on polymer networks. Further experiments on well-characterized samples are needed to test the generality of the theoretical predictions. In particular, relaxation experiments on networks in which the dangling-end distribution is known would be of significant interest.

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Appendix: Distribution of Chain Lengths

For a randomly cross-linked system, the probability Q_n of having a dangling chain end of exactly n monomers is given by[4]

$$Q_n = q(1 - q)^{n-1} \tag{1A}$$

For a lightly cross-linked system, q is simply the ratio of the cross-link density to the monomer density. In eq 8 we require the probability P_N of having a chain of $N = n/N_e$ segments. From eq 1A we can write

$$P_N = Cq(1 - q)^{N_eN-1} \tag{2A}$$

where C is a normalization constant to ensure that

$$\sum_{N=1}^{\infty} P_N = 1 \tag{3A}$$

From eq 3A we find that

$$C = [1 - (1 - q)^{N_e}]/q(1 - q)^{N_e-1} \tag{4A}$$

We now write

$$\begin{aligned}(1 - q)^{N_e} &= \exp[N_e \ln (1 - q)] \\ &\cong \exp(-N_e q)\end{aligned} \tag{5A}$$

where we have used the fact that $q << 1$. Substituting eq 5A into eq 4A and 2A leads to the desired result for large N

$$P_N \cong (e^p - 1) \exp(-Np) \tag{6A}$$

with p defined as

$$p = N_e q = N_e \rho_c / \rho_m \tag{7A}$$

For small p one can substitute integrals for summations on N and write

$$P_N \cong p \exp(-Np) \tag{8A}$$

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Self-Diffusion of Polystyrene Chains in Networks

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ABSTRACT: A holographic grating technique was applied to measuring self-diffusion coefficients D of polystyrene (PS) chains in PS networks. Friedel–Crafts cross-linking with *p*-dichloroxylylene was performed in concentrated and dilute solutions, the latter resulting in microgels of self-cross-linked macromolecules. The average number P_c of monomer units between cross-links was varied from 16 to 400. Mixtures of photolabeled linear PS and small particles of dry cross-linked PS were annealed in order to obtain dilute solutions of chains in network systems. The D values of PS chains measured in cross-linked PS at 177, 185, and 194 °C are found to be reduced by factors less than 4 relative to those in the un-cross-linked PS. The dependence of D upon the degree of polymerization P_n of the labeled PS could be described by a power law, $D \sim P_n^{-\alpha}$, where α depends somewhat upon the network preparation conditions. $\alpha = 2.07$ was found at 194 °C for $177 \leq P_n \leq 990$ in a microgel system having a network chain length P_c of 33.

Introduction

The reptation model of polymer chain motion[1] has been generally supported by self-diffusion[2-7] and dynamic mechanical[8] experiments. Inelastic neutron scattering data could be analyzed in terms of the Rouse model.[9] However, due to the limited space and time ranges accessible to this method, it is difficult to obtain sensible information upon slow whole chain motion. Numerical simulations of many-chain model systems[10] leave no doubt about reptation of a single chain in a "frozen" environment, but no reptation was found if all chains are free to move. Our current work on polystyrene (PS) chain diffusion as a function of the chain length of the surrounding matrix indicates that "tube renewal" effects are important even for chain lengths much longer than that of a relatively long diffusing chain. In order to clarify the tube concept, experiments where "fixed obstacles" are successively introduced by cross-linking should certainly be helpful. In particular, one can vary the number P_c of monomer units between cross-links and can thus test whether the number $P_e \sim 300$ of monomers between entanglements is related with the tube diameter in un-cross-linked entangled melts.

