Polymers bearing intramolecular photodimerizable probes for mass diffusion measurements by the forced Rayleigh scattering technique: synthesis and characterization

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A new photochromic probe, bis(9-anthryl methyl) ether (BAME) derivative, was synthesized and introduced as an effective probe for forced Rayleigh scattering (FRS) measurement. It is shown that BAME and polystyrene labelled with BAME exhibit a large change in refractive index under irradiation of u.v. light (363.8 nm). The self-diffusion of BAME and polystyrene labelled with BAME (PSA) were measured in various solvents. Results of PSA in good, marginal and poor solvents are consistent with those obtained from quasi-elastic light scattering (QELS). Since the photodimerization reaction of anthracene has been extensively studied in solution and crystal as well as in polymer matrix, unfavourable multistep photochemical reactions can be avoided. One such unfavourable case, which involves a fluorescence quenching solvent CCl_4, is demonstrated. A temperature dependence study of polystyrene in semi-dilute theta solution by FRS has suggested that the non-exponential intensity decay is due to large concentration fluctuations in the solution. The well known photochemistry, large refractive index change and temperature stability have made BAME a very promising probe for FRS measurements.

(Keywords: forced Rayleigh scattering; photodimerizable probe; diffusion; bis(9-anthryl methyl) ether; semi-dilute solution)

INTRODUCTION

Since the forced Rayleigh scattering (FRS) experiment was introduced for the measurement of polymer diffusion by Rondelez and co-workers[1,2], this technique has demonstrated its importance in the investigation of polymer dynamics[3–6]. In the FRS measurement of mass diffusion, a spatial modulation of refractive index is artificially created in a photosensitive sample by the interference pattern of a pulse of two coherent laser beams (writing beams). After this writing pulse, the optical grating in the sample is gradually smeared out by mass diffusion. This diffusion process can be directly followed by monitoring of the transient diffraction intensity from the sample with another laser (reading beam). According to the Fick law of diffusion, in a usual case, the decay of diffraction intensity should be a single exponential function with a corresponding characteristic time constant. The diffusion coefficient can be obtained from this time constant and the fringe spacing of the optical grating. However, the simple FRS technique described above seems to work only for some combinations of dye, polymer and solvent. In many cases, the decay of diffraction intensity appears as a non-exponential function of time. The origin of this non-exponentiality of the diffraction intensity is still not well understood. This is the most serious problem in obtaining the diffusion coefficients accurately by the FRS technique. The misinterpretation of the diffraction signal and hence the diffusion coefficient could obscure the important physical picture of the system under investigation.

To explain this unusual behaviour of the diffraction signal, Johnson *et al.* introduced the concept of wave-coupling theory[7], which was originally proposed by Kogelnik[8], to the FRS: under irradiation of light, some of the photochromic molecules may change chemical structure, resulting in two distinct species with different diffusion coefficients. This in turn will cause interference between the two diffraction fields and lead to a non-exponential decay of the diffraction signal. However, the same unusual diffraction signal was observed by Yu *et al.*[3] and by Deschamps and Leger[9] in experiments where the photochromic probes were attached to polymer chains and measurements carried out in specific solvents. It is unlikely that a small change in structure of the probe attached to a polymer chain can vary the diffusion coefficient of the chain in solution and form two distinct gratings, unless more complicated chemistry or physics are involved in this process.

In general, under irradiation of light, the probe which is photochromic in nature undergoes a photochemical reaction which changes the chemical structure of the molecule. For some cases, the change in structure results in a change of refractive index. However, this type of

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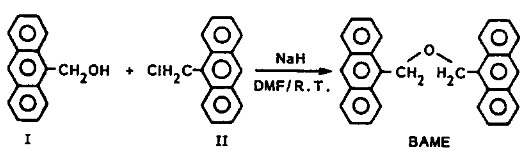


Scheme 1

photochemical reaction often takes place through several reaction steps in which a number of intermediates and/or photoproducts are involved. Furthermore, these intermediates and/or photoproducts may react with the surrounding chemical species and produce a more complicated situation. Consequently, multiple optical gratings may be formed at different times, resulting in a non-exponential diffraction intensity decay. The analysis of the decay to obtain diffusion coefficients for cases with complicated chemistry is therefore untractable unless the mechanism of the photochemical reactions is known and can be carefully analysed. We will discuss this case again below. For systems with complicated physics, such as double gratings or multiple relaxation times, it will be impossible to separate out individual mechanisms if complicated chemistry, as mentioned above, is occurring at the same time.

To eliminate difficulties and complications caused by an unknown mechanism of photochemical reaction involved in the FRS measurement, we introduced into this technique a new class of photochromic probes: the intramolecular photodimerizable bis(9-anthryl methyl) ether (BAME) derivatives. The photodimerization of anthracene has been studied extensively in solution[10,11], crystal[12] and, recently, bulk polymer matrix[13]. It can be known *a priori* whether a one-step or a complicated photochemical reaction will occur in a system. Therefore, multistep photoreaction systems can be avoided to favour the study of more complicated physical processes.

In a previous report[14], we have shown that polystyrene labelled with BAME derivative exhibits a large change in refractive index under irradiation of 363.8 nm Ar ion laser light and can be used as an effective probe for FRS measurements. In this paper, we show in detail the synthesis, characterization and wide applicability of these probes in various polymer systems. The procedures for synthesis of the probes and for labelling polystyrene are described, and the results of mass diffusion in various systems obtained by FRS with BAME and its derivative are demonstrated and compared with other measurement techniques.

EXPERIMENTAL

Sample synthesis

Bis(9-anthryl methyl) ether (BAME). The synthesis of this probe was carried out by the following reaction, described previously by Castellan *et al.*[15]:

9-Anthracenemethanol (I, see Scheme 1) and 9-chloromethyl anthracene (II) (both from Aldrich*) were recrystallized twice from benzene and toluene, respectively. DMF (Aldrich, HPLC grade) was distilled over magnesium sulphate. A solution of 2.38 g (10 mmol) of I in 250 ml of dried DMF was added dropwise into a solution of 0.2 g of NaH (60% in mineral oil, Aldrich, equivalent to 5 mmol) in 44 ml of dried DMF. The whole solution was stirred for an hour. The solution became orange-red in colour. Then a solution of 2.265 g (10 mmol) of II in 200 ml of DMF was added dropwise to this mixture. After stirring for another hour, the product was separated by adding water to the reaction mixture. Pure BAME was obtained from column chromatography of the crude product. The absorption spectrum of BAME in benzene is shown in *Figure 1*.

I.r.: 2900 cm^{-1} (CH_2); 1030 cm^{-1} (C–O).

H-n.m.r.: $\delta = 5.7$ ppm (4H, aliphatic).

9-10-hydroxymethyl anthryl methyl 9′-anthryl methyl ether (VI). Compound VI was prepared according to *Scheme 2*.

