of the deviations is to be attrributed to each cause.

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Diffusion of Labeled Macromolecules in Molten Polystyrenes Studied by a Holographic Grating Technique†

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ABSTRACT: A holographic technique for measuring small diffusion coefficients has been applied to polystyrene (PS) labeled with fluorescein, which is thermally stable at 180 °C but can be bleached with light ($\lambda = 458$ or 488 nm) from an Ar ion laser. The diffusion of short chains ($M_w = 4000$) decreases in a surrounding matrix of higher molecular weight, as predicted by the WLF equation taking into account the end-group free volume. For labeled PS chains of $1.8 \leq M_n \times 10^{-4} \leq 16.1$ in a high molecular weight matrix we find diffusion coefficients $4.2 \times 10^{-11} \geq D/\text{cm}^2\ \text{s}^{-1} \geq 4 \times 10^{-13}$ and $D \sim M_n^{-2.2}$ at 177 °C. The diffusion of labeled PS rings in the same matrix of linear PS depends upon sample preparation. We conclude that the rings can exist in a twisted pseudolinear shape that allows for rapid diffusion and in an open shape where a network is formed when long chains thread through more than one ring.

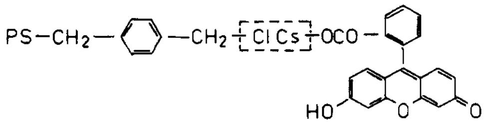
Introduction

In recent years, experimental studies of dynamical phenomena in matter have had increasing recourse to a laser technique[1] in which, by interference of two coherent beams, a grating is induced in the sample and the time evolution of this grating is monitored by light scattering. The terms *forced Rayleigh scattering*[2–4] and *holography*[5–7] have been used by different authors. We prefer the latter expression since we create the simplest possible hologram by partially bleaching the dye used for labeling the macromolecules, and we "read" this hologram as it changes due to macromolecular diffusion. There is some resemblance to the fluorescence bleaching technique where gratings have also been generated recently by interference of coherent light beams[8] or by applying an appropriate mask to the sample.[9] In holography, the diffusion length x can, in principle, be as small as the wavelength λ of the light. Thus, the lower limit of the diffusion coefficient D as given by eq 1 is $D \gtrsim (x/2\pi)^2 t^{-1} \sim 10^{-14}$ cm^2 s^{-1} if the diffusion time t is of the order of hours.

There are a huge number of problems related to macromolecular diffusion that can be solved after straightforward experimental methods have become available. The diffusants can be linear chains, rings, stars, combs, or block copolymers where the different blocks may vary drastically with respect to compatibility. The environment of the diffusants may consist of high or low molecular weight chains of the same or of different species, where the latter may be compatible or heterogeneous on a microscopic scale. Further, macromolecular diffusion in networks, porous systems, membranes, polymer liquid crystals, polyelectrolyte solutions, and many other environments is of interest. In the present paper, we describe the holographic technique as applied to diffusion of fluorescein-labeled molecules in molten polystyrene.[7] The first applications address the dependence upon the amount of labeling, the molecular weight, and the shape of the diffusant, as well as changes in the surrounding matrix.

Experimental Section

1. Fluorescein Labeling. Two different methods have been used in order to obtain polystyrene (PS) samples of narrow molecular weight (MW) distribution and labeled with fluorescein (FL). Labeling at the end group was achieved by terminating the anionic polymerization of styrene with dichloroxylylene and subsequent reaction of the chloromethyl end group with the cesium salt of fluorescein:[10]



Typically, a tetrahydrofuran (THF) solution of about 10 g of living PS in 200 cm^3 was terminated with a 40-fold surplus of di-

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† Dedicated to Professor W. H. Stockmayer on occasion of his 70th birthday.