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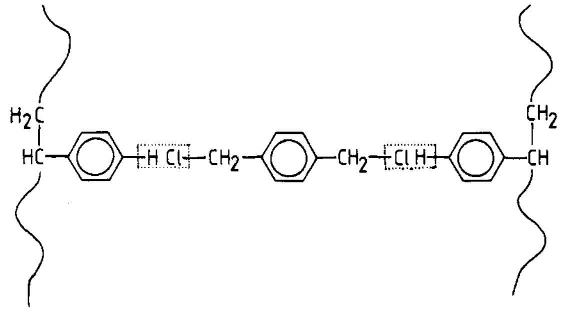
Since the network topology can be varied to a large extent by different preparation techniques, one can investigate further environmental influences upon chain diffusion. For cross-linking PS, essentially four different methods have been applied:[11-13] (1) anionic polymerization with bifunctional starters and bi- or polyfunctional termination, (2) radiation cross-linking, (3) chemical cross-linking by copolymerization of styrene and divinylbenzene, and (4) chemical cross-linking by Friedel–Crafts reaction of substituted benzenes having two chloromethyl groups in the para position with PS chains in solution.[12,13]

Friedel–Crafts cross-linking with *p*-dichloroxylylene[12] appears particularly attractive since the cross-link



is much more flexible than the phenylene cross-link from divinylbenzene. Since the PS phenyl groups should have equal probabilities of reacting with a chloromethyl group, one can expect rather homogeneous networks with a Schulz–Flory distribution of chain lengths between cross-links. Furthermore, one can perform the cross-linking at different solvent concentrations and can thus vary the network topology from the limit of self-cross-linked molecules obtained in dilute solution[13a] to the limit of entangled networks obtained in concentrated solution (see below). We give some details of our cross-linking procedures in the Experimental Section since they provide a very simple tool for preparing well-defined networks from linear PS.

The problem of dissolving chains in networks has previously been solved by preparing the networks in polymer systems where only a certain fraction of the chains carried linkable sites.[8,14,15] Thus, the networks formed around the dissolved chains. In principle, this method is applicable to PS which should be polymerized by anionic polymerization and terminated as described above (method 1) in a solution containing PS chains. However, it may be difficult to find a photolabel that is sufficiently stable during these reactions. Furthermore, any contact of the swollen gel with free solvent implies an osmotic force causing chain diffusion out of the gel. This also rules out any attempts to get chains into a gel by interdiffusion from a polymer solution. Therefore, we have chosen a method of chain diffusion into the dry gel by annealing a mechanical mixture of small gel particles with a fine powder of photolabeled linear PS. The experimental procedure is also described in the following section whereas details of the holographic grating technique are given elsewhere.[6,7]

