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Dynamics of Labeled Linear Polystyrenes in Semi-Dilute Polystyrene Matrices in the Uncross-Linked and Cross-Linked States

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Summary: Linear polystyrene chains that were labeled with a fluorescent dye were enclosed in a semidilute matrix of polystyrene in toluene. The matrix polymers used were suitably functionalized such that they could be photocross-linked in a stepwise and controlled manner without attachment of the tracer chains. The diffusion coefficient of the tracer chains was determined by fluorescence recovery after photobleaching while the state of the matrix was changing from a semidilute solution to a covalently cross-linked gel. The progress of the photocross-linking reaction was macroscopically monitored by rheology. The tracer chains were polystyrenes with molecular weights ranging from 50 000 to 2 000 000 g mol^{-1} and low polydispersity. They were labeled via polymer analogous reactions with the fluorescent dye 6-(7-nitrobenzfurazan-4-ylamino) hexanoic acid. The matrix polymers covered a similar molecular weight range. The results of these measurements show that the dependence of the diffusion coefficient on the tracer molecular weight in the gel can be described by a scaling law in the sense of the reptation theory whereas distinct deviations of this scaling behavior appear in the sol state. The ratio of the matrix molecular weight and tracer molecular weight in the initial sol state significantly influences the change of the probe dynamics during the sol-gel transition.

Keywords: diffusion; FRAP; photocross-linking; polystyrene; semidilute solution

Introduction

In the last decades, chain dynamics in melts, solutions and gels was investigated intensively by various techniques to obtain more information about the fundamental diffusion mechanisms of polymers. The dynamics of high molecular weight melts and concentrated solutions is dominated by intermolecular entanglements forming temporary junction points with finite lifetime. On a short timescale, such a system behaves similarly to chemically cross-linked polymers, where the junction points are permanent. One theory describing the transport mechanism of an unattached chain in a temporarily or permanently cross-linked system is the so-called reptation theory developed by de Gennes.[1–3] It predicts that the motion of the chain is restricted to a tube-like region defined by topological constraints of neighboring matrix chains in a way that the chain can only escape its tube by a curvilinear motion along its own contour. The simplest case is, therefore, the unattached chain in a network consisting of fixed obstacles. To describe the reptative behavior over wide ranges, scaling laws were developed and the diffusion coefficient in melts exhibiting long-living entanglements is related to the molecular weight M of a test chain by:

$$D \propto M^{-2} \quad \text{(melt state)} \tag{1}$$

Coming up with a prediction for a semidilute, entangled solution is a much harder problem, because, besides the

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molecular weight of the probe, additional parameters such as the concentration of the matrix and the molecular weight of the matrix have to be implemented in the scaling laws for good and for theta solvent conditions. The dependence of the diffusion coefficient is given by the following relations:

$$D \propto M^{-2} c^{-1.75} P^{0} \quad (\text{good solvent}) \tag{2}$$

$$D \propto M^{-2} c^{-3} P^{0} \quad (\text{theta solvent}) \tag{3}$$

where c denotes the concentration of the matrix and P is the molecular weight of the matrix polymers. Whereas the theory was confirmed for the melt state, there are still discussions about the applicability of the reptation theory to semidilute solutions because of additional hydrodynamic interactions existing in addition to topological restrictions in the sol state.

In our studies, we try to approach the ideal model of the unattached chain in a network by enclosing fluorescently labeled polystyrene tracer molecules in a semidilute, entangled solution of matrix polymers. The latter carry photocross-linkable groups such that the matrix can be cross-linked successively by irradiation. By studying the fluorescence recovery after photobleaching (FRAP), diffusion coefficients of an unattached test chain can be determined in every state of cross-linking during the transition from the sol to the gel. Using only polystyrenes as tracer and matrix polymers in the good solvent toluene, we are expecting minimized specific interactions between tracer and matrix polymers.

FRAP measurements are performed on a confocal laser scanning microscope that allows to monitor the fluorescence intensity with a high spatial and temporal resolution.

