Synthesis and characterization of polystyrene networks containing unattached photochromic polystyrene: preliminary results of self-diffusion measurements

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Using the forced Rayleigh light scattering technique, the self-diffusion coefficient, D_s, of polystyrene chains included in tridimensional structures was measured as a function of the molecular characteristics of the host polystyrene network, swollen at equilibrium. Photochromic linear polystyrenes were prepared anionically by deactivation of the living polymer with a spiropyran molecule. Polystyrene networks were obtained by copolymerization of living polystyrene with divinylbenzene. From swelling experiments, it was concluded that the addition of 8% labelled polystyrene to the network does not modify the elastic properties of the gel. We present preliminary results which demonstrate the feasibility of self-diffusion measurements on such systems, and reveal two different diffusion processes: a fast one that we attribute to chains free to move inside the network defects; and a slow one, corresponding to chains effectively entangled in the gel.

(Keywords: photochromic polystyrene; model network; self-diffusion; forced Rayleigh light scattering; gel structure)

INTRODUCTION

Over the past few years, a number of theoretical works have been published describing the dynamics of polymer molecules. One of the dominating concepts is based on the reptating chain introduced by De Gennes[1], and further developed by Doi and Edwards[2]. The tube model is able to make a number of predictions about the long-range configurational rearrangements of macromolecules. In particular, it leads to well defined molecular weight and concentration dependences of the self-diffusion coefficient, D_s, of the chains[3]. Several experimental techniques, essentially scattering techniques, have been used to investigate the applicability of these theories. Forced Rayleigh light scattering (FRS)[4–7], quasi-elastic light scattering[8] and pulsed field gradient nuclear magnetic resonance (n.m.r.)[9] have been used for dilute and semi-dilute solutions, while FRS[10], spatially resolved infra-red[11] and neutron scattering[12] have been used for polymer melts. Early experiments have given strong support to the model.

However, more recent results do show some deviations from the pure reptation predictions, which have been attributed to an additional freedom of the tube, related to the motion of all the surrounding chains[6,13,14]. These deviations are particularly important for chains that are not highly entangled. They have stimulated a strong debate about the validity of the reptation approach, and renewed theoretical interest. In view of this, it is tempting to follow the self-diffusion of linear chains trapped into chemically crosslinked gels, a model system much closer to the ideal reptation situation. Indeed, such experiments have been performed by Sillescu *et al.*[15] for polystyrene melts, but the case of swollen gels has not been studied. One important difficulty is to incorporate the free chain into a well defined tridimensional structure. Since diffusion of macromolecules into a network is difficult when the mesh size becomes smaller than the free chain radius[16], it is necessary to build up the network around the free chains. Of course, both have to be of identical chemical nature to elude microphase separation. Also, the concentration of the free chains has to be kept as small as possible to avoid additional defect formation during the synthesis of the network. Therefore, a sensitive technique has to be used to measure the self-diffusion coefficient.

In this paper, we report on the synthesis, the characterization and preliminary FRS self-diffusion measurements of polystyrene linear chains, chemically labelled with a chromophore, and inserted in polystyrene networks. Both the molecular weight of the labelled chains and the molecular weight between crosslinks have been varied. The preparation of appropriate samples was possible by the use of anionic synthesis and an end-linking technique.

EXPERIMENTAL

Materials

Styrene was purified by distillation on sodium wire at reduced pressure just before use. Divinylbenzene (DVB) and 1,1-diphenylethylene were dried by a column chromatographic technique using basic alumina. Benzene was stored over styryllithium and distilled before use.

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Tetrahydrofuran (THF) was distilled from a solution containing sodium benzophenone. The initiator, n-butyllithium, in solution in hexane, was used as received. The disodium salt of α-methylstyrene tetramer, used as difunctional initiator, was prepared by the reaction of α-methylstyrene with sodium in THF[17]. The concentration of the initiators was determined by titration, using the method of Eppley and Dixon[18]. The photochromic molecule, 1′,-(4-iodobutyl)-3′,3′,-dimethylindolino-6-nitrobenzospiropyran, kindly donated by Professor Gautron in Grenoble, was recrystallized from ethanol solution and dried in a vacuum oven for at least 24 h.