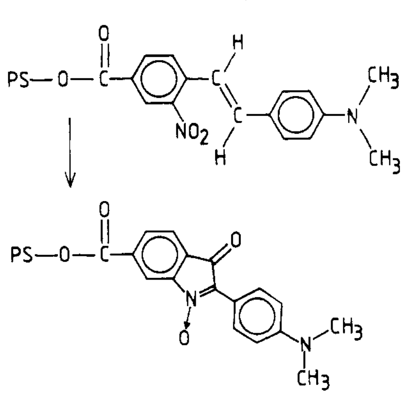
Experimental Section

1. Network Preparation. In our experiments, Friedel–Crafts cross-linking was performed in a solution of ~2 g of PS (M_w = 135 000, M_w/M_n = 1.06) in dichloroethane. Beforehand, the solvent was dried with CaH_2, and a well-defined quantity of water as one of the reactants could be added; for instance, cross-linking was performed with 5 μL of H_2O and 100 μL of $SnCl_4$ in 20 mL of solution. The dilute PS solution was first filtered through a 0.45-μm filter in order to remove dust and subsequently evaporated to the desired concentration of 20% or less by volume of polymer ($\phi_{PS} \lesssim 0.2$). The necessary quantity of twice-sublimated *p*-dichloroxylylene was dissolved at room temperature, and the solution was then heated to 60 °C. The cross-linking reaction was started by adding $SnCl_4$. The solution was stirred until gelation started after reaction times above 10 min and then kept at 60 °C for 24–72 h. The resulting soft gel was passed through a fine sieve in order to prepare well-defined particles which had an average size between 50 and 200 μm in the dry state, depending on the mesh size of the sieve. The catalyst was removed by twice treating the gel for 24 h with a mixture of 80% tetrahydrofuran and 20% 1 M HCl. The gel was then dried by precipitation from methanol and evacuation (~1 Pa) for 16 h at 175 °C. During this heat treatment, any residual CH_2Cl groups should have reacted by dehydrochlorination. However, we have also checked for residual CH_2Cl groups by performing our usual labeling reaction[6] with the Cs salt of the dye used as a photolabel at the CH_2Cl functionalized end groups of linear PS. No CH_2Cl groups could be detected in the networks by this procedure. Furthermore, we have performed the Friedel–Crafts reaction of PS with benzyl chloride, thus obtaining a random copolymer containing C_6H_5 and $C_6H_4CH_2C_6H_5$ side groups. The reaction was quantitative, and the copolymer had the same narrow M_w distribution as the parent PS (M_w = 230 000). The GPC analysis showed only 2% in a peak corresponding to $2M_w$. Thus, we feel sure that Friedel–Crafts cross-linking is free from unwanted side reactions under the conditions described above.

Friedel–Crafts cross-linking in dilute solution resulted in microgels of self-cross-linked PS molecules. Samples were prepared from PS having M_w = 135 000 and 230 000, respectively, and $M_w/M_n \lesssim 1.06$. The PS volume fraction was $\phi_{PS} = 0.01$ except for some highly cross-linked samples having P_c = 16.7 and 33.3, respectively, where $\phi_{PS} \leq 0.005$ was chosen. The GPC curves showed about 2–4% dimers in a small peak at $2M_w$ and an even smaller amount of trimers in a shoulder at $3M_w$. Measurements of the intrinsic viscosity exhibited a dramatic reduction of the hydrodynamic molecular volume for highly cross-linked molecules. The size reduction was confirmed by preliminary light scattering data, and first results of temperature-dependent ^2H NMR experiments with deuterated molecules. The much smaller size reduction found by Martin and Eichinger[13a] may be due to incomplete cross-linking under the conditions chosen in their experiments.

Macroreticular networks obtained by cross-linking with 1% and 3% divinylbenzene, respectively, were obtained from Bio-Rad (Bio-Beads SX1 and SX3). A corresponding product cross-linked with 2% divinylbenzene was obtained from Fluka (27821/x 2).

2. Sample Preparation. Photolabeled PS chains were prepared as before[6] from anionically polymerized PS, terminated with *p*-dichloroxylylene, and reacted with the Cs salt of a photosensitive acid, thus forming an ester bond. However, instead of fluorescein we used an orange *o*-nitrostilbene derivative which transforms into a blue isatogen on irradiation with an Ar ion laser (λ = 458 nm) at the temperatures of our experiments:



Some details of the labeling procedure are given elsewhere.[16] The stilbene label has an excellent thermal stability, is less bulky than the fluorescein dimer present in our previous experiments, and is free from secondary reactions of the chain ends with neighboring chains.[6] Thus, the accuracy of the measured diffusion coefficients is now estimated to be ±5%. It should be noted that we have corrected[6] for the polydispersity of our samples, and the corrected D values were found to be less than 5% larger than the uncor-

Table I
Apparent Activation Energies E_a for PS Chain Diffusion Coefficients D

	Friedel–Crafts Cross-Linked Networks							
ϕ_{PS}		0.01	0.01	0.2	0.2	0.2	0.2	0.2
$100p_c$	0	2	3	0.5	1	2	3	6
E_a/(kJ mol^{-1})	141	151	152	155	159	171	164	162
	Macroreticular Networks							
$100p_c$					1	2	3	
E_a/(kJ mol^{-1})					160	124	130	

rected ones. Diffusion experiments have been performed with seven samples of labeled PS having P_n values of 177, 261, 300, 341, 465, 572, and 990, respectively, and $M_w/M_n \lesssim 1.02$.