Experimental Part

Polystyrene Copolymers

Linear tracers were synthesized by polymer analogous hydroxyalkylation of polystyrenes with low polydispersities (Pressure Chemicals, Pittsburgh, PA, USA) and subsequent labeling with the fluorescent dye 6-(7-nitrobenzfurazan-4-ylamino) hexanoic acid by a Steglich esterification.[4,5] The degree of functionalization was kept low, in the range of 0.1 to 0.3 mol-%, as verified by UV/vis-spectroscopy.

The matrix polymers were synthesized using a two step polymer analogous reaction starting from linear polystyrenes to create poly(styrene-*co*-aminomethylstyrene) (p(s-*co*-ams)) carrying 0.3 to 0.5 mol-% photocross-linkable aminomethyl moieties (characterized using NMR spectroscopy).[6,7]

Figure 1 shows the structures of the tracer and matrix polymers. The degree of

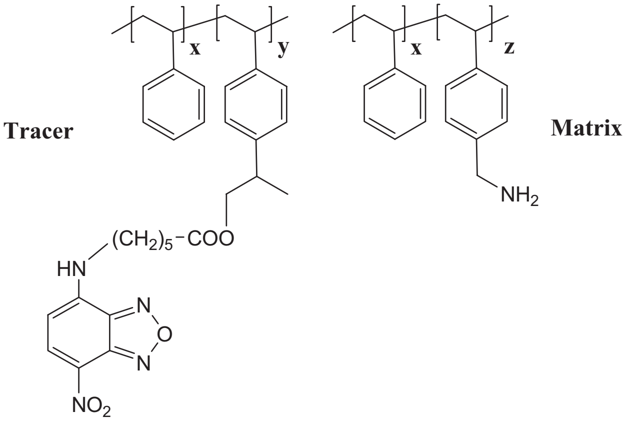

Figure 1.
Chemical structures of polystyrene tracer and P(s-*co*-ams); x/y ≈ 400–1100, x/z ≈ 200–300.

functionalization for both, tracer and matrix, was very low in order not to affect the properties of pure polystyrene perceptibly. The molecular weights of the tracer polymers covered a range from $M = 50\,000$ to $2\,000\,000$ g mol^{-1} and the molecular weights of the matrix polymers varied from $P = 123\,000$ to $900\,000$ g mol^{-1}.

Cross-linking of the Matrix Polymers

Polystyrene gels were obtained by irradiation (Xe arc lamp, 100 W, $\lambda = 370 \pm 18$ nm) of semidilute p(s-*co*-ams) solutions in toluene in the presence of thioxanthone as a photoinitiator. The random photocross-linking reaction is shown in Figure 2. It is initiated from the relatively stable triplet state of thioxanthone reached after excitation to a singlet state and subsequent intersystem crossing. This triplet state has an (n-π^*)-character in nonpolar organic solvents and it is known to be electrophilic and more reactive in hydrogen abstraction reactions than the (π-π^*) triplet.[8] After forming an exciplex with an aminomethylsytrene group, thioxanthone abstracts an electron, and a proton is subsequently transferred to the diarylketone producing a ketyl and an aminomethyl radical.[9,10] The aminomethyl radicals are able to dimerize leading to *N*-benzylidene benzylamine derivatives acting as tetrafunctional cross-links.

The gelation process was followed by oscillatory shear experiments on a rheometer (Gemini, Malvern / Bohlin Instruments GmbH) equipped with a quartz glass plate which allows for irradiation of the sample from the bottom during the rheological measurements. The shear frequency was 1 Hz and the applied stress was chosen between 0.5 and 1 Pa.

FRAP Measurements

Diffusion coefficients were determined by FRAP on a Leica TCS 2 confocal laser scanning microscope using a 10 × DRY objective with a numerical aperture NA = 0.3. In the scan mode, the fluorophores were excited with the 458 nm line of an Ar laser at 40–50% of its maximum power. To bleach the dye, the additional stronger laser lines at wavelengths 476, 488 and 514 nm were used with maximum intensity for 0.5 to 1 seconds depending on the mobility of the tracer. The recovery of the fluorescence was monitored by scanning the post bleach process (duration from 15 s to several minutes) at a resolution of 256×256 pixels and a line scanning speed of 400 or 800 Hz.

