Application of a photodimerizable probe to the forced Rayleigh scattering technique for measurement of self-diffusion of polymer chains

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A new type of photochromic compound, a bis-(9-anthrylmethyl) ether ((BAME), is introduced as a potential probe for the forced Rayleigh scattering (FRS) technique. Upon irradiation with ultra-violet (u.v.) light (~360 nm), BAME undergoes intramolecular dimerization which involves a large refractive index change in the visible region. The dimerization process is known to be essentially irreversible in the absence of short u.v. light (~250 nm) at room and moderately high temperatures. A derivative of BAME is synthesized and chemically attached to polystyrene chains. Some photochemical properties of the BAME-labelled polystyrene are reported together with the results of a preliminary diffusion measurement of polystyrene by the FRS technique.

(Keywords: self-diffusion; forced Rayleigh scattering; photodimerizable probe; optical recording material)

INTRODUCTION

Recently, the forced Rayleigh scattering (FRS) technique, which is also called the holographic grating technique or holographic relaxation spectroscopy, has been developed and used for the measurement of mass diffusion[1-4]. The principle of the technique is to follow the transient diffraction intensity from a sample containing photosensitive probes where the optical grating is created by a laser pulse. The decay of this diffraction intensity is, in a favourable case, due to the diffusional motion of probes which erase the gradient of complex refractive index in the sample. Consequently, the diffusion coefficient of polymer chains can be determined, in principle, from the decay rate of the diffraction intensity. However, the probes often undergo very complicated photochemical processes under irradiation of light, which sometimes leads to ambiguous results in diffusion measurements. Since its first application to mass diffusion studies[1], a few different photochromic probes have been used in this technique: such as spiropyran derivatives[2], azobenzene derivatives[1,3] and aminonitrostilbene[4]. Their photochemical properties, however, do not seem to be so well characterized as to render an easy and reliable interpretation of FRS signals.

In general, photochromic molecules undergo the following reaction:

$$\mathrm{M} \underset{\lambda' \text{ or } \Delta}{\overset{\lambda}{\rightleftharpoons}} \mathrm{M'} \tag{1}$$

where a molecule in the initial state M transforms to the quasistable state M′ under irradiation with light of wavelength λ and changes back to M under irradiation with light of wavelength λ' or by heat (Δ) in the dark. Often, reaction (1) is not simple and involves various intermediates which have their own characteristic lifetimes and optical properties. The lifetimes of these intermediates strongly depend on their chemical environments and temperature. For example, 1′,3′,3′-trimethylindolino-6-nitrobenzopyrylospiran changes to the quasistable merocyanine via at least one intermediate on the timescale of milliseconds, as shown in *Figure 1*, observed by a microsecond flash photolysis technique[5]. Those intermediates have generally different refractive indices and lifetimes. Consequently, the temporal diffraction intensity measured by the FRS technique can be affected by the presence of these intermediates of the probes, and this sometimes results in a non-exponential decay[6]. Furthermore, the lifetime of the quasistable state M′ becomes shorter as the temperature is increased due to the thermal reaction in the dark. These shortcomings of the usual photochromic probes have been a serious limitation in the measurement of diffusion in highly viscous media as well as at high temperatures by the FRS technique.

The objective of this paper is to demonstrate the use of a different class of photosensitive probe for FRS

