ g mol^{-1} (GPC)	$M_w/10^3$ g mol^{-1} (LS)	$\langle s^2\rangle_z^{1/2}$/nm	$R_h{}^a$/nm	$A_2/10^{-4}$ mol cm^3 g^{-2}	$k_b{}^b$/cm^3 g^{-1}	$[\eta]$/dL g^{-1}	$k_H{}^c$/cm^3 g^{-1}
VII/1	101	94 ± 2		8.17 ± 0.1	5.22	27	0.433	0.445
VII/2	103	103 ± 2		8.36 ± 0.1	5.0	29	0.413	0.406
VIII/1	460	433 ± 10	28.5 ± 1.5	18.46 ± 0.1	3.57	76	1.280	0.344
VIII/2	550	506 ± 10	28.0 ± 1.5	19.34 ± 0.2	2.9	69	1.224	0.337

[a] $R_h \geq \langle 1/R_h\rangle_z^{-1} = kT/6\pi\eta_0 D_z$. [b] $D_z(c) = D_z(c{=}0)(1 + k_b c)$. [c] $(\eta - \eta_0)/\eta_0 c = [\eta](1 + k_H c)$.

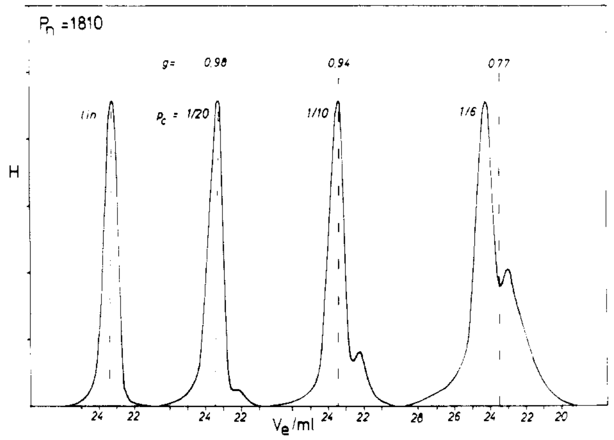


Figure 2. GPC curves of the samples VI/1–VI/4. The Zimm–Kilb factors g are calculated for the shift of the peak maximum by using universal calibration.

Results and Discussion

1. Solution Properties and Microgel Structure. In Figure 2, GPC curves are shown for some samples (see Table I), a linear parent PS of P_n = 1810 and the corresponding μ-gels with P_c = 20, 10, and 6 monomers between cross-links. The vertical dashed line represents the maximum of the curve for the uncross-linked polymer. The second peak and shoulder emerging on the right of the μ-gel curves indicate the presence of dimers and multimers due to intermolecular cross-linking. The shift of the main peak with respect to the dashed line is caused by the size reduction of the μ-gels. Using universal calibration,[22] one can calculate the Zimm–Kilb factor[23] $g_{ZK} = [\eta]_c/[\eta]_e$ where $[\eta]_c$ and $[\eta]_e$ are the intrinsic viscosities of the cross-linked and linear PS, respectively, which should be proportional to the hydrodynamic volumes of these molecules.

Viscosity and light scattering (LS) experiments have been performed with toluene solutions of PS samples having molecular weights (MW) of 10^5 and 5 × 10^5, respectively, the latter being sufficiently large for LS determination of the radius of gyration $\langle s^2\rangle^{1/2}$ in addition to the hydrodynamic radius R_h and M_w. For comparison the static and the dynamic LS measurements of the 5 × 10^5 molecular weight samples are shown in Figures 3 and 4, respectively, (a) always denoting the linear and (b) the cross-linked samples. The complete results are listed in Table II for linear and cross-linked (P_c = 20) PS. The average MW of the cross-linked samples is significantly increased, which obviously originates from the small contribution of intermolecular cross-linking also seen in the side peak of the GPC curves, cf. Figure 2. Qualitatively, the increased polydispersity of the cross-linked samples is also observed in dynamic LS where the correlation functions show larger deviations from the exponential than for linear PS. We also believe that the increase of R_h on cross-linking (see Table II) is caused by the intermolecular reaction product. In order to estimate the contraction of R_h on pure intramolecular cross-linking, we have performed the following simple calculation: (1) Assume that the high MW-fraction consists of two coupled chains, only. (2)