The measured intensity profiles were used to determine diffusion coefficients by applying solutions to Fick's second law for two-dimensional diffusion:

$$C(r,t) \sim I(r,t) = I_0(r,t) - \frac{A}{4\pi D(t+t_0)} e^{\frac{-r^2}{4D(t+t_0)}} \qquad (4)$$

C(r,t) is the concentration of the fluorophore that is proportional to the intensity

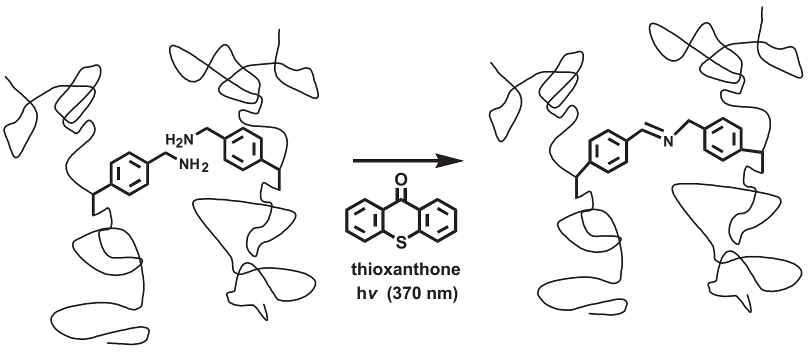

Figure 2.
Scheme of the stepwise photocross-linking reaction by dimerization of aminomethylstyrene groups.

$I(r,t)$. A is the amount of labeled polymer, $I_0(r,t)$ represents the prebleach intensity, r is the radial distance from the center of the bleached spot, D is the diffusion coefficient and t_0 denotes the time lag that has to be introduced because bleaching takes a finite time and, therefore, the starting conditions are not exactly defined. Equation (4) can only be applied in the case of a single diffusing species. In the investigated systems, particularly when cross-linking of the matrix has taken place, a distribution of diffusion coefficients is sometimes observed and a sum of Gaussian profiles is used to determine the diffusion coefficients of all species i:

$$I(r,t) = I_0(r,t) - \sum_i \frac{A_i}{4\pi D_i\left(t + t_{0,i}\right)} e^{\frac{-r^2}{4D_i\left(t+t_{0,i}\right)}} \qquad (5)$$

The complete fitting procedure is described in detail elsewhere.[11,12]

The samples were placed in 100 μm cuvettes. As a homogeneous network formation of the specimen is desirable, the concentration of the photoinitiator was adjusted to yield 90% transmission of the incident light to avoid any remarkable gradient of irradiation intensity. The concentration of the polymer tracers was in the range $c = 0.5$–1 g L^{-1}. This was in all cases low enough to ensure that there was no mutual overlap among fluorescently labeled tracer molecules.

Results and Discussion

Polymer Tracer Diffusion in Semidilute, Entangled Solution

Figure 3 shows the dependence of the diffusion coefficient of the probe polymer on the molecular weight of the matrix polymer P for several tracer molecular weights M in solution of pure polystyrene at $c = 100$ g L^{-1}. This concentration is above the overlap concentration c^* for all matrix polymers, hence the solutions are semidilute. However, the ratio c/c^* rises with increasing P because c^* is decreasing. c/c^* is about 2 for the lowest matrix molecular weight, $P = 50\,000$ g mol^{-1}, and reaches a factor of 5 around $P = 200\,000$ g mol^{-1}. The entanglement concentration c^e where entanglements become effective in the semidilute regime is typically reached at concentrations 2–5 times higher than c^*.[13] Hence at a concentration $c = 100$ g L^{-1} chosen in these experiments, the matrix is highly entangled at least for the longer matrix chains.