Compound III, 9,10-bis chloromethyl anthracene, was synthesized by the procedure described by Miller *et al.*[16] 25 g of anthracene (Wako Pure Chemical Industries, Japan) were purified by recrystallization twice from

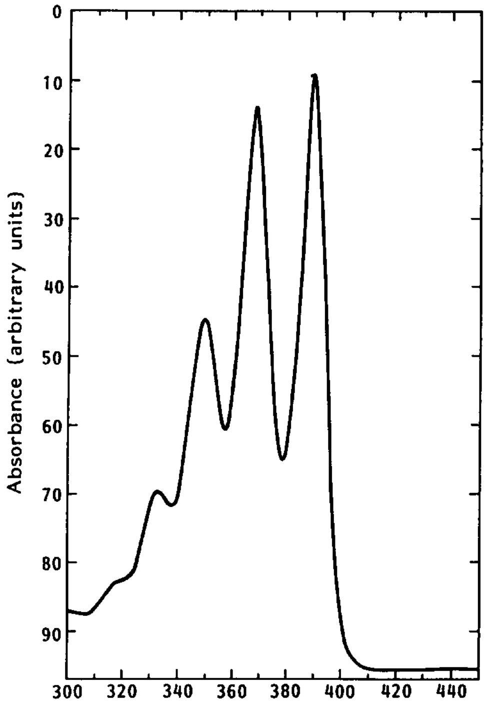
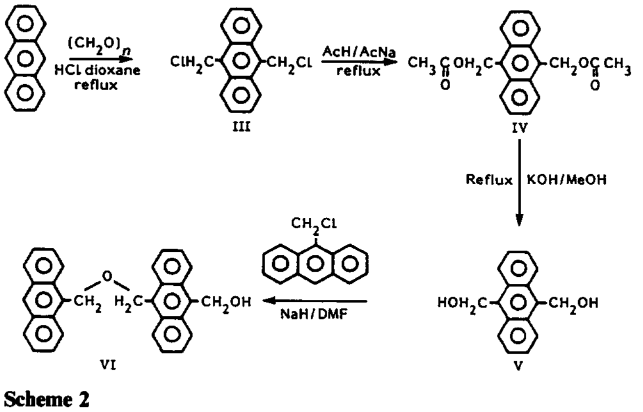


Figure 1 Absorption spectrum of BAME in benzene at 25°C



Scheme 2

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* Certain chemical materials and instruments are identified in this paper in order to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards

benzene solution. Anthracene thus obtained together with 21 g of paraformaldehyde (Nakarai Chemicals, Japan) were added into a solution of 34 ml of concentrated HCl and 200 ml of dioxane which was saturated with HCl gas. The whole mixture was refluxed at 150°C under a gentle flow of extra HCl gas. At the reflux temperature, anthracene and paraformaldehyde were dissolved to give a dark brown solution. After 2 h of reflux, HCl gas flow was stopped and the reaction solution kept at reflux for a further 3 h. Then the whole mixture was cooled to room temperature and left overnight.

The product, a yellow precipitate, was filtered and recrystallized twice from benzene. Yellow needle shaped crystals of compound III were obtained.

I.r.: 1240 cm^{-1} (C–Cl wagging).

H-n.m.r.: $\delta = 5.8$ ppm (4H, methylene proton).

Compound IV, 9-10-anthracene dimethanol diacetate, was prepared by the method described by Nakaya *et al.*[17] 1.51 g of 9,10-bis chloromethyl anthracene and 1.91 g of sodium acetate anhydrous were dissolved in 30 ml of acetic acid. The whole mixture was refluxed for 5 h. Then the whole mixture was cooled to room temperature. The bright yellow crystal was filtered and washed with water. The product was recrystallized twice from benzene before use in the next reaction.

I.r.: 1730 cm^{-1} (C=O).

H-n.m.r.: $\delta = 2.0$ ppm (methyl proton).

Compound V, 9,10 anthracene dimethanol, was also prepared by the procedure described by Nakaya *et al.*[17] A mixture of 1.18 g of compound IV and 3.56 g of 85% potassium hydroxide (Wako Pure Chemical Industries, Japan) in 93 ml of methanol was refluxed for 3 h. The product was then washed several times with water and dried.

I.r.: 3400 cm^{-1} (OH).

H-n.m.r.: $\delta = 5.5$ ppm (4H, doublet); 5 ppm (2H, triplet).

Compound VI, 9-(10-hydroxymethyl) anthryl methyl 9′-anthryl methyl ether, was prepared as follows. A solution of 0.394 g (1.66×10^{-3} M) of compound V in 40 ml of dried DMF was added dropwise to a solution of 0.066 g of 60% NaH in 15 ml of dried DMF. After the end of the addition, the solution was stirred for an hour. The solution became orange-red. Then, a solution of 0.375 g of 9-chloromethyl anthracene (1.66×10^{-3} M) in 35 ml of dried DMF was added dropwise to the reaction solution. The whole solution was stirred for another hour. The solution became yellow. The product was obtained by adding water into the solution and filtering. The crude product was a yellow powder. It was purified by gel filtration with Sephadex column and with DMF as solvent.

I.r.: 3400 cm^{-1} (OH), 2800 cm^{-1} (CH$_2$); 1030 cm^{-1} (C–O).

H-n.m.r.: $\delta = 8.5$–7.5 ppm (ring proton, 17H); $\delta = 5.7$ ppm (doublet, 4H); $\delta = 5.5$ ppm (doublet, 2H); $\delta = 5.0$ (triplet, hydrogene bonding proton).

Chloromethylation of polystyrene. Chloromethylation of polystyrene was carried out by following the procedure of Feinberg and Merrifield[18]. However, accompanying the attachment of chloromethyl groups on polymer chains, the alkylation reaction also causes intrachain cross-linking. This side reaction could cause a serious problem in the later measurement of mass diffusion. This cross-linking reaction can be minimized by carrying out the reaction at low temperature, low concentration (much less than the overlap concentration, C^*) and short reaction time. With this procedure we can obtain polystyrene with different degrees of chloromethylation of molecular weight up to 500 000 without an obvious change in molecular weight distribution of the precursor polymers. For example, 1 g of monodispersed polystyrene ($M_w = 1.02 \times 10^5$, $M_w/M_n = 1.04$, Toyo Soda standard sample) was dissolved in a mixture of 60 ml dichloromethane and 20 ml chloromethyl methyl ether (Aldrich). Then 0.1 ml of 1N dried THF solution of zinc chloride was added to this solution as a catalyst. The whole solution was stirred at 35°C for several hours. The degree of chloromethylation was checked by following the time evolution of the i.r. characteristic absorption band of the chloromethyl group (1260 cm)$^{-1}$) of the polymers obtained from different aliquots taken after appropriate reaction times. At the end of each reaction time, the corresponding solution was poured into ice water and chloromethylated polystyrene was obtained. The chloromethylated polystyrene was reprecipitated twice by using benzene and methanol. Finally, the molecular weight distribution was checked by g.p.c. and compared with the precursors.

Labelling chloromethylated polystyrene with BAME derivative. The coupling reaction between compound VI and chloromethylated polystyrene was carried out by the same procedure as used for synthesizing BAME. For example, a solution of 160 mg of compound VI in 100 ml of DMF was added dropwise to a solution of 10 mg of NaH in 40 ml of DMF. The whole solution was stirred for an hour. Then, a solution of 5.61 g of chloromethylated polystyrene ($M_w = 37\,400$, $M_w/M_n = 1.04$) in 100 ml of DMF was added dropwise to this solution. At the end of the addition, the solution was stirred at room temperature overnight. The labelled polymer was extracted by pouring water into the reaction solution. The polymer was precipitated twice by using benzene and methanol and finally checked with g.p.c. *Figure 2* shows the absorption spectrum of BAME labelled polystyrene in benzene at 22°C.

Sample characteristics

Solvents obtained from Aldrich (ACS reagent) were used in this work without further purification. Polydimethyl siloxane (Dow Corning), which has an average molecular weight of 4000, was purified by washing with benzene and methanol before use. BAME labelled polystyrene ($M_w = 37\,400$, $M_w/M_n = 1.04$) with a labelling ratio of 0.3 probe chain^{-1} was used.