Polymer synthesis and labelling

Linear polystyrene, PS, was prepared by anionic polymerization in THF at −70°C under dry nitrogen atmosphere. Mono- or difunctional initiator was used for labelling one or both ends, respectively. After one hour, the living polymer solution was divided into two parts: one fraction was classically killed with an excess of methanol, and the PS isolated To the other one, 1,1-diphenylethylene was added to reduce the reactivity of the polystyryl carbanion. Then the living solution was transferred to a dark flask containing the photochromic molecule in powdered form. The carbanions were allowed to react for about 1 h at −70°C, after which the resulting PS was purified by repeated precipitation into methanol and dried under vacuum. Labelling was carried out in the absence of light to avoid the opening of the pyranic ring and subsequent destruction of the photochromism[19]. The linear unlabelled polystyrene was characterized by gel permeation chromatography (g.p.c.) (Waters Associates 200, Styragel columns, THF). It was assumed that labelled and unlabelled polymers have identical molecular weights and dispersity. The concentration of spiropyran in PS was evaluated with a Cary 15 u.v.–visible spectrophotometer from absorption measurements at 605 nm.

Network synthesis

First, well defined polystyrene networks were obtained by anionic copolymerization of styrene and divinylbenzene, according to the method described by Weiss *et al.*[20]. In brief, styrene was polymerized in a 20/80 benzene–THF mixture at −60°C using the disodium α-methylstyrene tetramer. After completion of the polymerization, a small aliquot was sampled out for the determination of the molecular weight of the network precursor by g.p.c.

Second, labelling was achieved, in the absence of light, by addition of a solution of photochromic PS in dry THF to the reaction medium with efficient stirring at −60°C, immediately followed by the addition of a small amount of DVB. Gelation occurred within 1–2 min. The living gel was left for 30 min, and termination of the remaining carbanions was accomplished by exposure to atmospheric oxygen in a deep freeze (−30°C). The networks were characterized by their equilibrium swelling degrees in benzene and in carbon disulphide. Determination was made according to the conventional weighing method described previously[21]. Extractions were carried out with benzene in a Soxhlet apparatus and the sol-fractions were determined.

Forced Rayleigh scattering measurements

A detailed description of the experimental set-up has been given elsewhere[4,7]. The principle of the experiment is the following: the photochromic sample is excited with a pulsed interference pattern and generates a photo-induced grating which is selectively analysed with a second beam. The relaxation time of the diffracted light directly reflects the diffusion kinetics of the photoexcited species[22]. For these measurements, an argon laser beam ($\lambda_1 = 350.7$ nm) was used to write the grating, which was read with a helium/neon laser beam ($\lambda_2 = 632.8$ nm). The self-diffusion coefficient, D_s, is deduced from the relaxation time, t, of the diffracted intensity by:

$$t^{-1} = D_s q^2$$

where q is the wavevector of the interference pattern. The FRS measurements were performed on thin lamellae (1–2 mm) of swollen gel in carbon disulphide. This solvent was chosen because it has a refractive index ($n_D^{20} = 1.628$) close to that of polystyrene. Exchange of solvents from benzene–THF to CS_2 leads to satisfactorily clear samples.

RESULTS AND DISCUSSION

The molecular characteristics of the labelled polystyrene are given in *Table 1*. Sample C shows a relatively broad molecular weight distribution, probably due to its high molecular weight and to the use of a difunctional initiator. However, labelling at both chain ends is required to obtain a significant FRS signal. The estimation of the spiropyran content by elemental analysis of nitrogen[19] was not possible because it is below detection level. The values obtained from u.v. measurements, not confirmed by another technique, are only approximate. In fact, for this work, a qualitative visual test is sufficient, and is done by observation of the blue coloration which appears in benzene on irradiation, and the subsequent decoloration.

Three series of PS networks containing each of the labelled linear PS were prepared. Their molecular weight between crosslinks, M_c, and equilibrium swelling degree by volume, Q_v, in benzene and in CS_2 are reported in *Table 2*. *Figure 1* shows the variation of Q_v with M_c on a double logarithmic scale. In the same figure, values taken from the literature for model PS networks[23] are reported. *Figure 1* emphasizes that the experimental values of Q_v for networks with labelled chains are located on the same straight line as for the model networks. This implies that the presence of the labelled chains does not change the theoretically expected number of elastic chains and does not induce supplementary defects in the tridimensional structure.