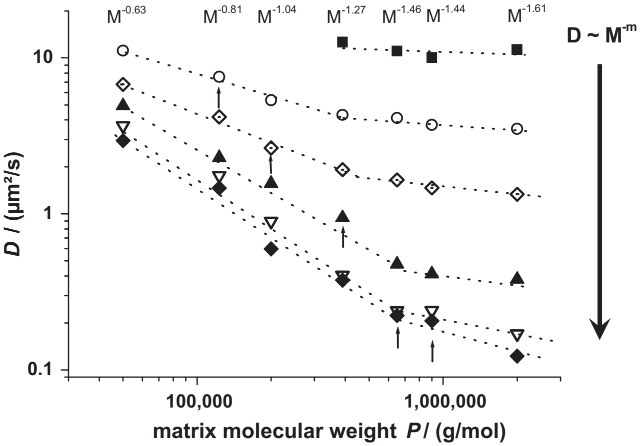

Figure 3.
Dependence of the diffusion coefficient of several polymer tracers on matrix molecular weight in semidilute solution, $c = 100$ g L^{-1}. Tracer molecular weights: ■: 50 000 g mol^{-1}, ○: 123 000 g mol^{-1}, ◇: 200 000 g mol^{-1}, ▲: 390 000 g mol^{-1}, ▽: 650 000 g mol^{-1}, ◆: 900 000 g mol^{-1}. Arrows indicate the situation when $M = P$.

From the data shown in Figure 3, two regions can be distinguished: There is one regime where the diffusion coefficient decreases significantly with increasing P, followed by a second regime (at high P) where the diffusion coefficient is practically independent of P or at least its dependence is significantly weaker than in the first regime. The small arrows in Figure 3 indicate the situation where $M=P$, i.e. the self-diffusion regime. The relation $D \sim P^0$ is one of the predictions of the reptation theory (cf. Equations (2) and (3)). However, it appears only when P is sufficiently larger than M. As known from literature, P should be at least $5M$.[14] Only if these conditions are met, the entanglements are lasting long enough to be experienced as long living junction points by the more mobile tracers.

Vertical sections through Figure 3 enable determination of the dependence of the diffusion coefficient on the tracer molecular weight in semidilute solution. Corresponding exponents obtained by fitting the data to a power law $D \sim M^{-m}$ are listed in the figure. In the polymer matrix with the highest molecular weight, we found $m=1.61$. m decreases gradually with decreasing the polymer matrix molecular weight. The reptation theory predicts $m=2$ for an unattached chain in an array of fixed obstacles or at least for very long-living entanglements such as those observed in melts. Deviations from this behavior are expected in the case of semidilute solutions. Furthermore, the deviations can be explained by the fact that the tracers with $M=650\,000$ g mol^{-1} and $900\,000$ g mol^{-1} are not yet in the regime where P is sufficiently larger than M. If only the shorter tracers with $M=123\,000$ g mol^{-1}, $200\,000$ g mol^{-1} and $390\,000$ g mol^{-1} are considered, a dependency $D \sim M^{-1.92}$ is obtained for the matrix with $P=2\,000\,000$ g mol^{-1}, indicative of reptative motion. Looking at matrices with lower molecular weight P, m drops to 0.63 for the shortest matrix polymers used in our studies. For the $2\,000\,000$ g mol^{-1} matrix, the concentration is far above the overlap concentration $c^* = 2.8$ g L^{-1} and also above the entanglement concentration c^e. However, for the matrices with lower P, the concentrations of the polymer system more and more approach the entanglement and overlap thresholds resulting in a matrix where the chain dynamics increase gradually leading to entanglements with shorter lifetimes. Then, the tracer molecules are no longer restricted solely to reptative motion and their dynamics deviate from the $D \sim M^{-2}$ dependence.

After all, it is not only the concentration that has to be considered when reptation-like behavior of tracer in different matrices is discussed, but also the relation of tracer molecular weight M to matrix molecular weight P is of significant importance.

Characterization of the Gelation Process

Figure 4 shows the course of G' for different matrices during the gelation process. The elastic modulus G' increases during irradiation and levels off to a plateau value G_0. The final modulus values are very similar, because the degree of functionalization is nearly the same. Only the matrix with the lowest molecular weight has a lower G_0 value due to a lower cross-linking efficiency.