Dilute solutions of the labeled chains in cross-linked PS were prepared as follows. The dried gel particles were mechanically mixed with 2–5% of a fine powder of labeled linear PS and pressed to a pellet of 8.5-mm diameter and 0.3–0.75-mm thickness using a modified IR pellet press. The pellet was placed into the sample holder[6] and annealed in vacuo (~1 Pa) at 180 °C for 4 days. It was checked that this period is sufficiently long by performing diffusion experiments after different annealing times Furthermore, one can calculate from the diffusion coefficients measured at 185 °C (see Figure 4) that the average distance traveled by a labeled chain in 4 days is between 20 and 100 μm. Although, this may not be enough for achieving completely homogeneous solutions, a sufficient volume of the gel particles is filled with chains in order to meet the condition of a *dilute* solution where deviations from interdiffusion are negligible. The self-diffusion coefficients were measured as described elsewhere[6,7] for linear PS. The grating distance was chosen between 2.2 and 3.8 μm. This implies that D is obtained from root-mean-square displacements $\langle r^2\rangle^{1/2} = (6Dt)^{1/2}$ averaged over about this distance, and no conclusions can be drawn from our present results with respect to possible spatial heterogeneities on a smaller distance scale.

Results and Discussion

In Figure 1, the dependence of D upon the average number of cross-links per monomer unit, $p_c = P_c^{-1}$, is shown for diffusant PS chains of $P_n = 177$ and labeled with the *o*-nitrostilbene label. Thus P_n is smaller than the entanglement distance $P_e = 310$ of un-cross-linked PS[8] but larger than most cross-link distances, varying in the range $16.7 \leq P_c \leq 400$. The full lines in Figure 1 connect the D values measured in microgel systems prepared from self-cross-linked PS molecules. The curves come down to a plateau in the range $0.01 \lesssim p_c \lesssim 0.03$, where D is reduced by only 25–35% compared with uncross-linked PS. The further reduction at $p_c = 0.06$ is probably due to reduced segment mobility of the networks since the glass transition temperature T_g was found to be increased by ~4 K for this system. The dashed lines in Figure 1 exhibit a much larger reduction of D in networks cross-linked in concentrated solution, $\phi_{PS} = 0.2$. Here, a minimum is attained at $p_c = 0.02$; remarkably, diffusion becomes faster for longer p_c and D becomes identical with the value obtained in the microgel system for the highest amount of cross-linking, $p_c = 0.06$, investigated in our experiments. Since the increase of D with increasing p_c was rather unexpected, we have repeated the cross-linking procedures in some solutions and have found excellent reproducibility. The D minimum at $p_c = 0.02$ corresponds to a maximum of the apparent activation energy E obtained from the linear Arrhenius plots of the data in Figure 1 and listed in Table I.

Apparently, the addition D reduction shown by the dashed lines in comparison with the full lines of Figure 1 must be related with the different network topology obtained by cross-linking in concentrated rather than dilute solution. It is tempting to ascribe this effect to the influence of "fixed" entanglements which can form in concentrated solution. "Trapped" entanglements have been introduced previously in order to augment the number of cross-links to an effective number necessary for a quantitative description of viscoelastic network properties.[8] Since these trapped entanglements were treated like additional cross-links, they cannot explain the *increase* of D in the region of $0.02 \leq p_c \leq 0.03$. Here, we infer from the "plateau" behavior of D in the microgel system that the sole addition of chemical cross-links has a marginal effect. However, it is conceivable that entanglements can be "fixed" in a region of low cross-link density, $p_c < 0.02$, and removed or replaced by additional cross-links in the region of $p_c > 0.02$. An example of a fixed entanglement having this property is shown in Figure 2, where the "strangulation" of the reptating chain should be released if a chemical cross-link to a third network chain is introduced in the region indicated by the arrow. It is also possible that the large influence of fixed entanglements is related with the "stacking" of phenyl groups between neighboring chains.[17] The large temperature dependence (see Figure 1 and Table I) also suggests a particular influence of intermolecular interactions. It should be noted