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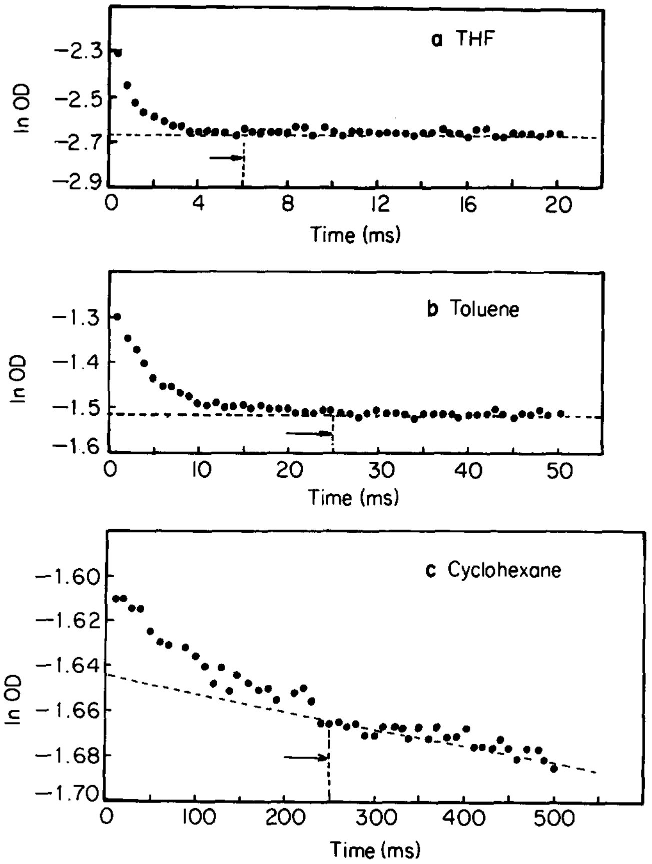
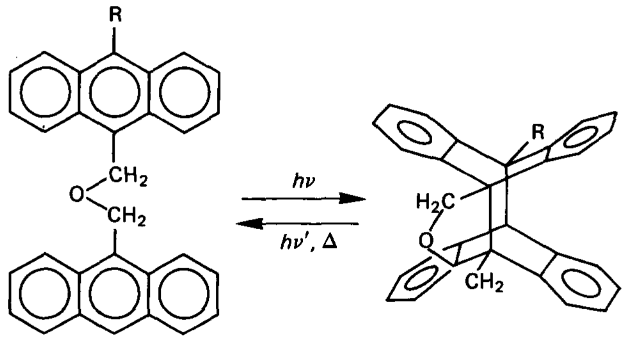


Figure 1 Transient decay of the triplet–triplet absorption of 1',3',3'-trimethylindolino-6-nitrobenzopyrylospiran (from Tokyo Kasei Co., Japan) in different solvents at 632.8 nm. The time constants of the fast components of the decay are 0.8 ms, 2.6 ms and 10 ms in (a) tetrahydrofuran, (b) toluene and (c) cyclohexane, respectively, at room temperature. The pulsewidth of the excitation Xe lamp flash is 20 μs. The broken line represents the decay of the metastable merocyanine of the same sample monitored by a Shimadzu photometer at 632.8 nm. These results indicate the existence of at least one intermediate with lifetime in the millisecond range which depends on the chemical environment (solvent). Concentrations of benzopyrylospiran are less than 10^{-4} mol l^{-1} for all cases

techniques, namely a derivative of bis-(9-anthylmethyl) ether (I) (BAME) which has well characterized photochemical properties.



(I) (2)

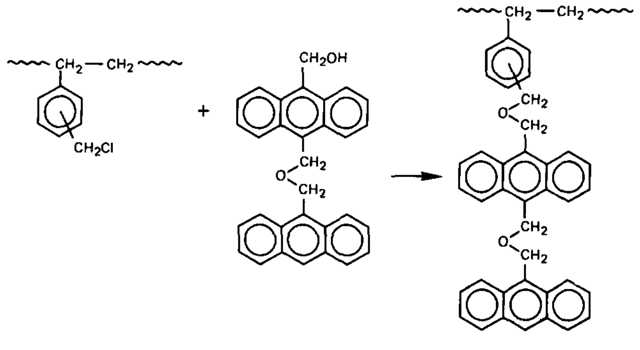
For more than a hundred years, anthracene has been known as a typical example for photodimerization reactions[7]. Under irradiation of light, anthracene dimerizes in concentrated solutions and also in crystals. In this photoreaction, as shown in equation (2), double bonds at the 9,9'- and 10,10'-positions of the two anthracenes are broken to form new single bonds as a bridge which links two anthracene rings together. In our case, R (=CH_2OH) is a functional group for the subsequent reactions to attach this probe to polymer chains. Since the conjugation of the π-electron system is destroyed in this process, there is a large change of absorption spectra in the u.v. region together with a refractive index change in the visible region. Although the refractive index change due to this photodimerization process has not been measured directly, a calculation based on bond refractivities predicted a large change in refractive index[8] which is proved by good FRS signals, as will be presented later. Furthermore, the resultant dimer is known to be stable even at high temperatures[9] and the photodimerization process has been well characterized, so that it is unlikely to have any complications due to long-lifetime intermediates. Therefore, we think BAME can be a very useful probe for FRS.