The asterisks in Figure 4 indicate the crossover of the elastic and the loss modulus and are, therefore, a rough estimate for the gelation threshold. The final shear modulus G_0 is a useful quantity for macroscopic characterization of the formed gels. It is a measure of the network density ν_{eff}, i.e. the effective number of network strands per volume, given by the Equation of the phantom network model:[15]

$$\nu_{eff} = \frac{G_0}{RT\left(\frac{f-2}{f}\right)} \qquad (6)$$

where f is the functionality of the junction points and in the case of tetrafunctional cross-links $f=4$. The network density can be used to calculate characteristic network parameters like the mesh size of the network. Static light scattering measurements showed that these gels are fairly homogeneous and comparable to a semidilute solution of unfunctionalized polystyrene.

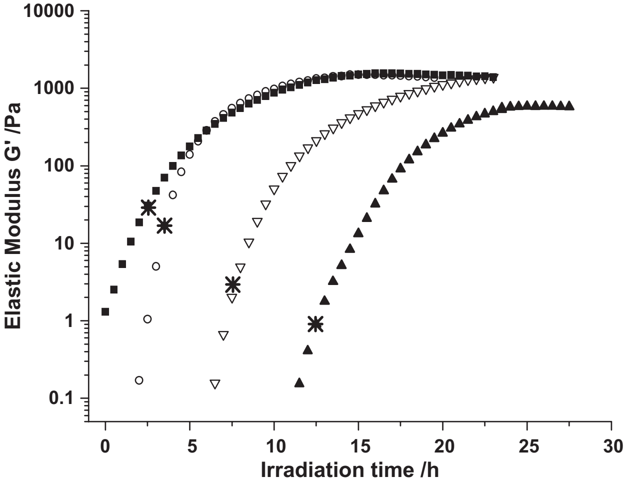

Figure 4.

Elastic modulus G' (1 Hz) as a function of irradiation time (progress of photocross-linking) for four different matrices with similar degree of functionalization, $c = 100$ g L^{-1}. Matrix molecular weight P: ▲: 123 000 g mol^{-1}, ▽: 200 000 g mol^{-1}, ○: 390 000 g mol^{-1}, ■: 900 000 g mol^{-1}. Asterisks indicate $G' = G''$ ($\approx$ gelation threshold).

Influence of the Molecular Weight of the Polymer Matrix on Probe Dynamics During Gelation

To investigate the influence of the initial matrix molecular weight on the diffusion behavior of polymer tracer chains during the sol-gel transition, fluorescently labeled polystyrene with molecular weight $M = 390\,000$ g mol^{-1} was enclosed in four different matrices with molecular weight P. Figure 5 shows the dependence of the diffusion coefficient on the progress of cross-linking. During the photocross-linking reaction, the diffusion coefficient decreases and finally reaches a similar value for all matrices. This decay is strong

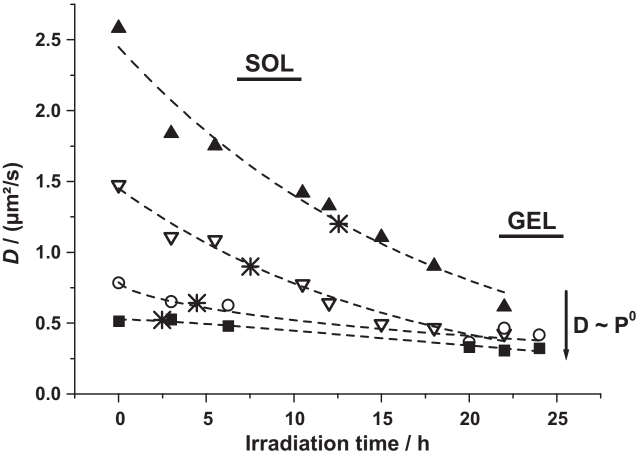

Figure 5.