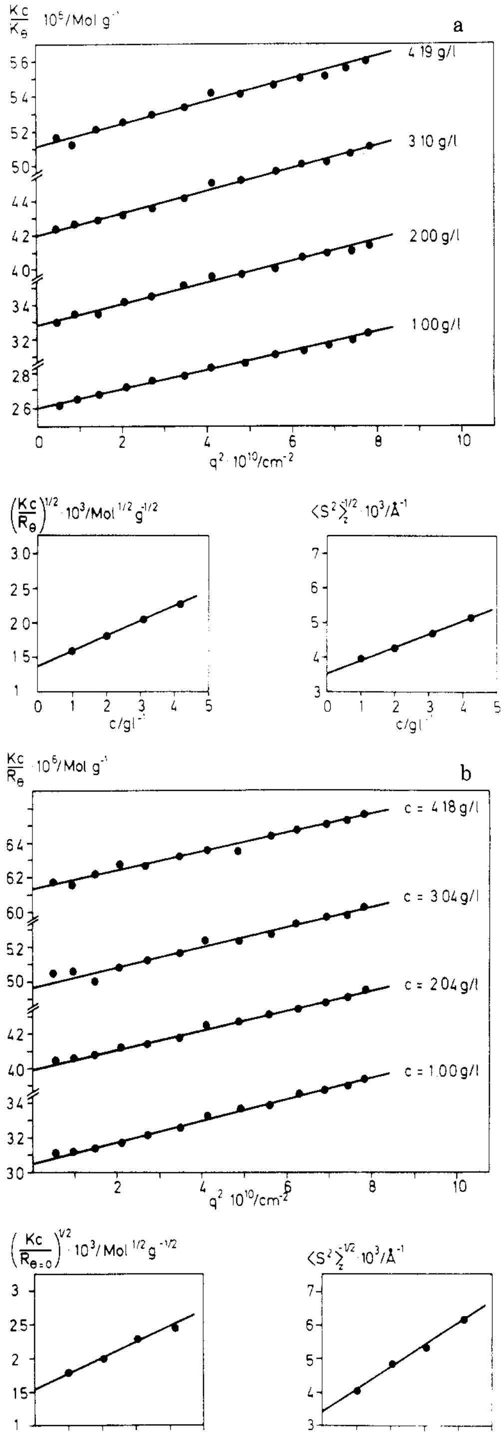


Figure 3. Zimm and Berry plots[2b] of the static scattering intensities for the linear (a) and cross-linked samples (b) VIII/1 and VIII/2, respectively.

Table III
Dimensions of Linear and Cross-Linked Polystyrene Molecules Corrected for Polydispersity (See Text)

sample	$M_w/10^3$ g mol^{-1}	x_1	R_h/nm	$\langle s^2\rangle_z^{1/2}$/nm	$[\eta]$/dL g^{-1}	$Q^a/10^8$
VII/1, calcd	100.5	0.93	8.53		0.455	1.946
VII/2, measd	103	0.93	8.36		0.413	1.938
VIII/1, calcd	494	0.86	20.08	32.8	1.41	2.049
VIII/2, measd	506	0.86	19.34	28.0	1.22	2.046

[a] $Q < \phi^{1/3} = (M[\eta])^{1/3}/R_h$.