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Table I
Characterization of Polystyrene Samples

M_w	M_w/M_n	M_n(label)[a]
4 000[b]		
16 000	1.10	
16 000[c]	1.03	
43 700	1.03	
21 000	1.06	18 400
30 200	1.07	27 100
34 500	1.06	31 200
39 200	1.08	35 500
61 152	1.15	48 400
64 200	1.06	59 500
100 800	1.27	63 000
91 300	1.18	72 300
198 600	1.16	161 200

[a] Number average for end-group-labeled molecules with $M_w/M_n \lesssim 1.02$ (see text). [b] Value as given by Pressure Chemical Co. [c] Ring molecules.[12,13]

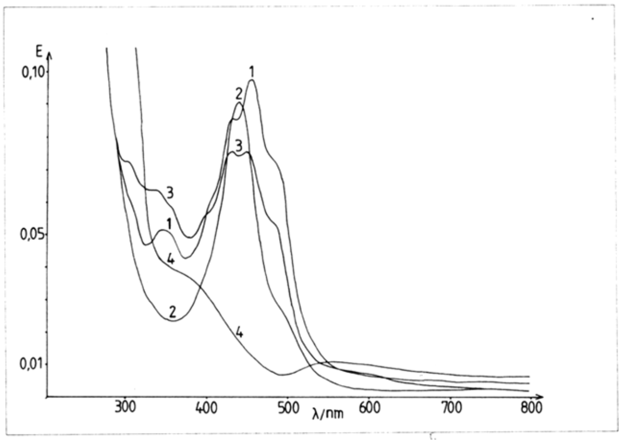

Figure 1. UV spectra of differently prepared samples of FL-labeled PS dissolved in CH_2Cl_2: 1, untreated PS-FL_2; 2, PS-FL after extraction of surplus FL; 3, PS-FL_2 obtained by mixing PS-FL and FL solutions; 4, spectrum obtained after 2 weeks' storage of PS-FL powder at room temperature. (E is extinction in arbitrary units.)

chloroxylylene in 400 cm³ of THF. The reaction with FL-Cs was performed in DMF solution. In the other method,[7,10] PS samples from Pressure Chemical Co. were labeled statistically at the phenyl groups by chloromethylation with chloromethyl methyl ether and subsequent reaction with FL-Cs. The MW distribution of all samples was determined by GPC. The end-group-labeled polystyrenes contained a fraction of unlabeled PS with double MW due to bifunctional termination. This contributes most of the polydispersity listed in Table I. The polydispersity of the labeled diffusant molecules could be determined from the MW distribution curves by subtracting the "bifunctional" peak, resulting in $M_w/M_n \leq 1.02$ for all end-group-labeled diffusants investigated. The samples of PS ring molecules[12,13] were labeled by the same procedure as the linear PS samples from Pressure Chemical Co.

In our diffusion studies, the FL concentration was typically about 2×10^{-3} M, which corresponds to one FL molecule per 5000 PS monomer units. The samples were prepared from a solution of labeled and unlabeled PS in THF by precipitation in methanol. Subsequently, the PS powder was pressed into pellets of 4.5-mm diameter and 0.3–0.75-mm thickness using a modified IR pellet press. In the course of our experiments we discovered that the samples prepared by this procedure contained the labels in the form of FL dimers. We were able to remove the additional FL by extraction with hot methanol–water mixtures. In Figure 1, the UV spectra are shown for solutions of samples prepared by these two different methods. Apparently, the complexed PS-FL_2 exists also in CH_2Cl_2 solution, and its spectrum differs considerably from that of the "purified" PS-FL. We have measured the diffusion of PS-FL with M_n = 18 400 diluted in a matrix of unlabeled PS with M_w = 110 000 at 177 °C. The diffusion coefficient was found to be about 35% larger than that of PS-FL_2 measured under the same conditions (see Figure 6). It should be noted that no dimers $(PS\text{-}FL)_2$ exist in bulk or in CH_2Cl_2 solution. Since PS-FL is unstable and was found to decay within 2 weeks at room temperature and within 2 h at 177 °C, we have done all diffusion experiments reported below with PS-FL_2, which is thermally stable for many days at 177 °C provided O_2 is removed from the sample. Dimerization in solution has been observed previously for FL and other dyes of similar structure.[14,15]