Comparison of diffusion coefficients of a polymer tracer with $M = 390\,000$ g mol^{-1} in matrices having different molecular weights as a function of progressive cross-linking; $c = 100$ g L^{-1}. Matrix molecular weight P: ▲: 123 000 g mol^{-1}, ▽: 200 000 g mol^{-1}, ○: 390 000 g mol^{-1}, ■: 900 000 g mol^{-1}. Asterisks indicate $G' = G''$ ($\approx$ gelation threshold).

when the molecular weight of the initial polymer matrix is small, but it is barely perceptible when the polymer matrix has a high molecular weight. As discussed above, in the sol state two situations need to be distinguished: When the molecular weight of the polymer tracer is appreciably lower than that of the polymer matrix ($M < P$), reptation-like motion is dominant because of long-living entanglements and the relation $D \sim P^0$ may be valid. On the other hand, when the polymer tracer chains are longer than the polymer matrix chains ($M > P$), the tracer dynamics is slower than the polymer matrix dynamics in the semidilute solution, resulting in marked deviations from reptation behavior.

The asterisks in Figure 5 indicate the crossover of the elastic and the loss modulus (gelation threshold) after which the sample no longer consists only of sol but also of a significant amount of gel which increases as cross-linking proceeds. The gel point has no distinct effect on the course of the diffusion coefficient during successive cross-linking.

The decay of the diffusion coefficient depends on the ratio of the chain lengths of tracer and matrix polymers in the initial sol state. This change is significant if polymer tracer chains are longer than polymer matrix chains in the sol, whereas only a small difference of the diffusion coefficient is observed if the polymer tracers are sufficiently shorter than the polymer matrix in semidilute solution. This behavior can be explained by the increase of the effective molecular weight of the polymer matrix upon successive cross-linking. Short-living entanglements in a polymer matrix with low P are converted to permanent junction points and the initial situation $M > P$ is concurrently inverted to a $M < P$ situation during the sol-gel transition because P approaches infinite molecular weight. If the polymer tracer is already shorter than the matrix polymer in solution, subsequent cross-linking does not affect the situation significantly. That is why in this case the probe dynamics is not so drastically affected by gradual photocross-linking.

Furthermore, the polymer tracer dynamics in the gel state, regardless of the polymer matrix used, is similar to the diffusion behavior of the same tracer in a semidilute solution of a matrix polymer with very high molecular weight. The diffusion coefficient in the gel is $D_{gel} \approx 0.3\ \mu m^2\ s^{-1}$, which is nearly identical to the diffusion coefficient determined for the same tracer in a 2 000 000 g mol^{-1} semidilute solution ($D_{sol} = 0.38\ \mu m^2\ s^{-1}$). Thus, it is possible to approach the situation in the cross-linked state simply by enclosing the probe chains in a polymer matrix consisting of very long polymers showing a $D \sim P^0$ behavior.

Dependence of the Diffusion Coefficient on the Molecular Weight of the Polymer Tracer During the Sol-gel Transition

To investigate the dependence of the polymer tracer dynamics on their molecular weight upon cross-linking of the polymer matrix, we studied six different polymer tracers with molecular weights between $M = 50\,000$ and 2 000 000 g mol^{-1}, each enclosed in a p(s-*co*-ams) matrix ($P = 390\,000$ g mol^{-1}) at a polymer concentration of $c = 100$ g L^{-1}. The overlap concentration of the matrix polymer is $c^* \approx 10$ g L^{-1} and hence the polymer tracers are enclosed in an entangled system. In Figure 6, we compare the diffusion coefficients of the enclosed polymer tracers in the initial sol state and in the final gel state after photocross-linking.

Considering the behavior in the sol first (open squares), the data are separated into two regimes by the vertical dotted line. On the left hand side of the line, the molecular weight of the polymer tracer is below that of the polymer matrix ($M < P$), and we observe essentially a scaling law dependence. On the right hand side, where $M > P$, the polymer tracer dynamics is slower than the polymer matrix dynamics and these data points deviate significantly from the scaling behavior in the $M < P$-regime. Upon photocross-linking of the polymer matrix, the polymer tracer diffusion coefficients are represented by solid dots. Now a single power law, $D \sim M^{-1.83}$, is observed. The