The solvent extraction data are also presented in *Table 2*. After 5 d of continuous washing, the amount of linear network precursor was found to be approximately 0.5%, i.e. it was of the same order of magnitude as for model end-linked networks. Complete extraction of the linear PS chains was not attained. Two reasons may explain our results: first, duration of extraction may be too short for high molecular weight chains ($> 100\,000$ g mol^{-1}) combined with networks having small mesh-size[24]. However, it is not yet established that longer extraction time would have allowed a complete recovery of the trapped unattached chains. Second, despite the care taken during synthesis, some carbanion may have attacked the merocyanine group (open form of the spiropyran), leading to grafting of the linear PS chains to the network. One may also note that, contrary to the swollen gels, the sol-fractions no longer show any

Table 1 Characteristics of photochromic polystyrene chains

Sample code	$10^{-3}M_w$ (g mol^{-1})	$10^{-3}M_n$ (g mol^{-1})	M_w/M_n	Label position	Label content (label chain^{-1})
A	80	65.5	1.22	One end	0.34
B	329	271	1.21	Both ends	0.62
C	683	478	1.43	Both ends	0.55

Table 2 Characteristics of the polystyrene networks

Sample code[a]	M_c (g mol^{-1})	Q_v (benzene)	Q_v (CS_2)	Sol fraction labelled PS[b]
451A	5400	8.59	10.60	2.91
467A	8900	10.14	–	3.32
468A	10 300	12.52	–	5.65
491B	6400	7.75	7.86	2.48
492B	10 800	11.04	10.60	3.03
493B	32 600	26.10	–	6.14
494B	44 400	33.55	28.53	7.45
495C	5600	7.57	7.65	2.66
496C	9600	10.98	9.59	3.37
497C	14 300	16.03	14.43	4.99
498C	24 400	22.28	–	5.32

[a] Letter refers to code of photochromic PS
[b] Initially, 8% labelled PS introduced

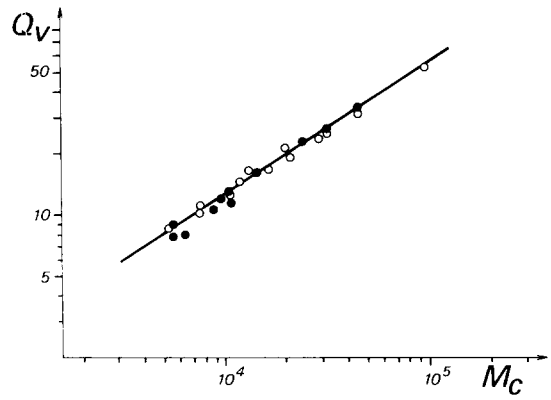

Figure 1 Equilibrium swelling degree for model polystyrene networks (○) and for PS networks containing 8% labelled chains (●) *versus* molecular weight between crosslinks

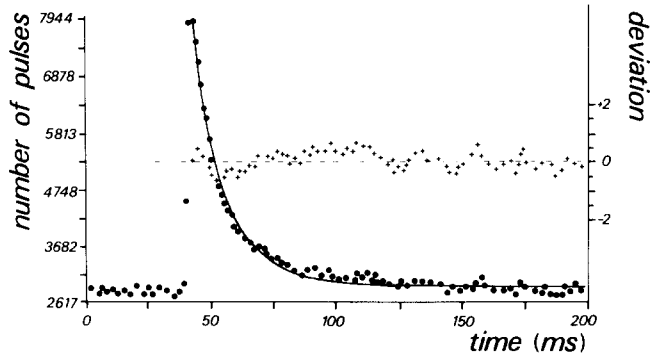

Figure 2 FRS diffracted intensity *versus* time plot for PS network code 492. The continuous line is the best fit to the decay profile using a single exponential function. The distribution of the deviation between experimental and calculated values indicates the quality of the fit

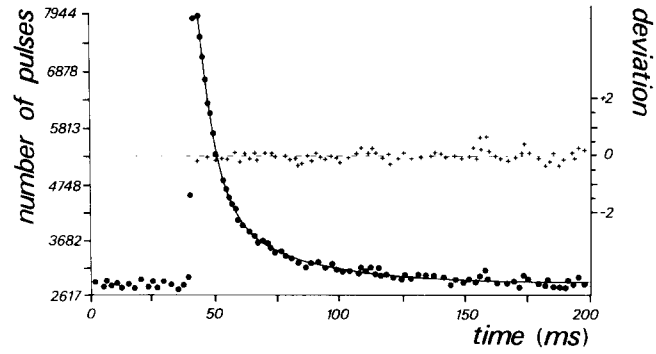

Figure 3 The same plot as in *Figure 2* with data fitted by a sum of two exponentials

photochromic behaviour, most likely due to light and temperature degradation during extraction.