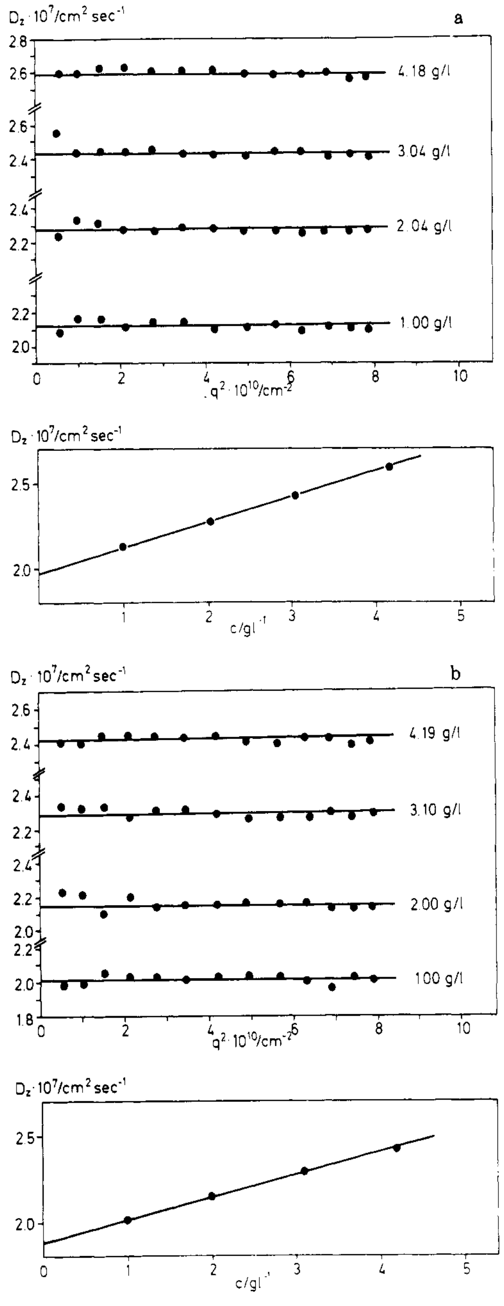


Figure 4. Angular and concentration dependence of the reduced first cumulant Γ/q^2 as measured by dynamic light scattering for the linear (a) and cross-linked samples (b) VIII/1 and VIII/2, respectively.

Table IV
Contraction of Polystyrene on Cross-Linking

sample set	$g^{1/2\,a}$	h^b
VII		0.980
VIII	0.853	0.963

[a] $g = \langle s^2\rangle^{(\mu\text{-gel})}/\langle s^2\rangle^{(\mathrm{lin})}$. [b] $h = R_h^{(\mu\text{-gel})}/R_h^{(\mathrm{lin})}$.

Correct the MW of the cross-linked samples for the portion of cross-linking agent, which will not contribute to the contour-length of the chain, hardly influencing the dimensions. (3) Calculate the mass fraction of intermolecularly cross-linked chains from the difference in MW from

$$M_w = x_1 M_1 + (1 - x_1)2M_1$$

where M_1 is the MW and x_1 the mass fraction of the precursor polymer. Approximately the same x_1 is obtained from the GPC elugrams. (4) Calculate the hydrodynamic and geometric dimensions of the linear polymer with the same fraction $(1 - x_1)$ of molecular weight $2M_1$, according to

$$\langle 1/R_h\rangle_z = \frac{x_1 M_1/R_h(M_1) + (1 - x_1)2M/R_h(2M_1)}{x_1 M_1 + (1 - x_1)2M_1}$$

$$\langle s^2\rangle_z^{1/2} = \left[\frac{x_1 M_1\langle s^2\rangle(M_1) + (1 - x_1)2M_1\langle s^2\rangle(2M_1)}{x_1 M_1 + (1 - x_1)2M_1}\right]^{1/2}$$

$$[\eta] = x_1[\eta](M_1) + (1 - x_1)[\eta](2M_1)$$

The unknown quantities $R_h(2M_1)$, $\langle s^2\rangle(2M_1)$, and $[\eta](2M_1)$ can be evaluated from the exponents a_X of the known relations[23-25] $X = \text{const} \times M^{a_X}$ with $a_X = 0.574$, 0.605, and 0.788 corresponding to $X = R_h$, $\langle S^2\rangle^{1/2}$, and $[\eta]$, respectively. Thus, $X(2M_1) = 2^{a_X}X(M_1)$

In Table III these polydispersity-corrected properties of the linear chains are now compared to the measured properties of the cross-linked polymer. It is clearly seen that the effect of cross-linking on the hydrodynamic and geometric dimensions is very small and almost within the experimental error, except for the intrinsic viscosity measurements. This could be expected, since $[\eta] = \phi R_h^3/M$ provided ϕ remains constant. As seen from almost constant Q values ($Q = M[\eta]^{1/3}/R_h$) in Table III, the change in the viscosity exactly matches the change in R_h^3, which demonstrates the consistency of the present measurements. The increase of Q with increasing molecular weight is generally expected for polymers in a good solvent and originates from the molecular weight dependence of the excluded volume. Defining the contraction of $\langle S^2\rangle$ and R_h on cross-linking by the ratios g and h as given in Table IV,[27-29] we see that the size of the μ-gels is, indeed, somewhat reduced in comparison with the linear parent PS molecules, and the reduction increases with increasing molecular weight. Although the experimental accuracy of g is rather poor, our data suggest that $g < h^2$. This could be expected, since the ratio g/h^2 is known to depend on the topology of the polymer chain. As mentioned earlier, Martin and Eichinger[13] investigated a similar system of intramolecular cross-linked polystyrene of $M_w = 500\,000$ and reported an h factor of $h \approx 0.94$, somewhat smaller than our value of 0.963 given in Table III. However, their data were measured under Θ conditions and cannot be quantitatively compared to the present data. It is remarkable that Martin and Eichinger[13] found the h-factor almost independent of the number of cross-links in a range of $10 \leq m \leq 100$ which corresponds to $250 \geq P_c \geq 25$ monomers between cross-links. The value of $P_c = 20$ chosen in our LS experiments compares with their highest