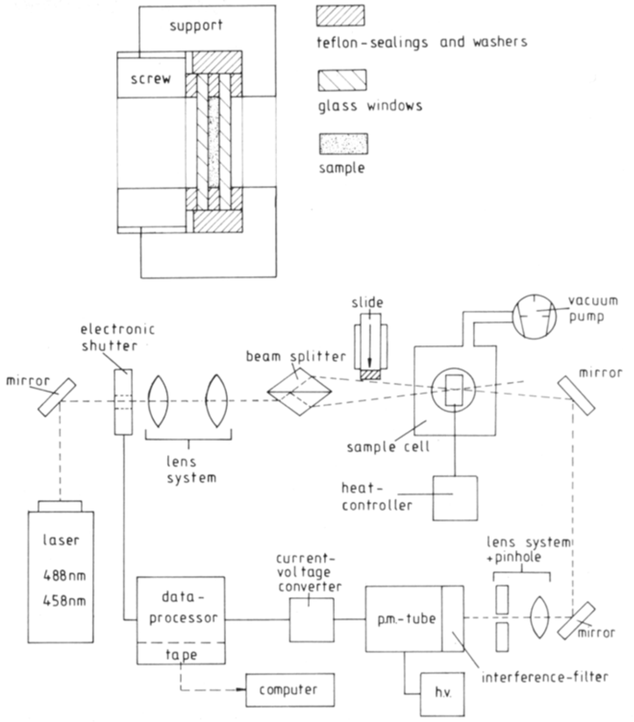

Figure 2. Experimental setup: block diagram and enlarged drawing of the probe assembly.

2. Experimental Setup. The essential components of the holographic technique used in our experiments are shown in Figure 2. The laser beam was generated by an argon ion laser (Coherent Radiation CR 90-2) operating in single mode at a wave length λ of 488 or 458 nm. The beam was focused by the lens system to a spot size of about 1 mm within the sample. A beam splitter produced two coherent beams of equal intensity crossing at an angle θ (0–8°) in the sample cell, thus creating an optical interference pattern with a grid spacing of $d = \lambda/(2 \sin(\theta/2))$. Hologram formation was achieved by irradiating light intensities of typically 10 mW for times of less than 0.2 s. To read the hologram, we employed a slide that shut off the upper beam and attenuated the intensity of the lower beam by a factor of 10^3. Thus, we diffracted the lower beam from the hologram (forced Rayleigh scattering), and in accordance with Bragg's law, the diffracted light followed the same path that the upper beam had in hologram formation. In order to avoid further bleaching, we applied the attenuated reading beam for periods of less than 50 ms using an electronic shutter timed by the data processor that also stored the diffraction intensity on magnetic tape. The diffracted light was detected by a photomultiplier after stray light was reduced by a filter system.

The sample cell could be evacuated and flushed with Ar for removing O_2. The probe was attached to a stabilized heating device that allowed temperature control to ±0.1 K. Before the probe was placed in the sample cell, it was preheated to ~110 °C, and the screw was fastened in order to achieve a transparent sample in good contact with the glass windows.

3. Decay Curves. The intensity $I(t)$ of light diffracted from the hologram and stored by the data processor was analyzed by fitting it to the equations[3]

$$I(t) = (Ae^{-t/\tau} + B)^2 + C$$
$$\tau^{-1} = (2\pi/d)^2 D + \tau_d^{-1} \qquad (1)$$