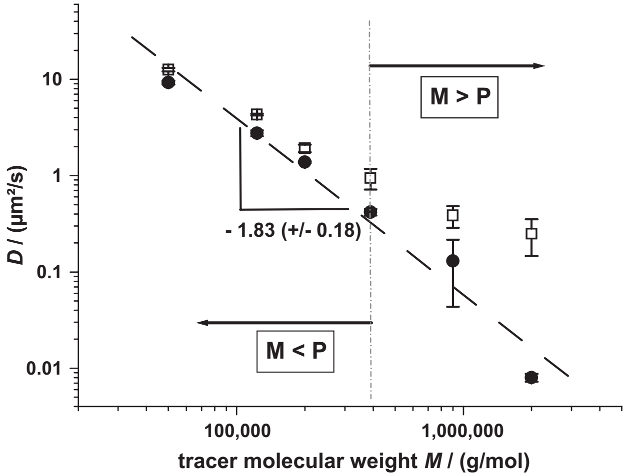

Figure 6.
Dependence of the diffusion coefficient on the molecular weight of the polymer tracer in $P = 390\,000$ g mol^{-1} P(s-*co*-ams); $c = 100$ g L^{-1}; ☐: sol state (before photocross-linking), ●: gel state (after photocross-linking).

data obtained in the sol follow essentially the same line as long as $M < P$ (left side), while the diffusion coefficients measured in solution are appreciably larger than those in the gel, when $M > P$. This means that for a polymer tracer chain embedded in a polymer matrix of longer chains, it does not make any noteworthy difference whether the polymer matrix is or is not cross-linked. On the other hand, when the polymer matrix chains are shorter than the tracer molecules, the strong dynamics of the matrix enhances the mobility of the polymer tracers significantly. Cross-linking of the polymer matrix then cancels this effect, leading to appreciable differences between sol and gel data, as seen on the right hand side of Figure 6.

In a polymer network built up by fixed obstacles, de Gennes predicted a scaling law behavior $D \sim M^{-2}$. Indeed, in the gel state a scaling-law dependence can be observed over the whole range of the used tracers and the slope in a double logarithmic plot is -1.83 ± 0.18. This value is in good agreement with the theoretical inverse square dependence of the molecular weight of the polymer tracer and reptation-like motion can be assumed.

A lot of studies dealt with the dependence of the diffusion coefficient on the molecular weight of the polymer tracer in semidilute solutions and networks. In many investigations, the slope was determined to be between -2 and -3.[14,16–21] Only few investigations measured weaker dependences on M.[22,23] Muthukumar tried to explain these findings by the structure of the network.[24] He carried out computer simulations on probe dynamics in homogeneous and heterogeneous network structures and found that a stronger dependence of the diffusion behavior on the molecular weight of the polymer tracer ($D \sim M^{-3}$) is due to a more inhomogeneous structure of the gel. In a fairly homogeneous network, the reptation prediction $D \sim M^{-2}$ is expected. Static light scattering measurements revealed that the networks in our studies are fairly homogeneous (there is no appreciable difference in scattering intensity between gels and solutions), presumably because they are built up by random cross-linking of preformed macromolecules in a good solvent in the entangled regime.

Conclusion

Our investigations demonstrate that FRAP is an appropriate technique to study the dynamics of fluorescently labeled polystyrenes in a chemically nearly homogeneous system consisting of polystyrene probe molecules, polystyrene matrix polymers and the solvent toluene which is a good solvent for polystyrene. The stepwise photocross-linking reaction provides a suitable means to study diffusion behavior during the transition from the sol state to the network because every stage of successive network formation can be investigated by simply interrupting or continuing the irradiation of the samples.

The results of the measurements reveal a dependence of the diffusion coefficient on the molecular weight of the polymer tracer that can be described by a scaling-law behavior in accordance with de Gennes' reptation theory. The experiments of the probe dynamics in different matrices during successive cross-linking demonstrate the strong influence of the ratio of the molecular weights of polymer tracer to polymer matrix in the initial sol state on the change of the dynamics during the sol-gel transition. These measurements also show that the chain dynamics in semidilute solution converge with those in gels when the molecular weight of the matrix polymers is sufficiently high to give rise to long-living entanglements.

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