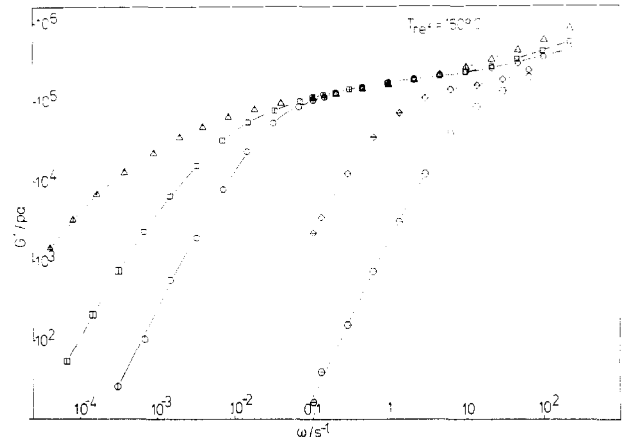


Figure 5. Storage modulus $G'(\omega)$ of bulk polystyrenes measured at 150 °C (symbols with horizontal bar) and 170 °C (symbols with vertical bar), respectively. (○) sample II; (◇) III; (○) VI/1; (□) VI/2; (△) VI/3.

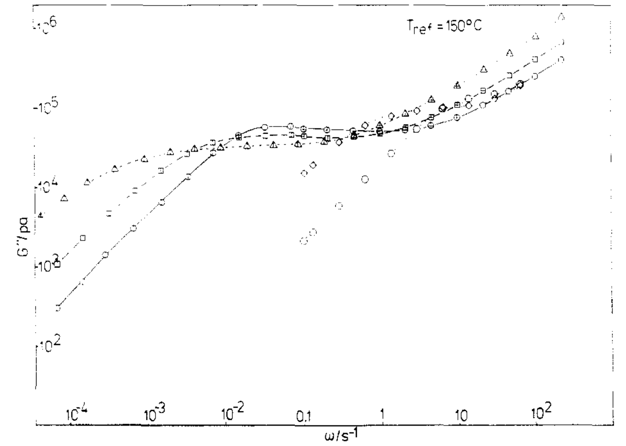


Figure 6. Loss modulus $G''(\omega)$ (legend, see Figure 5).

cross-link density. The Zimm–Kilb factors g_{ZK} shown in Figure 2 for smaller PS molecules (M_w = 194 000) indicate that much higher cross-linking is necessary in order to achieve larger size reductions. However, this would imply higher contributions of dimers and multimers, unacceptable for LS analysis. It should be noted that we have listed in Table II and the LS second virial coefficient A_2 and the constants k_D and k_H characterizing and the concentration dependence of dynamic LS and viscosity, respectively. Though small changes caused by cross-linking were observed, no interpretation can be given at present.

It is rather puzzling why the considerable amount of intramolecular cross-linking by *p*-bis(chloromethyl)benzene has such a small effect upon the coil size in solution whereas cross-linking of precursor sites distributed at random along the chain produces the expected large size reduction.[14] The formation of small rings as suggested by Martin and Eichinger[13] cannot be excluded. With Stuart models, we could make the smallest tension-free ring from five styrene units. However, it is hard to conceive why such rings should not be knitted to networks for high cross-link densities, in particular, since macroscopic networks are easily formed at higher concentrations by intermolecular cross-linking.[12,15] A more extensive discussion will be given in the next section.