In this paper, some photochemical properties of BAME-labelled polystyrene are shown and preliminary results of measurements of self-diffusion of this polymer by the FRS technique are demonstrated.

EXPERIMENTAL

Materials

Chloromethylated polystyrene is prepared according to the procedure of Feinberg and Merrifield[10] with dichloromethane and chloromethyl methyl ether as solvents and zinc chloride as the catalyst. By varying the amount of catalyst, reaction time and temperature, the number of chloromethyl groups on a polymer chain can be controlled. Polystyrene used in this work is the NBS SRM 1478 with $M_w = 37400$ and $M_w/M_n = 1.04$. The probe used to label the polystyrene is a derivative of BAME, namely 9-(10-hydroxymethyl)anthrylmethyl 9'-anthrylmethyl ether (II). The coupling reaction between chloromethylated polystyrene and compound II in DMF leads to the BAME-labelled polystyrene of the following equation:



(II) (3)

Instruments and data analysis

Absorption spectra of the samples are measured by a Shimadzu photometer model 200-S. Samples are deaerated and sealed under vacuum in a 1 cm path-length quartz cuvette and the absorption spectra are taken after various irradiation times. A 200 W Nihon Denchi high-pressure mercury lamp is used to induce photodimerization at a distance of 10 cm from the sample and a Corning CS-052 filter is used to cut off all light of wavelength shorter than 340 nm from the light source.

In the forced Rayleigh scattering experiment, the writing beam is operated at 363.8 nm from a coherent Innova model 90-5 Ar-ion laser. The intensity and pulsewidth of the writing beam do not exceed 20 mW and 20 ms, respectively. The reading beam is operated at 488 nm from a Lexel model 75 Ar-ion laser. The fringe spacing of the interference pattern is varied between 5 and 25 μm by changing the crossing angles of the two writing beams and 5 mm path-length quartz cuvettes are used for sample cells. All the decays of diffraction intensity are fitted to the following four-parameter model function[1-3] by a nonlinear least-squares regression program:

$$I(t)=(Ae^{-t/\tau}+B)^2+C \tag{4}$$

and the diffusion coefficient is determined from the slope of $1/\tau$ vs. q^2 according to the following equation:

$$\frac{1}{\tau}=Dq^2+\frac{1}{\tau_p} \tag{5}$$

where τ_p = lifetime of the quasistable form of the probe, which should be infinite if we have a truly irreversible change in complex refractive index; q = magnitude of the wavevector of the holographic grating, which is given by:

$$q=\frac{2\pi}{d}=\frac{4\pi\sin(\theta/2)}{\lambda} \tag{6}$$

d = fringe spacing of the interference pattern; θ = crossing angle between the two writing beams; and λ = wavelength of the writing laser. Details of the dye synthesis and photochemical properties of labelled polymers as well as FRS instruments will be published in the future.

RESULTS AND DISCUSSION

Photochemical properties of BAME-polystyrene

The absorption spectrum of BAME-polystyrene in deaerated benzene solution is shown in *Figure 2a*. The number of BAME molecules attached to polymer chains is determined from the absorbance of the sample with molar extinction coefficient ε of 11 100 (at 395 nm in dimethylformamide, DMF), which we obtained from the DMF solutions of BAME (II). The number of BAME per polystyrene chain used in this work is found to be rather small, 0.3 probes/chain. Photodimerization of BAME-polystyrene is observed in dilute solution as well as in bulk. The effect of photodimerization of BAME on the absorption spectrum of BAME-polymer in benzene solution is shown in *Figure 2a* after 15 min of irradiation at room temperature. The absorbance at 395 nm decreases down to 11% of the initial value. In bulk, 50% of BAME attached to polymer chains dimerized after 15 min of irradiation at 45°C in the film of host polystyrenes cast from benzene, as shown in *Figure 2b*. These results indicate that BAME attached to polystyrene chains is dimerized efficiently even in the bulk at temperature less than T_g. The high quantum efficiency of photodimerization of this probe reflects Hirayama's C-3 rule for intramolecular excimer formation[11] and also the flexibility of the ether linkage between two anthracenes, though substitution with bulky groups at the 10- and 10'-positions was reported to decrease the quantum yield of the dimerization reaction[12]. From these results, we can conclude that BAME is a suitable probe for the FRS measurement of self-diffusion of polymer chains in dilute solutions as well as in bulk.