FRS analyses were made for the three series of gels to check the molecular weight dependence (M_c of the network, M_n of the labelled chains) of D_s. *Figure 2* presents a typical relaxation of the diffracted intensity after the flash excitation. Contrary to what happens in semi-dilute solutions, the relaxation process is quite complex. Attempts to fit the data to the analytical form expected for a single-exponential relaxation[4,6,7] appeared rather unsuccessful (*Figure 2*). Therefore, we fitted our data with a sum of two exponentials:

$$y(t) = A(B_1 e^{-\alpha_1 t} + B_2 e^{-\alpha_2 t}) + C$$

where α_1 characterizes a fast process and α_2 a slow process. In *Figure 3*, the best fit curve using this model function is drawn for the same sample as in *Figure 2*. The deviation between experimental and calculated values, also reported in *Figure 3*, is an illustration of the quality of the fit. The observed dependences of α_1 and α_2 on the interfringe spacing i allow us to conclude that both relaxations correspond to a diffuse process, i.e. $\alpha_{1,2} = D_{1,2}q^2$, with $q = 2\pi/i$.

The corresponding diffusion coefficients $D_{1,2}$ are summarized in *Table 3*. The primary observation to be made is that the D_1 value obtained for the fast process remains almost constant when the molecular characteristics of the gels are changed, and that it has the same order of magnitude as the self-diffusion coefficient of free labelled chains. On the other hand, the self-diffusion coefficient corresponding to the slow process systematically increases with increasing molecular weight between crosslinks. As no signal shows up for the solvent surrounding the gel, we are tempted to explain these results by ascribing the fast process to linear chains trapped in voids or defects of the gel structure, with size larger than or comparable to the interfringe spacing. The slow process would be attributed to linear chains really entangled into the gel. An interesting observation is that the amplitude ratio between the two processes depends strongly on the place of the sample examined. This means that the gels are not homogeneous at a microscopic level, and that the relative amount of defects varies from place to place. This strongly complicates a quantitative analysis of the results. Surprisingly, the dependences of the diffusion coefficient corresponding to the slow process on

Table 3 Self-diffusion coefficient measured in swollen PS networks

Sample code	$10^{-3} M_c$ (network)	$10^{-3} M_n$ (label)	$10^8 D_s$ ($cm^2 s^{-1}$) Fast process	Slow process
451A	5.4	65.5	270	15.7
467A	8.9	65.5	–	–
468A	10.3	65.5	85	5.7
491B	6.4	271	22.2	5.4
492B	10.8	271	27.8	5.9
493B	32.4	271	–	8.9
494B	44.4	271	–	12.6
495C	5.6	478	–	5.3
496C	9.6	478	–	5.8
497C	14.3	478	–	6.9
498C	24.4	478	–	7.7

both the molecular weight of the linear chains and the molecular weight between crosslinks appear weaker than the reptation predictions. These data have to be considered as very preliminary, owing to the difficulty of separating with a good degree of confidence two diffusion processes having characteristic times not separated by more than one decade.

To gain information on the diffusion of linear chains entangled into the gels, it appears necessary to improve the homogeneity of the gels at a microscopic level in order to suppress the fast relaxation process. In any case, the forced Rayleigh light scattering experiments provide quite a sensitive test of the homogeneity of the gel on the micrometre scale, and further experiments are under progress to see if a characteristic size of the defects can be detected in the 0.5–50 μm range.

CONCLUSION

The most difficult problem for forced Rayleigh light scattering measurements is the preparation of appropriately labelled samples. Using anionic synthesis, great progress has been achieved regarding the introduction of long polymeric chains bearing one spiropyran molecule at each end into a tridimensional structure. The procedure which was developed leads to sufficient photochromism for analysis by the FRS technique. The main problem which still remains is data processing since the signal is sensitively influenced by the molecular weight distribution and the inhomogeneities of the samples. Currently, we are not able to answer the question: 'Do the linear chains reptate inside the network matrix?'. But the technique may reveal a useful tool for characterizing gel inhomogeneities in the micrometre range.

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