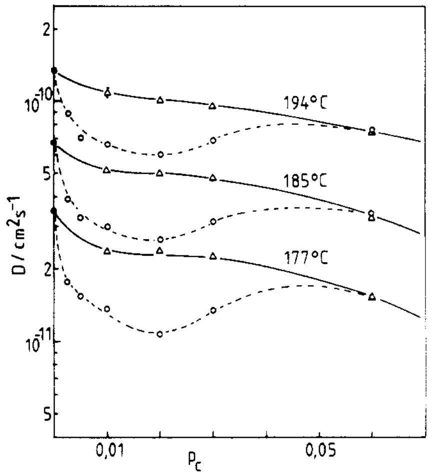


Figure 1. Self-diffusion coefficients of labeled linear PS (P_n = 177) in PS networks drawn vs. the fraction p_c of cross-links per monomer unit. Triangles: microgel networks cross-linked in dilute solution, $\phi_{PS} \leq 0.01$. Circles: networks cross-linked in concentrated solution, $\phi_{PS} = 0.2$. The error bar indicates the estimated accuracy of ±5% for all results in Figures 1–5. The D reduction shown by the dashed lines indicates the influence of fixed entanglements (see text).

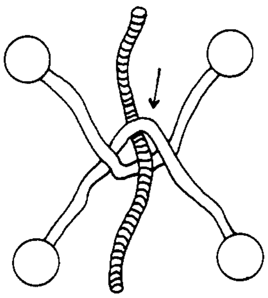


Figure 2. "Strangulation" of diffusant chain in a fixed entanglement.

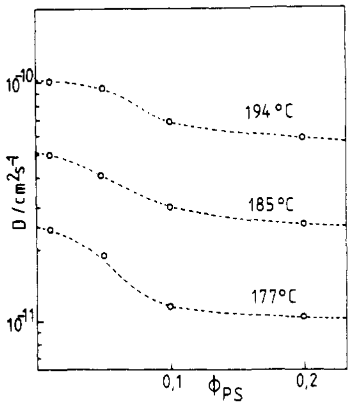


Figure 3. Self-diffusion coefficients of labeled linear PS (P_n = 177) in PS networks (P_c = 50) drawn vs. the volume fraction of PS at cross-linking, ϕ_{PS}. The D reduction due to fixed entanglements sets in well below the entanglement concentration ϕ_e = 0.25.

that in poly(dimethylsiloxane) (PDMS) networks the mechanical relaxation of dissolved PDMS chains was found to be "dramatically" slowed down in comparison with the un-cross-linked environment,[18] and the swelling of PDMS networks in molten linear PDMS was found to become faster on increasing the cross-link density.[15] These effects can perhaps also be explained by the conception of fixed entanglements.

The dependence of D upon the PS mole fraction at cross-linking, ϕ_{PS}, shown in Figure 3 indicates that the particular D reduction discussed above starts at the overlap concentration ϕ^* separating the dilute and semidilute concentration regimes. However, this crossover is complicated by the fact that intramolecular cross-linking yields a size reduction of the molecules thus increasing ϕ^* whereas intermolecular cross-linking results in macroscopic gel formation at a yet unknown critical concentration. Nevertheless, it is apparent from Figure 3 that the fixation of entanglements causing the D reduction occurs at concentrations well below the entanglement concentration $\phi_e = P_e/P_n = 0.25$, where $P_n = 1220$ refers to the chains being cross-linked and $P_e = 310$ is the entanglement distance as obtained from shear viscosities.[8] It should be noted that "fixed entanglements" like the defect shown in Figure 2, can be formed in concentrated solutions though $P_n < P_e/\phi_e$ provided $P_n > P_c$. We should further note that the D difference between entangled and microgel networks cannot be explained by the effect of "interfaces" between self-cross-linked molecules since this effect should be largest at high cross-linking whereas the merging full and dashed lines in Figure 1 reveal a vanishing effect at p_c = 0.06.