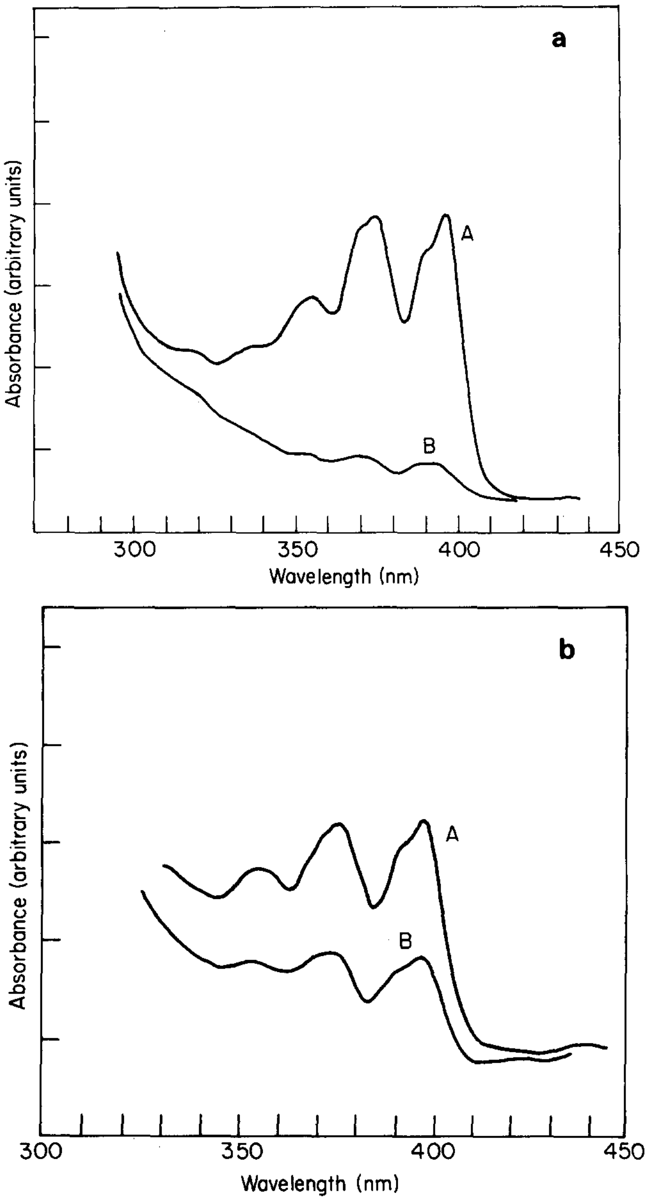


Figure 2 Photodimerization of BAME-polystyrene: (a) in benzene—A, before irradiation, B, after 15 min of irradiation; (b) in host polystyrene film at 45°C—A, before irradiation, B, after 15 min of irradiation

Forced Rayleigh scattering

The self-diffusion of polystyrene labelled with BAME is measured at 21.5°C in benzene at concentration 0.55 wt%. In this experiment, all the decay of diffraction intensity at various fringe spacings is single exponential, i.e. corresponding to fitting the decay to equation (4) with B equal to zero. As an example, the decay of diffraction intensity measured at 6.86 μm in fringe spacing ($\theta = 53.1$ mrad) is shown in *Figure 3*. The q^2 dependence of $1/\tau$ obtained by changing the crossing angles between two writing beams is shown in *Figure 4*. The self-diffusion coefficient calculated from this slope, according to equation (5), is $(6.1 \pm 0.2) \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$, which is in reasonable agreement with the interpolated literature value of $6.6 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$ at infinite dilution[13]. The fact that the straight line passes through the origin in *Figure 4* indicates a long lifetime of the photodimer of BAME. This is also confirmed by the fact that the absorption spectrum of the irradiated sample was unchanged after more than a week at room temperature in the dark. It is worth noting