2. Dynamic Mechanical Measurements. The storage modulus G', the loss modulus G'', and the dynamic viscosity η^* are shown in Figures 5–7 for some samples of linear and intramolecular cross-linked PS. The usual temperature frequency shift procedure[30] was applied in order to combine measurements at 150 and 170 °C to the common reference temperature of 150 °C. Of particular interest is the comparison of a linear polymer (M_w = 194 000) with corresponding μ-gels having different degrees of cross-linking (P_c = 10 and 20). In the high-frequency range, G' and G'' of the μ-gels are shifted to lower frequencies with respect to the curves of linear PS. This shift can be partly explained by the increased glass transition temperatures T_g of the μ-gels. The T_g shifts of 6 and 12 K given in Table I for the μ-gels with P_c = 20 and 10, respectively, correspond to frequency shifts of log ω = 0.2 and 0.7, which accounts for most of the G' and G'' differences in the transition zone, cf. Figures 5 and 6. In addition to the shift, there is a broadening of the transition zone which is perhaps caused by the heterogeneity introduced on a local scale by the cross-links. This conclusion is supported by preliminary ^{2}H NMR results obtained in our laboratory.

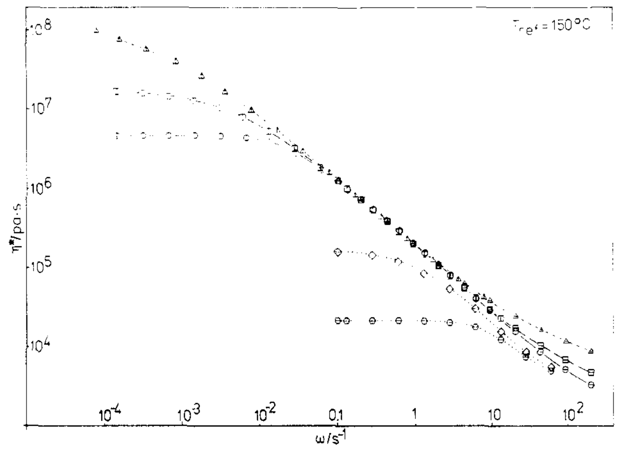


Figure 7. Dynamic viscosity $\eta(\omega)$ (legend, see Figure 5).

In the *plateau zone*, the storage modulus is not affected by cross-linking, the plateau modulus G°_N remains constant up to the high cross-link density given by the average number of P_c = 10 monomers between cross-links. Application of the most simple network assumption predicts[30]

$$G^\circ_N = \nu kT$$

ν being the number of effective network strands per unit volume. If the chemical cross-links would just add to the entanglements causing the plateau modulus in linear PS, one should expect an increase of G°_N by a factor of about $1 + P_e/P_c$ where $P_e \approx 180$ is the number of monomers between entanglements; this is an increase by a factor of 19 for P_c = 10. Surprisingly, we find no increase in our μ-gel samples whereas other workers have observed very large equilibrium shear moduli above 10^7 Pa in densely cross-linked polymers.[30,31] A possible explanation for the lack of increase of the modulus could be the formation of relatively small rings as discussed in case of the light scattering results. However, a recapitulation of results of the other model polymer topologies as star,[32] ring,[10] comb,[33] and H-shaped[34] polymers shows that the influence of chain branching or cyclization is always given by a decrease of the plateau value compared to that of an analogous linear chain.[35] Accordingly, a "multi-loop-molecule" should have a lower plateau modulus. In addition it seems not very probable that the two effects balance in a way that the modulus is independent of the cross-linking density. Edwards and Graessley have introduced the contour-length concentration to compare the plateau values of different polymer systems.[38] However, within this description it is also not straightforward to understand why different polymer topologies show a different behavior in the plateau region. An alternative view is that the conception of en-

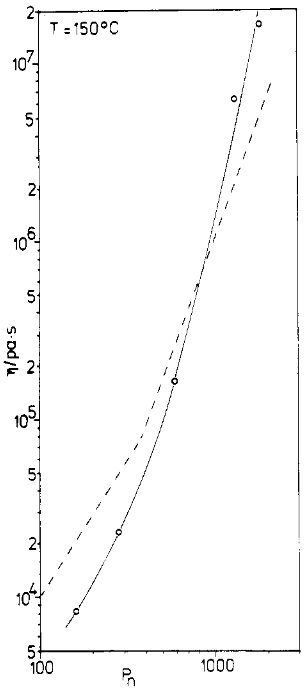


Figure 8. Extrapolated values of the zero-shear viscosity η_0 at 150 °C versus the degree of polymerization P_n for the samples I, II, III, V, and VI/2. The viscosity of the sample I is shifted according to its different glass transition temperature. The shift parameters and values of analogous linear chains represented by the dashed line are taken from ref 9. T_g differences of the full and the dashed curve due to the different T_g's are not taken into account (see Table I).