The dependence of self-diffusion in networks as a function of the chain length P_n of the labeled PS chains is shown in Figure 4. The fit to a power law $D \sim P_n^{-\alpha}$ yields α values 2.22, 2.07, and 1.82 for the un-cross-linked PS matrix (M_w = 110 000), the microgel network (P_c = 33, ϕ_{PS} = 0.005), and the entangled network (P_c = 50, ϕ_{PS} = 0.2), respectively, all at 194 °C. α = 1.82 was also found for the entangled network at 185 and 177 °C whereas the corresponding α values in the un-cross-linked PS matrix were found[7] to increase in this temperature range to a value of 2.35 at 177 °C. We have shown above (Figure 1) that the difference between entangled and microgel networks also increases with decreasing temperature for P_n = 177 whereas this difference becomes smaller for longer chains and seems to vanish at 194 °C for $P_n \gtrsim 1000$. This would imply that the "fixed entanglements" affect preferably the chain ends. Although this interpretation is admittedly speculative, there can be no doubt about the existence of environmental effects in entangled networks and in un-cross-linked PS, which cannot be explained without modification of the reptation model. On the other hand, all assumptions of the reptation model with "fixed obstacles" should apply in the microgel system, where the experimental α value of 2.07 is in good agreement with the model value α = 2.

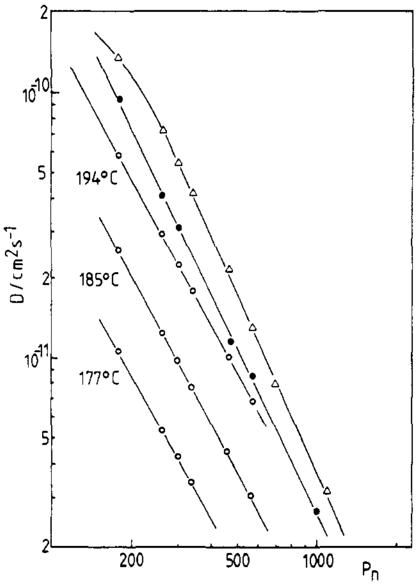


Figure 4. Self-diffusion coefficients of labeled PS chains drawn vs. their degreee of polymerization, P_n. Open circles: PS networks with p_c = 0.02 and ϕ_{PS} = 0.2. Full circles: PS networks with p_c = 0.03 and $\phi_{PS} \leq 0.01$ at 194 °C. Triangles: un-cross-linked PS matrix with M_w = 110 000 at 194 °C. At 194 °C, the slopes α are 2.22, 2.07, and 1.82, respectively, indicating that the reptation model (α = 2) is most suitable for chain diffusion in networks prepared from dilute solution.

Macroreticular networks are prepared by copolymerization of styrene and divinylbenzene in partly demixed solvent–nonsolvent systems, thus causing large spatial fluctuations of the polymer and cross-link densities in the swollen network which is tailored for GPC applications. The macroreticular structure is characterized by regions of high cross-link density and "pores" filled with short chains (dangling ends) tethered in the high-density regions. The large number of end groups in the porous regions should provide additional free volume, causing high mobility in the dry state at the temperatures of our diffusion experiments. Thus, the *local* mobility in these regions should be very high as in a short-chain melt, where we have found[6] chain diffusion coefficients 1 order of magnitude larger than for the same diffusant in long-chain melts used as un-cross-linked PS (M_w = 110 000) in the present investigation. This increased local mobility can provide an explanation for the peculiar behavior of the experimental diffusion coefficients shown in Figure 5. For PS chains (P_n = 177) carrying the *o*-nitrostilbene label, D is reduced at p_c = 0.01. Apparently, the hindrance by fixed entanglements outweighs the increased mobility of the dangling ends. The enormous increase at p_c = 0.02 can be understood if we assume that the limit of high cross-linking with no fixed entanglements is already reached in the regions of high cross-link density, and further, the diffusant chains move preferably in the end group rich porous regions. The latter effect should increase with the label size, thus explaining the behavior of fluorescein-labeled PS shown in Figure 5b. The assumption of increased local mobility is supported by the temperature dependence where an apparent activation energy reduced to 124 kJ