Instruments and data analysis

A block diagram of the FRS instrument used in this work is shown in *Figure 3*. A coherent Innova Model 90-5 Ar ion laser operated at 363.8 nm was used for the writing of the transient grating and a Lexel Model 75 Ar ion laser operated at 488 nm was used for reading. The power of both writing and reading beams in our experiment was about 20 mW c.w. The writing pulse was generated by an

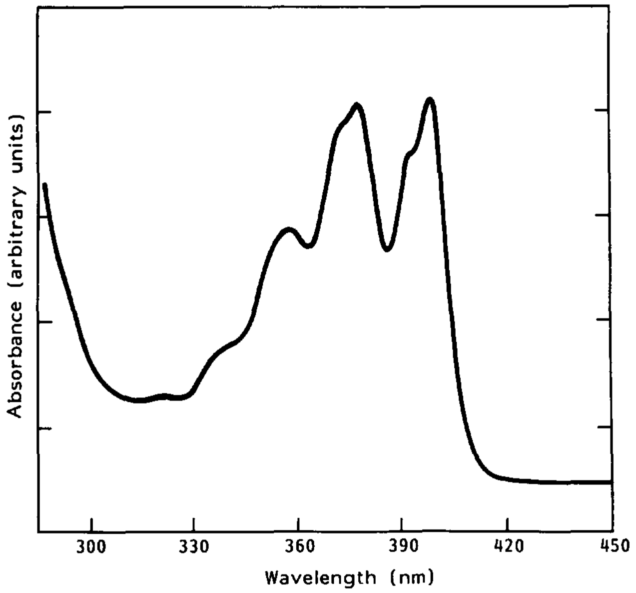

Figure 2 Absorption spectrum of BAME labelled polystyrene ($M_w = 102\,000$, $M_w/M_n = 1.02$) in benzene at 22°C

electric shutter and had a pulse width of about 20 ms. In this set-up, the fringe spacing of the interference pattern can be varied between 5 and 25 μm. The decay of diffraction intensity is digitally recorded and analysed by a nonlinear least squares regression program with the following model function[19]:

$$I(t) = (A\mathrm{e}^{-t/\tau} + B)^2 + C \tag{1}$$

where A, B, C and τ are fitting parameters.

Background of the forced Rayleigh scattering experiment

In the FRS experiment photochromic molecules are often used to create a sinusoidal modulation of refractive index. In the simplest case, the photochromic molecules undergo a change in structure through a one-step reaction:

$$\mathrm{M} \underset{h\nu' \text{ or } \Delta}{\overset{h\nu}{\rightleftharpoons}} \mathrm{M}^* \tag{2}$$

The backward reaction determines the lifetime τ_p of M*, i.e. the natural lifetime of the optical grating generated in the FRS experiment. The spatial modulation of concentration of M* after the light pulse is given by:

$$C^*(X,0) = C_0\left(1 + \cos\frac{2\pi}{d}X\right) \tag{3}$$

where C_0 is the initial concentration of M and d is the fringe spacing. For simplicity, we consider the one-dimensional case. After the light pulse, if the probe molecules undergo photochromic change following reaction (2), the diffusion of species M* in the sample can be described by Fick's law with a sink term caused by the finite lifetime τ_p of M*:

$$\frac{\partial C^*(X,t)}{\partial t} = D_{\mathrm{self}}\nabla^2 C^*(X,t) - \frac{C^*(X,t)}{\tau_p} \tag{4}$$

The solution of equation (4) under the initial condition (3) is:

$$C^*(X,t) = C_0\mathrm{e}^{-t/\tau_p}\left\{1 + \cos\frac{2\pi}{d}X\exp\{(2\pi/d)^2 D_{\mathrm{self}}t\}\right\} \tag{5}$$

The diffraction field caused by a grating of refractive index differences is then:

$$E_{\mathrm{diff}}(t) \propto \eta C_0\{C^*(0,t) - C^*(\tfrac{1}{2}d,t)\} \tag{6}$$

where η is the diffraction efficiency of the grating. This quantity depends on the characteristics of the photochemical probe.

Finally, the time-dependent diffraction intensity is:

$$I_{\mathrm{diff}}(t) \propto E^2_{\mathrm{diff}}(t) = (A\mathrm{e}^{-t/\tau} + B)^2 + C \tag{7}$$

where:

$$\frac{1}{\tau} = D_{\mathrm{self}}q^2 + \frac{1}{\tau_p} \tag{8}$$

$$q = \frac{2\pi}{d} = \frac{4\pi}{\lambda_w}\sin(\theta/2)$$

τ = decay time constant of the diffraction intensity;
q = magnitude of the scattering vector of the grating;
λ_w = wavelength of the writing beam;
θ = crossing angle between the two writing beams;
A = prefactor depending on properties of the grating;
B = coherent background;
C = incoherent background.

By measuring the decay time constant τ at different angles, the diffusion coefficient can be obtained from equation (8). As mentioned above, equation (4) can only describe diffusion of species obeying the simple photochemical reaction (2). When more than one photoproduct or intermediate is involved multiple optical gratings may be formed. Equation (4) becomes a set of simultaneous differential equations which will result in complicated solutions. Depending on the refractive indices of the species at the reading wavelength, the decay of the diffraction intensity may be non-exponential. Consequently, details of the photochemical reaction mechanism are required before it is possible to analyse the decay and extract the diffusion coefficient. An example of

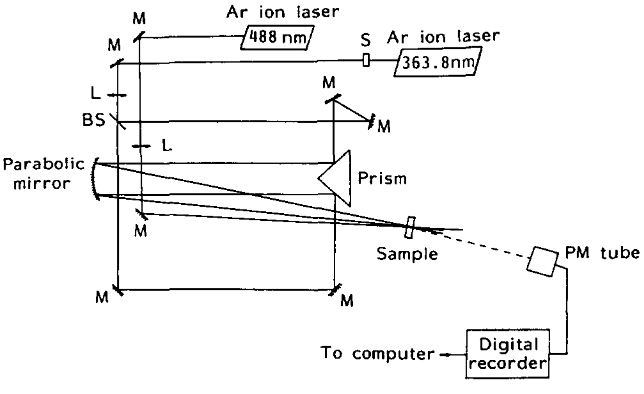

Figure 3 Block diagram of FRS instrument: L, lens; BS, beam splitter; S, shutter; M, mirror

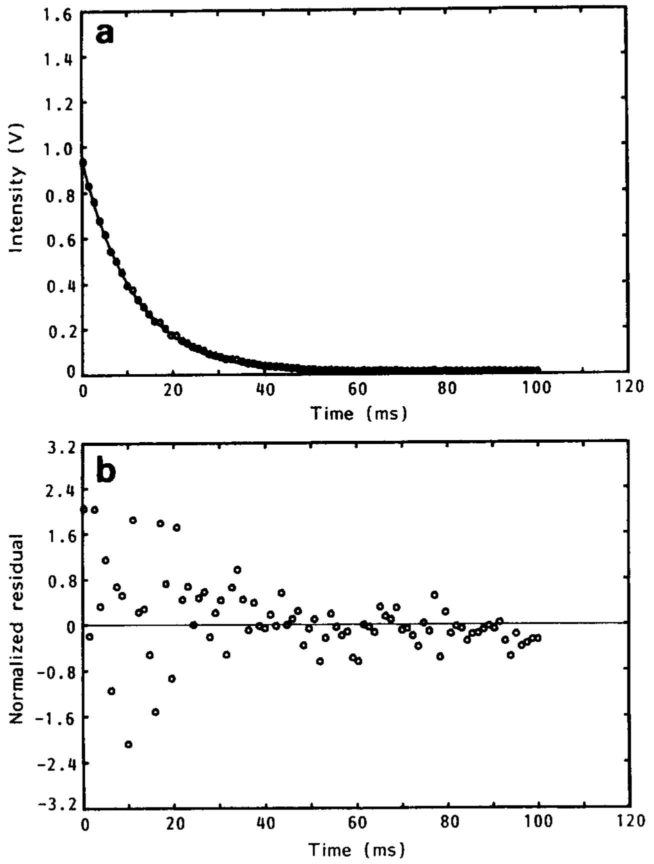

Figure 4 (a) Decay of diffraction intensity of BAME in t-decalin at 22°C; $c=2.9\times10^{-5}\,\mathrm{mol\,l^{-1}}$. ○, Experimental data points; ———, curve obtained by fitting with equation (1). $\theta=21.71$ mrad; $d=16.76\,\mu\mathrm{m}$; $D=3.1\times10^{-6}\,\mathrm{cm^2\,s^{-1}}$; (b) normalized residual plot for the data in (a), r.m.s. residuals = 5.448×10^{-3}

this will be shown later for BAME, in the discussion section.