tanglements acting as physical cross-links in a network of independently moving Gaussian chains only applies to length scales above the entanglement spacing $P_e^{0.5}a_0$ where a_0 is the monomer size. If the entanglement coupling is viewed as a cooperative multichain phenomenon,[36] it is possible that any "wriggling motion"[37] within distances smaller than the entanglement spacing is just slightly affected by *flexible* cross-links. In this view the elastic response of polymer melts is seen as a cooperative process of many chains, and in certain limits (such as small distances between cross-links) network theories working with monocatenar Gaussian springs should not be applicable. A more detailed discussion of this problem is prohibited by the restricted data set. Further tests will include dynamic light scattering experiments in the bulk state and other networks having different topologies in order to avoid possible peculiarities of our present systems. Thus, we are studying permanent and ionomer networks prepared by ionic polymerization and networks obtained by emulsion polymerization. First results indicate that the usual picture of a rubberlike entanglement network is too simple and may not be applicable in all cases.

The *terminal zone* shown at frequencies $\omega < 0.1\ s^{-1}$ in Figures 5–7 is shifted to lower frequencies with increasing cross-linking. Though the molecular weight distribution remains narrow (see Figure 1) the transition from elastic to viscous behavior becomes very broad for the μ-gel samples (from one-half to more than two decades in frequency). A similar broadening has been observed in samples of star, ring, and H-shaped polymers.[10,32–34] The broadened terminal zone indicates motional heterogeneities on a size scale of a polymer molecule possibly caused by different conformations or by local environments. However, these heterogeneities have no influence on the diffusion experiments since the longest terminal relaxation times are much smaller than the times for diffusion over distances

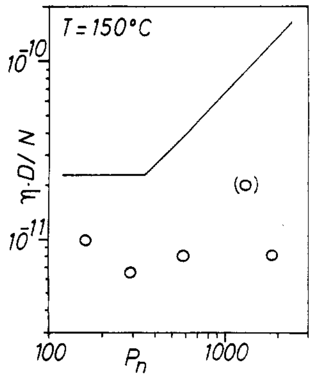


Figure 9. Plot of the product ηD versus the degree of polymerization shifted to 150 °C. The full line indicates the behavior of linear chains.

set by the holographic grating technique. Since we find exponential forced Rayleigh scattering decay curves[6] we can be sure that all μ-gel molecules move with the same diffusion coefficient when averaged over lengths of the order of the grating distance $d < 300$ nm.

In Figure 8, we have compared the zero-shear viscosity η_0 of five μ-gel samples having $P_c = 20$ (see plateau values in Figure 5) with η_0 of linear PS at 150 °C. The differences are more pronounced than between ring-shaped and linear PS where η_0 for rings is only slightly smaller at low and possibly larger at high M_w (see ref 10 and 11). More instructive is the consideration of the product $\eta_0 D$, where D is the self-diffusion coefficient. Since D has been measured at 194 °C, we have calculated the values at 150 °C using the WLF equation[30] with $c_1 = 13.7$ and $c_2 = 48$ K determined from viscosities in linear PS.[39] The product $\eta_0 D$ should be independent of the monomer friction factor which may depend somewhat upon the density and the molecular weight.[40] For the PS μ-gel samples, Figure 9 shows that η_0D remains constant over the M_w range of almost one decade. If our result is compared with the Stokes–Einstein expression, $D\eta_0 = kT/6\pi r_{\mathrm{eff}}$, one obtains an effective radius of $r_{\mathrm{eff}} = 0.24$ nm for the largest μ-gel having $M_w = 194\,000$. This is remarkably small if compared with the bulk sphere radius $r = 4$ nm of a corresponding "collapsed" μ-gel. The small r_{eff} reflects the high flexibility of the μ-gels which could alternatively be described by some "local" viscosity smaller than η_0. The constant $D\eta_0$ clearly excludes reptative μ-gel diffusion since $D\eta_0$ should then be proportional to M as indicated by the full line in Figure 9.