A, B, and C determine the amplitudes of the signal, the coherent,

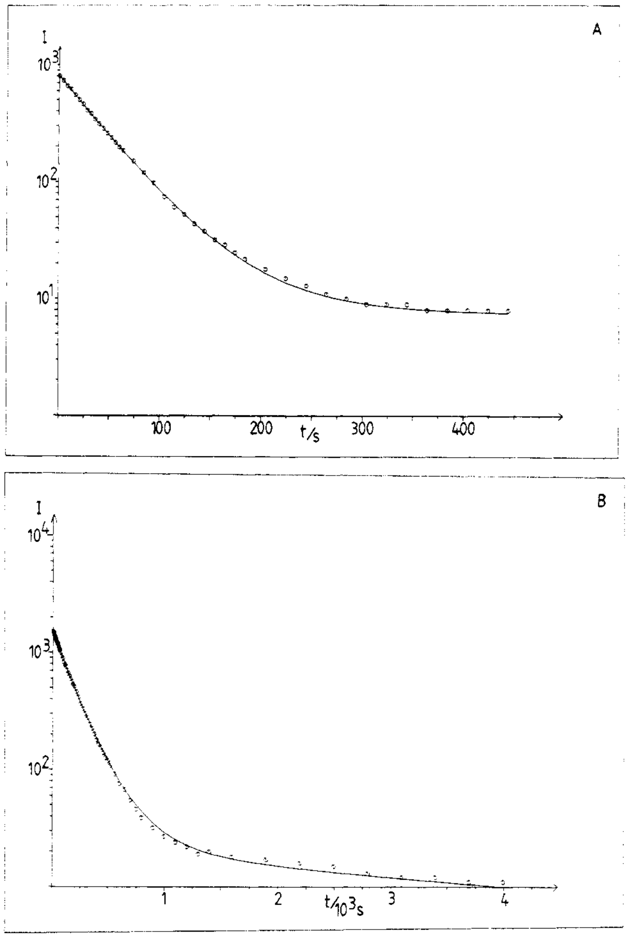

Figure 3. Decay of diffracted intensity due to diffusion of labeled PS at 177 °C: circles, experimental values; full lines, fit corresponding to eq 2. (A) M_w = 16 000; d = 4.03 μm; τ = 84 s. (B) M_n = 31 200; d = 3.78 μm; τ_1 = 295 s; τ_2 = 6520 s; A_2/A_1 = 0.08.

and the incoherent background, respectively. The decay time τ_d for thermal decay of the dye label could be set to infinity in our experiments. The grating distance d can be varied between 3.5 and ~50 μm in our present experimental setup. A typical decay curve $I(t)$ is shown in Figure 3A. Ten weight percent of labeled PS with M_w = 16 000 was diluted with PS of M_w = 100 000 and the diffusion measured at 177 °C. For λ = 488 nm and d = 4.03 μm we obtain $D = 4.9 \times 10^{-11}$ cm^2 s^{-1}. For samples with higher label concentration or higher molecular weight we encountered decay curves that were nonexponential in the long-time region and dependent upon the bleaching time. We believe that this is due to secondary reactions where products are formed that may even increase the hologram efficiency, depending on their spatial concentration distribution.[6] We found that the decay curves become independent of the bleaching time if we work with the laser line at 458 nm. This may be related to the differences in the spectra of PS-FL and PS-FL$_2$; cf. Figure 1. However, at 458 nm we obtained decay curves with a long-time tail that could be described phenomenologically by a second exponential, as shown in Figure 3B. In this manner, we evaluated the decay curves for determining the molecular weight dependence of D shown in Figure 6. Here, we also checked whether τ is proportional to d^2 as required by eq 1 for $\tau_d \gg \tau$. For some samples d was varied between 3.8 and 9.6 μm. Thus, we believe that the D values of Figure 6 have an accuracy indicated by the error bars. The absolute accuracy may be somewhat less for some of the results given in Figures 4, 5, and 7 determined at 488 nm.

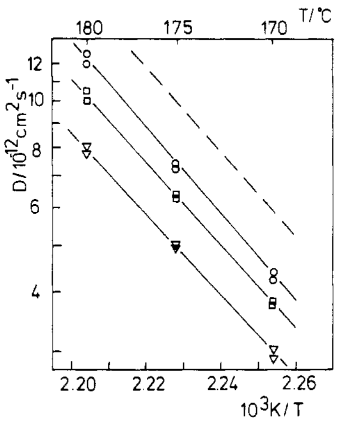

Figure 4. Diffusion coefficient of statistically labeled PS. The average numbers $\bar{n}$ of labels per labeled PS molecule are 1.0, 1.6, and 2.1 for ○, □, and ▽, respectively. (See text for dashed line.)

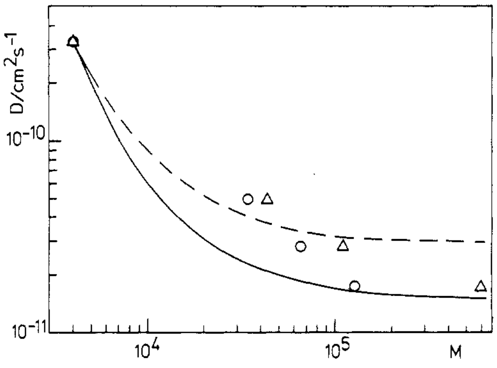

Figure 5. Diffusion coefficients of labeled PS (M_w = 4000) drawn vs. the matrix molecular weight (triangles, $M = M_{\text{matrix}}$) and vs. the number-average molecular weight (circles, $M = M_n$). Theoretical curves drawn vs. M_n. Full line: c_1 = 13.7, c_2 = 48.0 K. Dashed line: c_1 = 10.8, c_2 = 42.9 K. t = 150 °C.