Characterization of BAME as a probe for FRS

Diffusion of BAME in various solvents. To demonstrate the validity of BAME as a probe for FRS, the self-diffusion of BAME in various solvents has been measured. A single exponential decay of diffraction intensity as a function of time is always observed. For example, the diffraction decay of BAME in t-decalin is shown in *Figure 4*. The q^2-dependence of the decay time constants obtained from the curve fitting process (equation (1)) is linear, as shown in *Figure 5*. The straight line passing through the origin confirms the fact that the lifetime τ_p of the dimer form of BAME is infinite, which is consistent with the irreversibility of anthracene dimers even at high temperatures reported previously by Chandross[12]. Diffusion coefficients of BAME in various solvents are plotted *versus* solvent viscosity in *Figure 6*. It is worth noting that the diffusion coefficient of BAME in cyclohexane obtained by FRS has the same order of magnitude as that estimated from the reaction rate of fluorescence excimer formation of 9-acetoxyanthracene[20], provided that 9-acetoxyanthracene is a sphere with radius 0.4 nm. The linear relationship between diffusion coefficient of BAME and viscosity of solvents does not hold, indicating that specific intermolecular interactions between BAME and solvents exist. This kind of interaction, which cannot be described by a simple Stokes–Einstein model, is beyond the scope of this Paper.

Diffusion of BAME in polymer melts. To test the applicability of BAME in polymer melts, we used PDMS as an example. *Figure 7* shows the decay of diffraction intensity from BAME in PDMS at 22°C. The data can clearly be represented by a single exponential function, as shown by the solid line in *Figure 7(a)* and by the residual plot in *Figure 7(b)*. The diffusion constant obtained from the $1/\tau$ *versus* q^2 plot shown in *Figure 8* is $9.6\times10^{-7}\,\mathrm{cm^2\,s^{-1}}$.

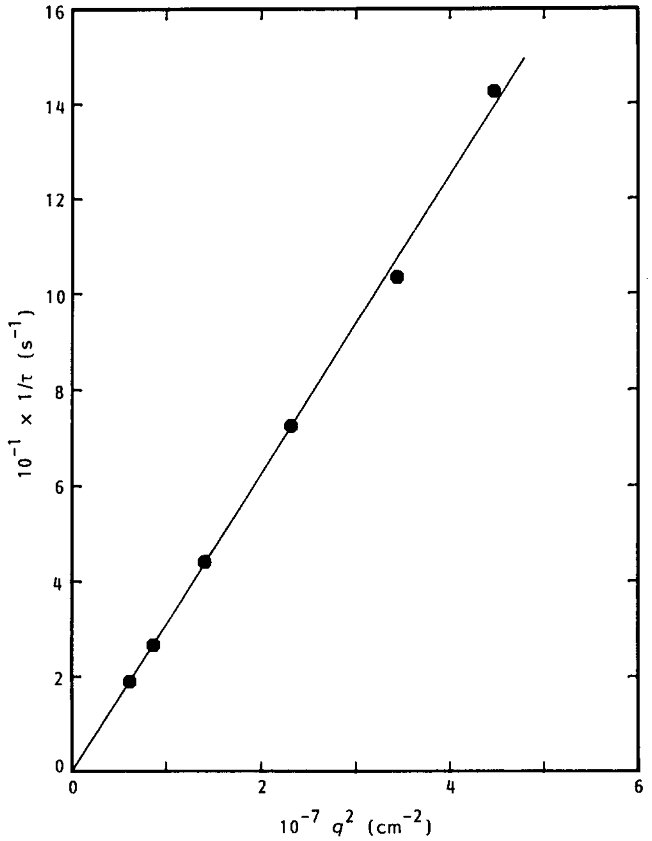

Figure 5 q^2 Dependence of decay time constants of BAME in t-decalin at 22°C

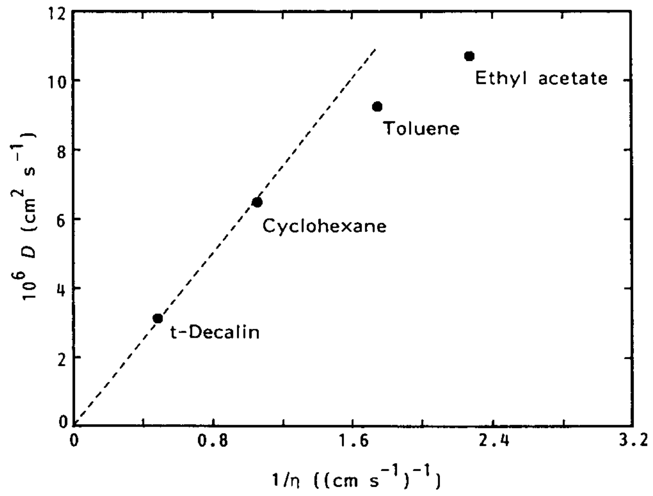

Figure 6 Relation between translational diffusion constants of BAME and viscosity of various solvents at 22°C

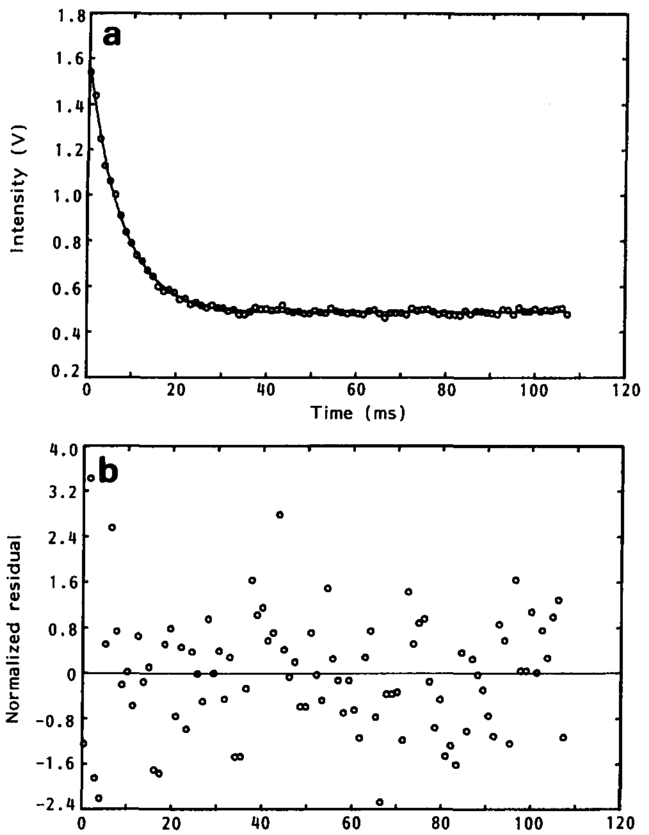

Figure 7 (a) Decay of diffraction intensity of BAME in PDMS (average $MW \approx 4000$) at 22°C. ———, Curve obtained by fitting with equation (1). $\theta = 48.20$ mrad; $d = 7.55\,\mu$; $D = 9.6 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$; (b) normalized residual plot for the data in (a), r.m.s. residuals $= 1.125 \times 10^{-2}$