3. Chain Diffusion in a Microgel Network. In the Doi–Edwards theory of entangled chain systems the self-diffusion coefficient D is given by[1,2]

$$D = N_e l^2 / N^2 \tau_0$$

where l is the size of an elementary unit and τ_0 the time constant to move it. N^2 reflects the size dependence of the mobility and is a probe-specific parameter. Therefore the matrix influence is represented by N_e. With the setting (ρ being the density)

$$G^\circ_N = \rho RT/M_e$$

N_e is proportional to the inverse of the local compliance, or the elasticity of the local environment which surrounds the probe chain. Hence diffusion measurements should be a sensitive possibility to detect small differences of the local compliance. In a network with P_c monomers between cross-links, we should expect that D becomes inversely proportional to $1/P_c + 1/P_e$ if entanglements are treated as physical cross-links. In Figure 10 we have compared this expectation with experimental results obtained for the

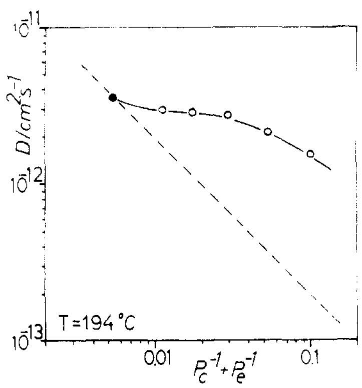


Figure 10. Diffusion coefficients of a linear polystyrene chain with M_w = 103 000 g/mol within five different μ-gel environments IX2–6 and the linear reference IX 1 (full symbol). The dashed line represents the expectation calculated from the tube model.

diffusion of linear labeled PS chains with M = 103 000 g/mol in five different μ-gel matrices (IX 2-6) with $160 \geq P_c \geq 10$ at 194 °C. The small decrease of D at high cross-linking can be related with reduced segment mobility due to the increased glass transition temperature T_g, cf. Table I. The lack of decrease of D in μ-gel networks parallels the lack of increase of the plateau modulus G°_N discussed above, cf. Figure 5. The same behavior was found in our previous publication for chain diffusion in highly cross-linked μ-gel and continuous networks. Furthermore, the crossover from reptative (DP_n^{-2}) to Rouse-like (DP_n^{-1}) scaling behavior occurs at $P_n \approx P_e$ even in a network having $P_c \ll P_e$, see Figure 2 of ref 5. In experiments with singly and doubly labeled short chains we have shown that this crossover is no artifact of chain labeling.[41] Thus, we find that the tube size of the Doi–Edwards model is given by the entanglement length irrespective of further chemical cross-linking. Currently we are preparing differently cross-linked networks in order to examine the influence of the network topology to show whether this behavior is universal for PS networks or some pecularity of the systems treated here.

Conclusions

Investigations of structural and dynamical properties of PS microgels have revealed surprisingly small changes in comparison with linear PS even for large cross-link densities where the average number of monomers between cross-links is only P_c = 10. The assumption that a high proportion of small rings is formed in the Friedel–Crafts cross-linking reaction[13] can explain some experimental results but leaves too many open questions. Since the smallest tension-free ring (from Stuart models) needs five styrene units, the assumption of having these rings along the chain implies a random copolymer

where the chain length is reduced to 50% of the non-cross-linked PS chain for P_c = 10. It is difficult to understand why only the smallest possible rings should be formed and why no intramolecular ring–ring cross-linking should occur for high cross-link densities.

The dynamic mechanical and diffusion results in molten microgel PS can be understood if we assume that the entanglement spacing P_e = 180 rather than P_c is the smallest unit determining the tube size in the Doi–Edwards model. However, this model may only be useful for describing linear polymers, and no satisfactory theory is presently available for describing cooperative motion in microgel systems.

Acknowledgment. We thank J. Mertes, BASF, Ludwigshafen, and T. Pakula, MPI für Polymerforschung, Mainz, for their friendly help during some experiments and W. W. Graessley, EXXON, Research and Engineering Company, NJ, for many helpful comments. Support by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 41) is gratefully acknowledged.

Registry No. (PS)(4-$ClCH_2C_6H_4CH_2Cl$) (copolymer), 30446-12-9.

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