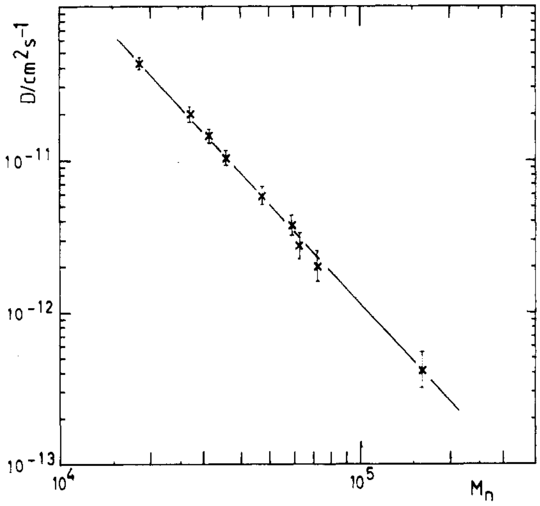

Figure 6. Diffusion coefficients of labeled PS chains in a high molecular weight matrix at 177 °C.

Results and Discussion

1. Amount of Labeling and Temperature Dependence. In Figure 4, the diffusion coefficients of statistically labeled polystyrene (PS) diluted with PS of the same M_w (43 700) are shown for different numbers of labels per PS molecules. We have defined the number $\bar{n}$ as an average over the labeled molecules of a Poisson distribution. Thus, $\bar{n}$ = 1 corresponds to only singly labeled molecules whereas for $\bar{n}$ = 2.1, we have 37% single, 32% twofold, 19% threefold, and 8% fourfold labeling. Apparently, the influence of the label upon the diffusion coefficient is much larger than should be expected from the small increase in molecular weight even if we take into account that each label is a FL dimer (see above).

The average activation energy of 167 kJ/mol obtained from the Arrhenius plots of Figure 4 is in excellent agreement with the value of 170 kJ/mol determined by

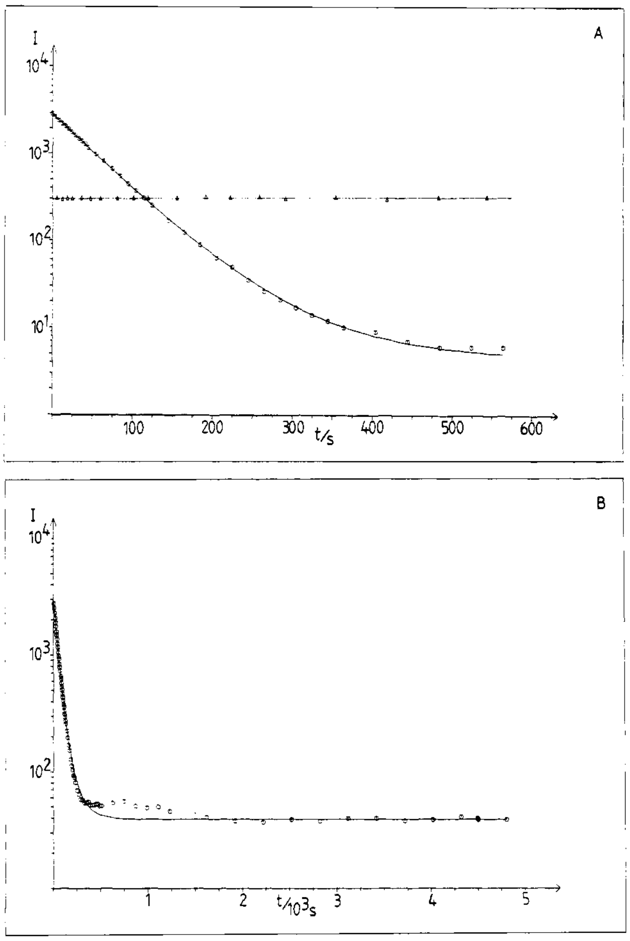

Figure 7. Decay curves for the diffusion of labeled PS rings in a high molecular weight matrix at 177 °C. (A) sample prepared by precipitation (O) or evaporation (▲) from THF solution; (B) sample containing about 5% of diethyl phthalate.