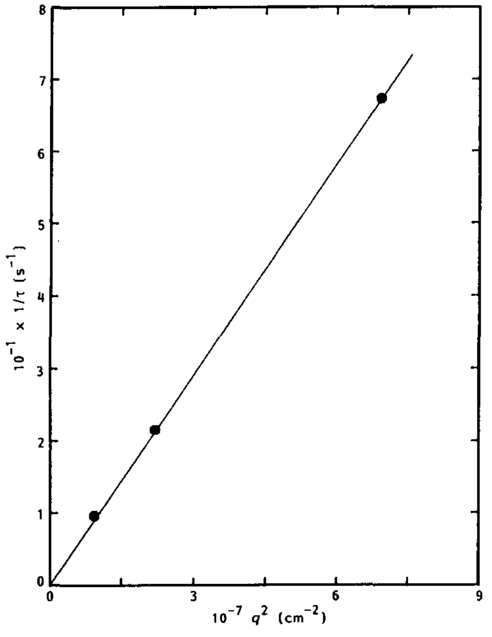

Figure 8 q^2 Dependence of decay time constant of BAME in PDMS at 22°C

Self-diffusion of BAME labelled polystyrene in various solvents. To test the applicability of BAME as a probe for polymer diffusion, three typical solvents, benzene (good solvent), ethyl acetate (marginal solvent) and t-decalin (poor solvent) were selected. All measurements were carried out at room temperature (≈22°C). As shown in *Figures 9–11*, the behaviour of the diffraction intensities of BAME labelled polystyrene in these solutions is normal, i.e. a single exponential function of time. From the q^2-dependence of decay time constants, shown in *Figure 12*, the self-diffusion coefficients of polystyrene in these solvents are calculated. The validity of these diffusion constants was checked against the quasi-elastic light scattering (QELS) measurements of the precursor chloromethylated polystyrene in the same solvent and at the same temperature and concentration. Results obtained from the two sets of measurements agree within 10%, as shown in *Table 1*.

Unusual behaviour of BAME labelled polystyrene in fluorescence quenching solvents. In this section, multiple gratings caused by multistep photochemical reactions will be illustrated. In carbon tetrachloride, a solvent with external heavy atom effect, the diffraction signal from BAME labelled polystyrene behaves abnormally, as shown in *Figure 13*. After the end of a 20 ms writing pulse, the diffraction intensity continuously rises for another 100 ms and then starts to decay with small oscillation at long time. One possible reason for this abnormal behaviour is the reaction between anthracene and solvent (CCl_4) under the irradiation of u.v. light, as reported many years ago by Bowen and Rohatgi[21] and later by Kallman-Oster[22]. According to these works, after excitation to the singlet state, anthracene removes the chlorine atom from the solvent and allows the formation

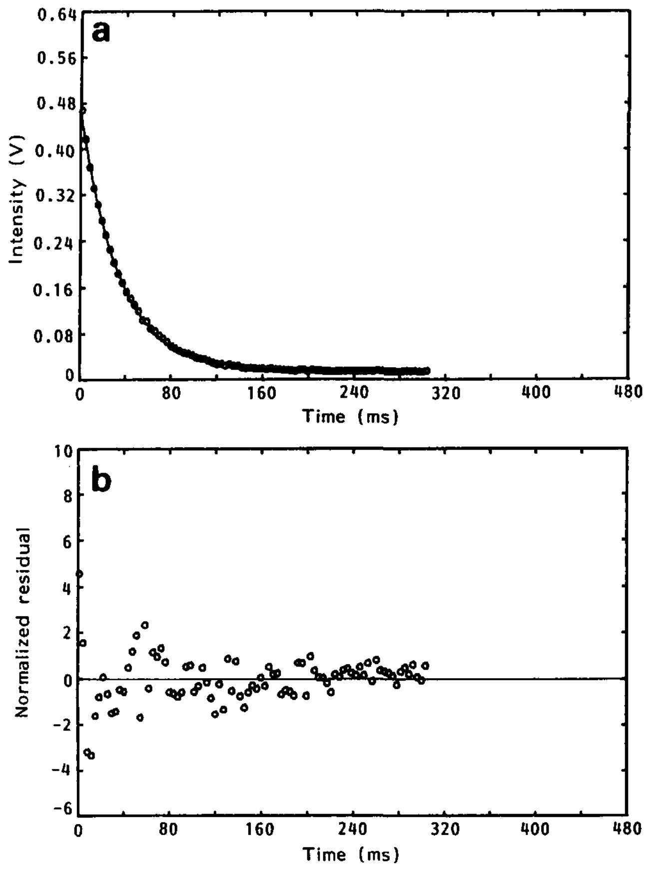

Figure 9 (a) Decay of diffraction intensity of BAME labelled polystyrene (PSA-1) in benzene at 22°C; $c = 0.55 \times 10^{-2}$ (g/g). ———, Curve obtained by fitting with equation (1). $\theta = 29.91$ mrad; $d = 12.16\,\mu\mathrm{m}$; $D = 6.1 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$; (b) normalized residual plot for the data in (a), r.m.s. residuals $= 1.724 \times 10^{-3}$

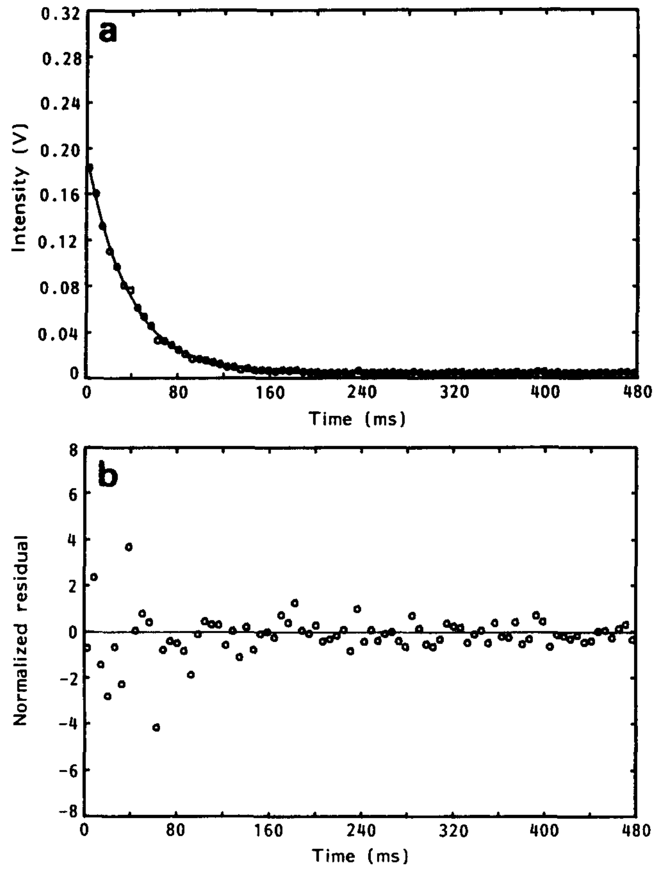

Figure 10 (a) Decay of diffraction intensity of PSA-1 in ethyl acetate at 22°C; $c = 53 \times 10^{-2}$ (g/g). ———, Curve obtained by fitting with equation (1). $\theta = 20.76$ mrad; $d = 17.52\,\mu$m; $D = 1.1 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$; (b) normalized residual plot for the data in (a), r.m.s. residuals $= 1.361 \times 10^{-3}$