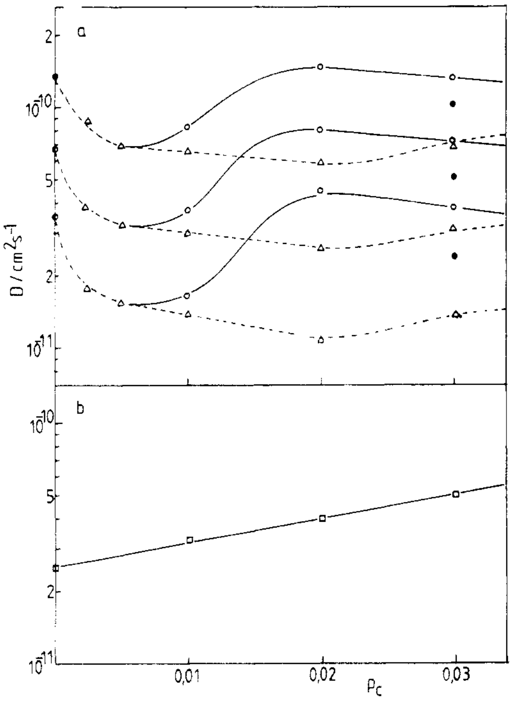


Figure 5. Self-diffusion coefficients of labeled PS chains (P_n = 177) in macroreticular PS networks (full lines) as compared with Friedel–Crafts cross-linked PS. Circles and triangles: *o*-nitrostilbene label. Squares: fluorescein label. Full circles: filled networks (see text).

mol^{-1} is obtained for p_c = 0.02 (see Table I). The end group density of the "porous" regions can be reduced by "filling" the networks with unlabeled long chains. Thus, we have annealed 100 mg of the highly cross-linked macroreticular networks (p_c = 0.03) with 10 mg of linear PS (P_n = 1040) and 4 mg of labeled PS (P_n = 177) for 9 days at 175 °C. The resultant reduction of D shown in Figure 5 confirms our interpretation. Nevertheless, we should emphasize that alternative explanations are possible and further experiments are necessary in order to fully explore the influence of network topology upon chain diffusion. In particular, deformed networks should be probed dynamically by measuring the diffusiontensor of dissolved chains. Further work in networks swollen by good solvents or, alternatively, by oligomers of the same polymer should supply information upon dynamic effects of the osmotic forces in these spatially heterogeneous systems.

Conclusions

We have shown that Friedel–Crafts cross-linking of PS with *p*-dichloroxylylene provides a very useful tool for preparing networks in solutions of linear PS. In particular, the simple accessibility of self-cross-linked PS molecules obtained by cross-linking in dilute solution opens up new opportunities that go far beyond the purpose of this paper. The most striking features of chain diffusion in these microgel systems are the small D reduction and the fact that for the highly cross-linked case (P_c = 16.7) D coincides with the value obtained in a corresponding network prepared in concentrated solution, ϕ = 0.2. Thus, we find no "interfacial" effects on diffusion of chains dissolved in the microgel systems. The relatively large additional D reduction (see Figure 1) found in networks prepared at ϕ_{PS} = 0.2 for P_c = 50 is tentatively interpreted in terms of fixed entanglements which eventually can "strangulate" reptating chains (See Figure 2). The small total reduction and the chain length dependence of D are in harmony with the reptation model of chain diffusion. As a matter of fact, it is hardly conceivable how a chain of P_n = 990 could move other than by reptation in a network with P_c = 33. The surprising increase of D in macroreticular networks has been explained by the assumption that the diffusing chains move preferably in "porous" regions characterized by an abundance of dangling ends tethered in the highly cross-linked regions which form the macroreticular structure.

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Registry No. PS (homopolymer), 9003-53-6; (*p*-dichloroxylylene)·(styrene) (copolymer), 30446-12-9.

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