Allen and Fox[16] for the inverse viscosity in this temperature range. The diffusion coefficients indicated by the dashed line in Figure 4 have been obtained by multiplying the value of $D_{230} = 5 \times 10^{-10}$ cm^2 s^{-1} given by Bachus and Kimmich[17] for the diffusion coefficient at 230 °C with the viscosity ratio η_{230}/η taken from the data of Allen and Fox.[16] The good agreement seems fortuitous in view of the uncertainties of the different experimental methods. Thus, the viscosities published by Casale and Porter[18] are smaller by a factor of 3.4 than those of Allen and Fox[16] at 200 °C. On the other hand, small diffusion coefficients determined by the NMR pulse gradient method tend to be larger than those determined by other methods.[17]

2. Matrix Influence. In order to study how the diffusion coefficient of a labeled diffusant depends upon the molecular weight of the surrounding matrix, we have labeled PS of $M_w = 4000$ to a degree of 1 label per 2.2 PS molecules and have prepared samples that were diluted to 2.6% by weight with unlabeled PS of the same and higher molecular weights. The diffusion coefficients at 150 °C are shown in Figure 5. The large decrease of D in a high molecular weight matrix is in marked contrast to the findings of Klein in polyethylene melts,[19] where the diffusion coefficient is independnet of the matrix, provided its M_w is not smaller than that of the diffusant. The difference can be explained by the influence of end-group mobility, which is large at temperatures not far above the glass transition. von Meerwall and collaborators[20] have obtained an excellent fit of their experimental diffusion coefficients in polyisoprenes with an equation derived from the WLF equation of the free volume theory.[21] Thus, the diffusion coefficient in a matrix of number-average molecular weight M_n is given by

$$D = D_\infty \exp\left(\frac{-c_1 c_2 \ln 10}{c_2 + T - T_{g\infty} + k/M_n} \right) \tag{2}$$

where c_1 and c_2 are the WLF parameters and k determines the M_n dependence of the glass transition temperature $T_g = T_{g\infty} - k/M_n$. At $T \gg T_g - c_2$, the diffusion coefficient D approaches the limiting value D_∞, which depends only upon the molecular weight of the diffusant. Apparently, this limit applies to the results of Klein in polyethylene melts.[19] In PS, $T_{g\infty} = 373$ K and $k = 10^5$ are accepted values[22] though a somewhat different M dependence has recently been published.[23] The WLF parameters c_1 and c_2 used in Figure 5 were taken from viscosity[16] (full line) and photon correlation spectroscopy[24] (dashed line) data, respectively. The fair agreement indicates that the matrix effect is caused by the free volume introduced by the polymer chain end groups. More extensive experiments including oligomers and diffusants labeled at both end groups not only should provide a further test of the free volume picture but should be aimed at finding a quantitative parametrization of the label influence.

3. Molecular Weight Dependence. We have measured the diffusion coefficient D of end-group-labeled PS chains for molecular weights M_n between 18400 and 161200 (see Table I) at 177 °C. In order to avoid the end-group free volume influence discussed above, we diluted the samples with unlabeled PS of sufficiently high molecular weight, $M_w = 110000$, except for $M_n = 161200$, where the undiluted sample was measured. The results, shown in Figure 6, can be described by the relation $D \sim M_n^{-\alpha}$ with an exponent of $\alpha = 2.2$. Since the label influence (cf. Figure 4) decreases for higher molecular weights, α should be larger by perhaps 0.2 for unlabeled PS chains. More accurate values of α should become available from a quantitative determination of the label influence and from measurements in the molecular weight regime $M_n > 10^5$, which will be possible with an improved experimental setup where the laser beams intersect at an angle of $\theta = 90°$, thus reducing the grating distance to $d = 0.3$ μm. It is apparent from Figure 6 that we find no change of the slope $-\alpha$ at the critical molecular weight $M_c = 32000$, where the corresponding slope of the shear viscosity η changes from 1 to 3.4.[16] This has been found previously for self-diffusion in polyethylene oxide and poly(dimethylsiloxane) at room temperature[25] and for PS at 230 °C.[17] Thus, no simple relation between D and η should exist for $M \lesssim M_c$. Graessley[26] has estimated the diffusion coefficient of molten polyethylene from experimental values of η and the plateau modulus within the framework of the Doi–Edwards theory[27] and has found fair agreement for $M \gtrsim M_c$. A corresponding estimate for PS of $M_w = 43700$ from the η values of Allen and Fox[16] results in D values that are only about one-fourth the experimental values shown in Figure 4. In comparing our diffusion results with those of Bachus and Kimmich,[17] we should note that the end-group free volume may influence the D values at 230 °C. Although the applicability of the WLF equation can be questioned at temperatures far above T_g, the WLF parameters of PS were determined by Allen and Fox[16] from η values at temperatures up to 220 °C. With these parameters, eq 2 predicts a decrease of the diffusion coefficient by a factor of 0.64 if diffusant molecules of $M_n = 10^4$ are placed in a high molecular weight matrix at 230 °C. Thus, the exponent $\alpha = 2.0$ as determined for self-diffusion[17] should become considerably smaller if the end-group free volume effects are removed. The results of Bachus and Kimmich[17] are also different from those of von Meerwall et al.[20] for self-diffusion in polyisoprenes at $M < M_c$, where $\alpha = 1.0$, provided the end-group effects are described by eq 2. Finally, we should notice the considerable influence of polydispersity effects[28] in determining the exponent α. In our experiments we had $M_w/M_n \lesssim 1.02$, and no polydispersity effect upon α was detected, although the fit of the decay curves (Figures 3 and 7) could be improved by assuming a Gaussian molecular weight distribution with M_w/M_n, given by Table I, and $\alpha = 2.2$. The large polydispersity of the polyethylene fractions investigated so far[17,19] impedes comparison of experimental and theoretical exponents, where the latter are predicted as 2,[29] 2.4,[30] 3,[31] and 3.4,[32] respectively.