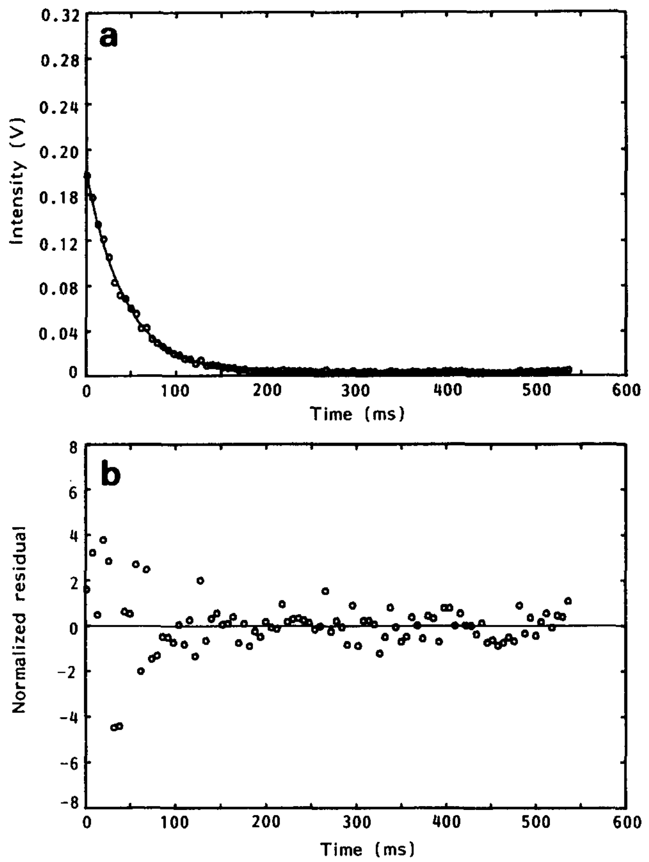

Figure 11 (a) Decay of diffraction intensity of PDSA-1 in t-decalin at 22°C; $c = 0.58 \times 10^{-2}$ (g/g). ———, Curve obtained by fitting with equation (1). $\theta = 40.34$ mrad; $d = 9.02\,\mu$m; $D = 2.3 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$; (b) normalized residual plot for the data in (a), r.m.s. residuals $= 1.299 \times 10^{-3}$

of free radicals. These free radicals react with the anthracene ring through successive steps to produce complicated chlorinated polynuclear products. The total quantum yield of these reactions is very high, about 0.4. There is also a possibility that these free radicals react with polymer chains to form cross-links. Owing to the refractive index difference of those photoproducts, multiple optical gratings may be created, which could result in non-exponential decay of the diffraction intensity. Since we do not have a complete knowledge of the photochemical reaction mechanism and the refractive index of different photoproducts at the wavelength of the reading beam, analysis of this complicated time dependence of diffraction signal is not possible. However, if we neglect the early increasing data values and carry out the analysis with the later data values only, the unusual decay of diffraction intensity in *Figure 13* can be fitted very nicely to equation (7), as shown in *Figure 14*. But, the resulting diffusion coefficient is $1.4 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$, which is about one third of the value of $5.26 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$ obtained by pulse field gradient n.m.r. under very similar experimental conditions[23]. Therefore, caution must be exercised if one wishes to truncate the early part of an unusual decay of FRS data. It is worth noting that in other fluorescence quenching solvents such as dimethyl aniline we could not observe the diffraction signal from BAME. This confirms that dimerization of anthracene takes place via an excited singlet state, with excimer as an intermediate.

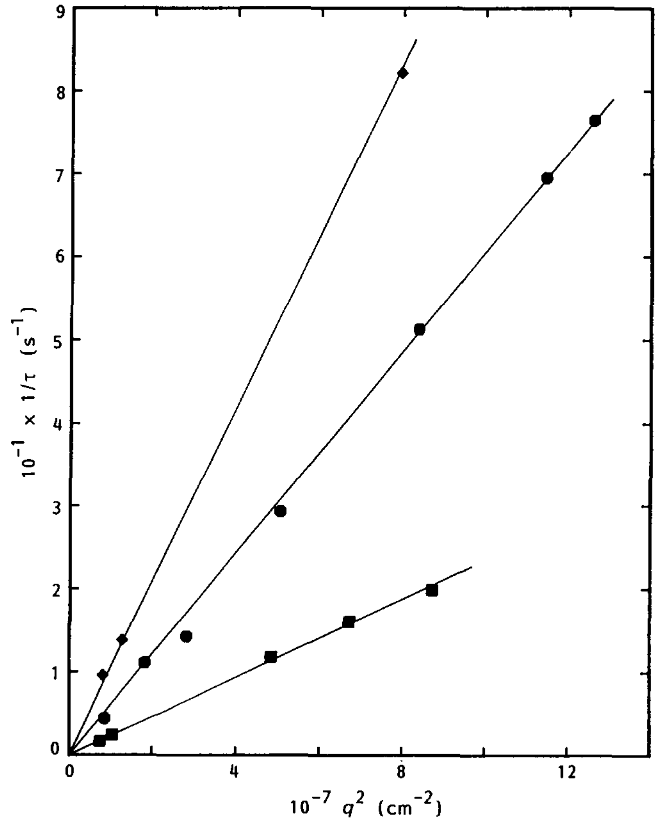

Figure 12 q^2 Dependence of decay time constants of PSA-1 in benzene (●), ethyl acetate (◆) and t-decalin (■)

Table 1

Solvents	C (g/g)	D (cm^2 s^{-1}) (FRS)	D (cm^2 s^{-1}) (QELS)
Benzene	0.55×10^{-2}	6.1×10^{-7}	6.6×10^{-7}
Ethyl acetate	0.53×10^{-2}	1.0×10^{-6}	1.1×10^{-6}
t-Decaline	0.58×10^{-2}	2.3×10^{-7}	2.5×10^{-7}

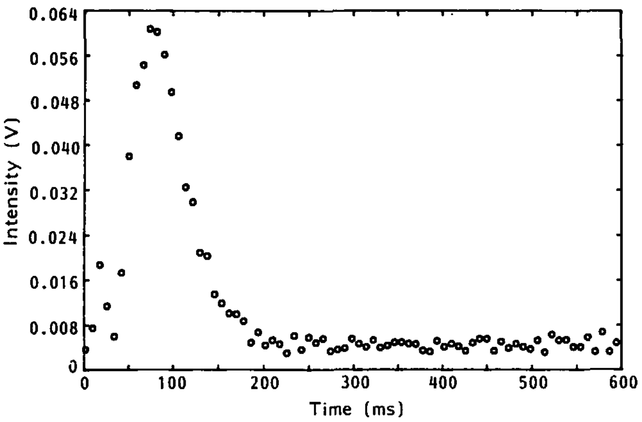

Figure 13 An unusual diffraction decay from PSA-1 in CCl_4 at 22°C. Pulse width, 20 ms; concentration of polymer, $c = 0.5$ wt%; $\theta = 51.67$ mrad; $d = 7.04\,\mu$m

Self-diffusion of BAME-labelled polystyrenes in t-decalin under semi-dilute conditions. Self-diffusion of BAME-labelled polystyrene with several different molecular weights ($M_w = 9500$, 37400 and 102000; $M_w/M_n \leqslant 1.05$; labelling ratios 0.2, 0.5 and 1.0 dye chain^{-1}) has been carried out by FRS in matrixes of entangled and unlabelled polystyrenes in t-decalin at several different temperatures. For unlabelled chains, NBS-705 polystyrene ($M_w = 173000$, $M_w/M_n = 1.07$) was chosen, since the static properties of this polymer in t-decalin have been carefully studied by Nose and Chu[24]. Concentration of unlabelled chains in the matrix is kept constant at 0.101 g/g, which is $\approx 3c^*$, where c^* was calculated from $c^* = M_w/N_A\rho_s 4\pi/3Rg^3$ ($= 0.037$ g/g). The concentration of labelled chains in all solutions is $\approx 1.22\times10^{-3}$ g/g.