4. **Diffusion of Labeled Ring Molecules.** PS rings[12,13] of $M_w = 16\,000$ have been labeled to a degree of 1 label per 2 ring molecules and diluted to 10% with unlabeled PS of $M_w = 110\,000$. The samples were prepared by precipitation from a 0.5% THF solution, and the diffusion was measured at 177 °C under conditions identical with those described for the labeled PS chains of the same molecular weight (see Experimental Section and Figure 3). The value of $D = 4.3 \times 10^{-11}$ cm^2 s^{-1} is only 12% smaller than that of the chains. In each case, the fit of the decay curve to eq 1 is remarkably good (cf. Figures 3 and 7), and the given D value is an average of three independent measurements that agree within ±2%. The rapid ring diffusion can be understood within the reptation model only if we assume that the rings are present in a pseudolinear, possibly twisted, shape. In order to test this assumption, we have prepared a sample by slowly evaporating a THF solution and drying under vacuum at 110 °C. Here, no diffusion of the rings was observable for a time of at least 16 h. Thus, we conclude that $D < 10^{-14}$ cm^2 s^{-1} for this sample. This result suggests that the chains thread through the rings as the solution in the good solvent THF becomes more and more concentrated. Since the long chains can thread through more than one ring, a network is formed where the rings are unable to more over a distance of the order of the grid spacing d. On the other hand, precipitation from a relatively dilute solution may lead to a "collapse" of the rings into a twisted shape that can reptate in a manner similar to that of a linear molecule. We have tried to "open up" the rings by adding a small droplet of diethyl phthalate on both sides of the pellet before placing it between the glass windows (Figure 2). The probe was then annealed for 16 h at 177 °C before the diffusion experiments were performed. Thus, the sample could be considered as a homogeneous solution of about 5% of the diluent. The resulting decay curve (Figure 7B) shows an initial decay that yields a diffusion coefficient of $D = 4.9 \times 10^{-11}$ cm^2 s^{-1}, somewhat faster than without diluent. However, the long-time region exhibits a tail that could be reproduced in three different bleaching experiments in the same sample. We believe that it originates from a small fraction of ring molecules that are slowed down by the onset of the threading mechanism described above. Further experiments on diffusion and viscosity of ring–chain systems with varying diluent concentration[13] will provide a more quantitative basis of our conclusions. A more direct proof for the transition from a twisted to an open shape should be possible with neutron scattering methods, which so far have been applied only to ring systems where the open shape was found.[33]

Conclusions

We have shown that the holographic grating technique can be applied to measuring very small diffusion coefficients that occur in bulk polymer systems above the glass transition. Our diffusion experiments with labeled PS chains support the reptation model if the influence of the label and of the end-group free volume is properly taken into account. The photochemistry of the fluorescein label could not be fully resolved, and further applications may require a more thorough investigation of secondary reactions unless a different label can be found where these difficulties can be avoided.

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Registry No. Polystyrene, 9003-53-6; fluorescein, 2321-07-5.

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