For the solution with labelled chain molecular weight 9500 at 22°C, the diffraction intensity keeps growing for 60 ms after the end of the writing pulse before it starts to decay, as shown in *Figure 15*(*a*). This so called 'unusual' behaviour of diffraction intensity has been previously observed for azobenzene labelled polystyrene in cyclohexane at 35°C[3] and spiropyran labelled polystyrene in cyclopentane at 23°C[9], both in semi-dilute conditions. In our experiment, however, this unusual intensity growth gradually decreases with increasing temperature and finally disappears at 29.5°C for 9500 labelled polymer, as shown in *Figures 15*(*b*) and (*c*), respectively. The diffusion coefficient at 9.5 K in NBS-705 matrix was obtained as 6.6×10^{-8} cm^2 s^{-1} by fitting the diffraction intensity from *Figure 15*(*c*) with a four-parameter fit (equation (7)), as shown in *Figure 16*. For labelled chains of higher molecular weights, the unusual rise persists even at 41.3°C (for labelled chains of $M_w = 102000$), though the rise time after the pulse tends to decrease gradually with increasing temperature, as shown in *Figure 17*.

Since BAME dimerizes in t-decalin with a simple one-step photoreaction, these results suggest that semi-dilute solutions under θ-condition might not be completely homogeneous, as reported recently by Koberstein *et al.*[25], who showed by small angle neutron scattering (SANS) that there exists, in semi-dilute solutions of polystyrene under θ-condition, a long range concentration fluctuation in the region of $qRg < 1$. Therefore, we currently believe that the unusual behaviour of FRS signals observed in semi-dilute solutions under θ-condition with azobenzene[3], spiropyran[9] and BAME probably originates from the inhomogeneity of the system. But we can not rule out another, unlikely, cause of this abnormality of diffraction intensity at θ-temperature. This is the double grating from the photo-unreacted and photoreacted labelled chains due to different chemical structures of the photochromic probes before and after irradiation (for spiropyran: neutral colourless form/merocyanine (blue form) carrying electrostatic charges, *trans*-azobenzene (hydrophobic)/ *cis*-azobenzene (hydrophylic); and for BAME: monomer (opened form)/photodimer (closed form)). These differences in θ-temperature might be enough to cause the formation of some transient clusters which modify the refractive index gratings in the experiment. We would like to point out here that, with writing pulse widths < 50 ms, we could not obtain normal single exponential decay even at 29.5°C for 9500 labelled chain in NBS-705 matrix. This fact suggests that there exists a certain structural

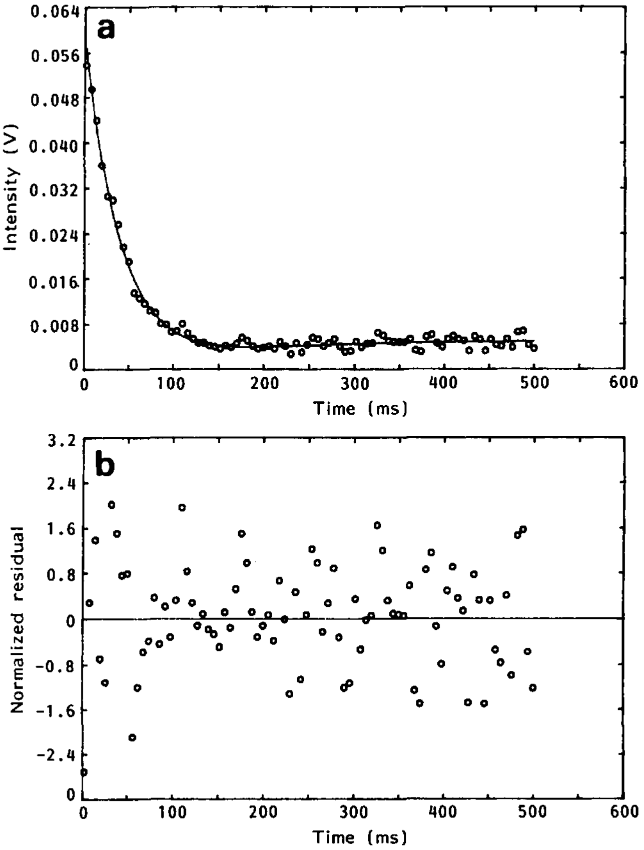

Figure 14 (a) A single exponental fit to the later part of the unusual diffraction decay of *Figure 13*. The apparent diffusion coefficient obtained is $D = 1.4\times10^{-7}$ cm^2 s^{-1}; (b) normalized residual plot for the data in (a), r.m.s. residuals $= 1.122\times10^{-3}$

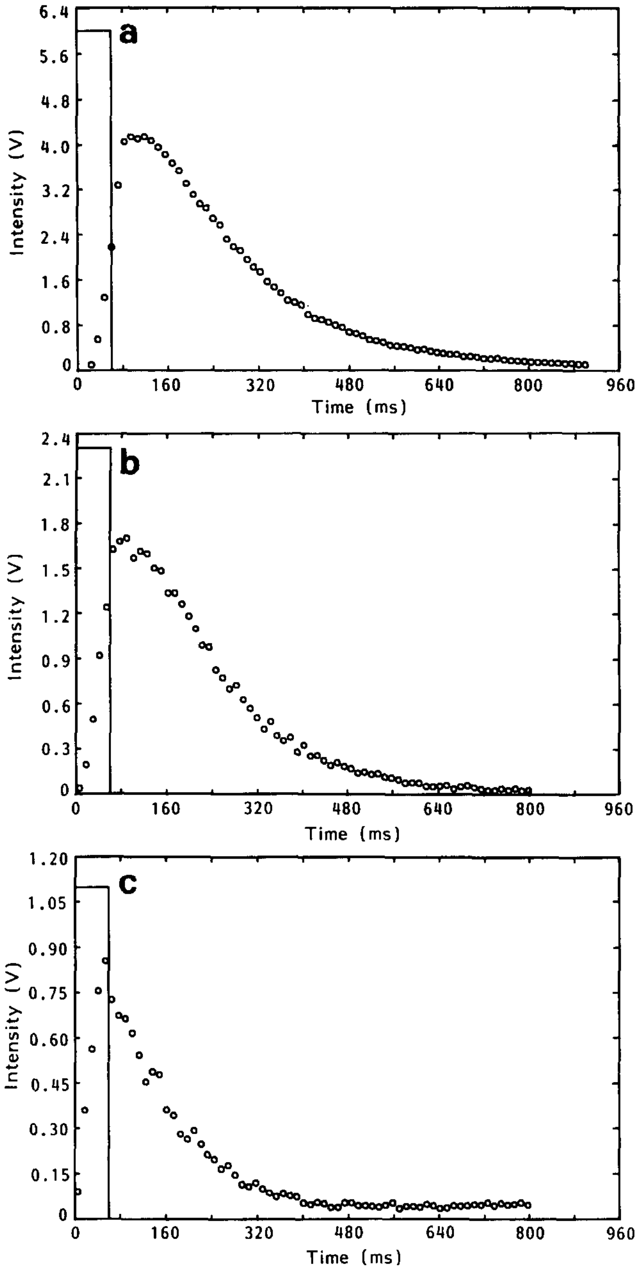

Figure 15 Decay of diffraction intensity of BAME labelled polystyrene with molecular weight $= 9.5 \times 10^3$ at $c = 1.22 \times 10^{-3}$ g/g in a matrix of semi-dilute polystyrene solution in t-decalin with matrix molecular weight 173×10^3 and $c = 0.101$ g/g at temperatures of (a) 22°C, (b) 24°C, (c) 29.5°C. (a) $\theta = 38.17$ mrad; $d = 9.53$ μm. (b), (c) $\theta = 37.84$ mrad; $d = 9.61$ μm

relaxation with relaxation times of the order of several tens of milliseconds over a region of 10 μm in semi-dilute solutions of polystyrene under θ-condition.

DISCUSSION AND CONCLUSION

We have presented synthesis procedures and some experimental results of using BAME as a new probe to change the refractive index under irradiation for mass diffusion measurements by the FRS technique. In FRS experiments, generally, there are many factors which could be responsible for the 'unusual' diffraction decay. One is the complicated photoreactivities of a photochromic probe, giving, under irradiation with light, several photoproducts with different refractive indices as well as different sizes, as demonstrated for BAME-labelled polystyrene in dilute solution of halogenated solvents (CCl_4, CH_2Cl_2, etc). Therefore, we think that simple and well characterized photochromic probes are necessary to obtain the right diffusion coefficient and to separate the effects of unfavourable photochemical reactions from the physical nature of any experimental system under investigation. By doing so, we believe that there is a much better chance to understand a more complicated physical process which itself gives non-exponential diffraction signals in FRS experiments. We believe that BAME satisfies this critical requirement because the dimerization reaction of anthracene has been extensively studied in solutions[10,11], crystals[12] and bulk polymers[13]. It is generally known *a priori* whether an unfavourable multistep photochemical reaction will happen and hence it can be avoided.

In comparison with other photochromic probes, the advantages of BAME are as follows:

(1) BAME undergoes very simple (one step) and well characterized photoreaction in most organic solvents. This unique property fulfils the critical requirement for the FRS experiment: a single grating of refractive index.

(2) BAME has high quantum yields of intramolecular photodimerization even in bulk polymers at room temperature. This photodimerization also provides a large refractive index change, as predicted[14,26]. Therefore, FRS experiments can be carried out at a very low label concentration of the order of 10^{-6} mol l^{-1}, as described earlier. These characteristics of BAME make FRS experiments available at a very small labelling ratio,

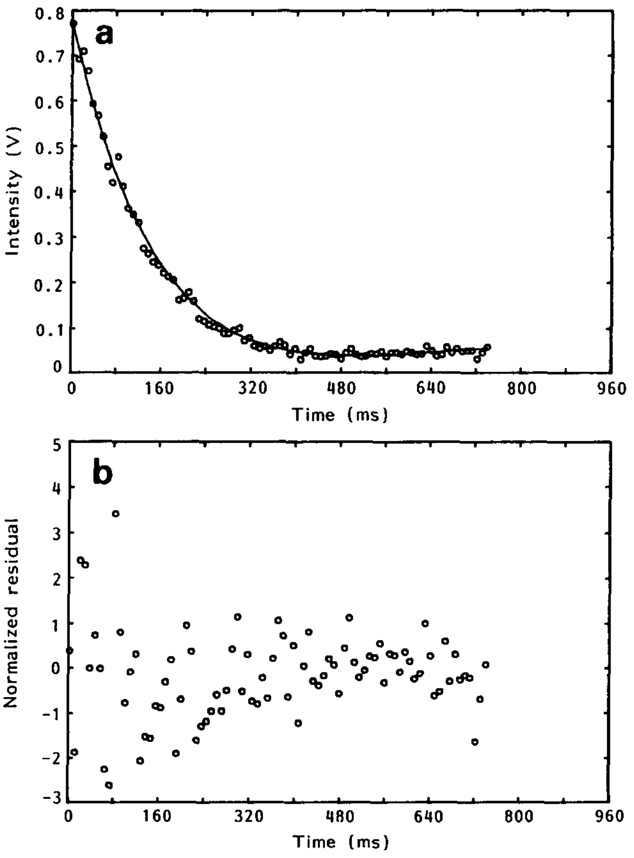

Figure 16 (a) A single exponential fit to data from *Figure 15(c)*. The diffusion coefficient obtained is 6.6×10^{-8} cm^2 s^{-1}; (b) normalized residual plot for the data in (a), r.m.s. residuals $= 1.445 \times 10^{-2}$

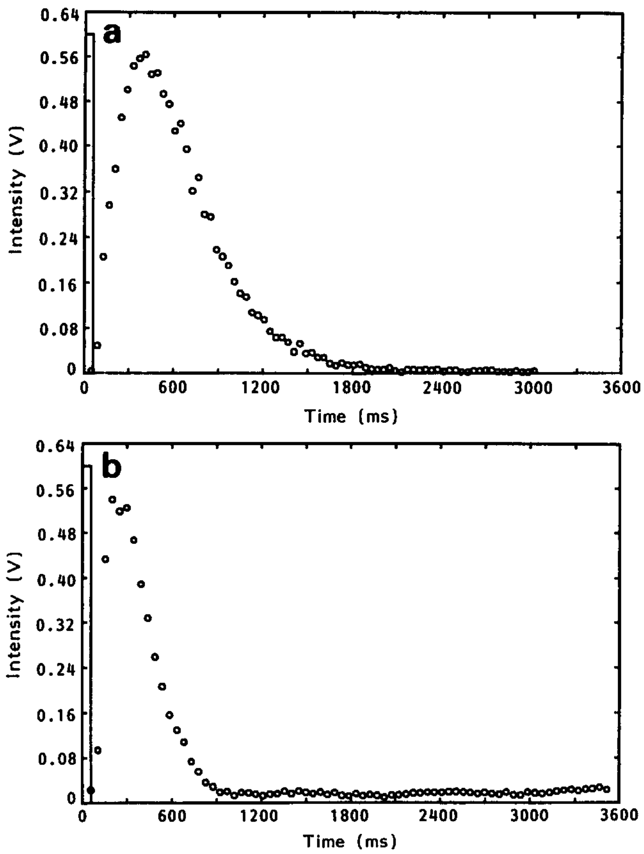

Figure 17 Decay of diffraction intensity of BAME labelled polystyrene with molecular weight $10^2 \times 10^3$ at $c = 1.22 \times 10^{-3}$ g/g in a matrix of semi-dilute polystyrene solution in t-decalin with matrix molecular weight 173×10^3 and $c = 0.101$ g/g at temperatures of: (a) 29.5°C; (b) 41.3°C. $\theta = 37.84$ mrad; $d = 9.61$ μm

which does not affect seriously the nature of the system under investigation.

(3) The most important and superior property of BAME is the thermal stability of photodimer (the closed form), which is stable at very high temperatures ($\approx$240°C). This unique property provides the capability of measuring very slow diffusion of polymer chains (10^{-13}–10^{14} cm^2 s^{-1}) in polymer blends at high temperature as well as probe diffusion near glass transition.

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