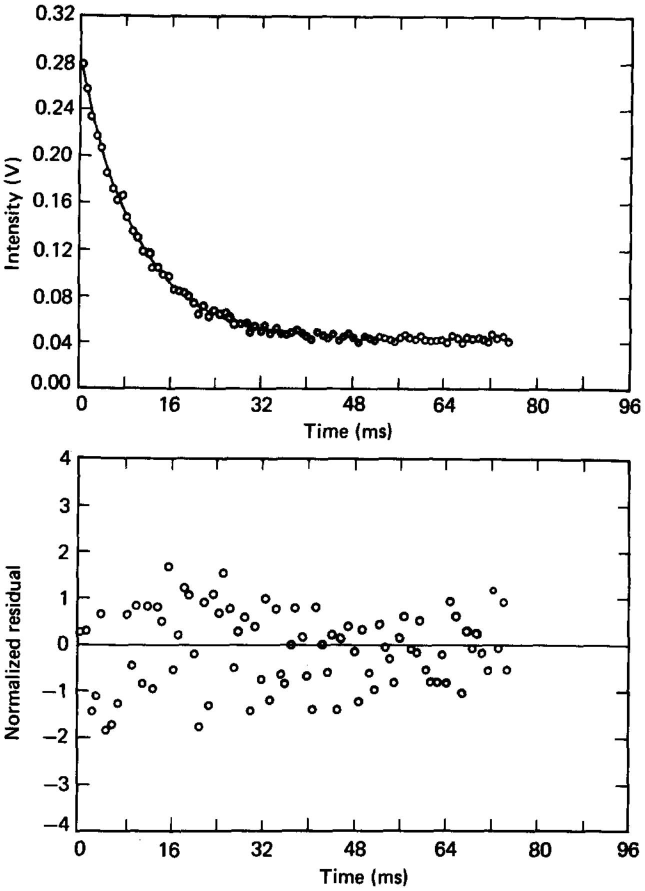


Figure 3 Decay of the diffraction intensity from BAME-polystyrene in benzene solution at 21.5°C: polymer concentration, $4.86 \times 10^{-3}\,\mathrm{g\,ml^{-1}}$; fringe spacing, $d = 6.86\,\mu\mathrm{m}$; $\theta = 53.06$ mrad. The curve is obtained by fitting data points to the model function equation (4) with $B = 0$. RMS residuals $= 3.027 \times 10^{-3}$

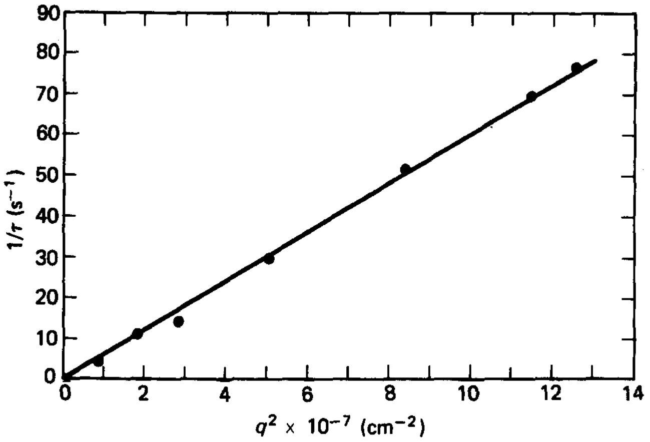


Figure 4 $1/\tau$ vs. q^2 plot for BAME-polystyrene in benzene solution at 21.5°C: polymer concentration, $4.86 \times 10^{-3}\,\mathrm{g\,ml^{-1}}$; $D_{\mathrm{app}} = 6.1 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$

that the temperature for the thermal photodecomposition of the photodimer of anthracene was reported as 200°C (ref. 9). In this work, the total concentration of BAME used for FRS measurement is less than $10^{-5}\,\mathrm{mol\,l^{-1}}$. Nonetheless, we are able to obtain good signals, which indicates that the photodimerization of anthracene involves a large change in refractive index, as predicted[8]. Therefore, we conclude at this moment that BAME is a very sensitive probe for FRS measurements. It should be pointed out that Tomlinson and coworkers have attempted to use the photodimerization process with various polycyclic aromatic hydrocarbon crystals to produce spatial patterns of varying refractive index for the purpose of reversible phase holographic recording[8]. However, our work is the first attempt to use the intramolecular photodimerization process for studying mass diffusion by the forced Rayleigh scattering technique.

In summary, we demonstrated that intramolecular photodimerizable BAME can be used as a suitable probe for the forced Rayleigh scattering technique. The difficulties sometimes encountered in FRS experiments caused by the photochemical intermediates and/or secondary photoreaction products might be eliminated in this case, because the lifetime of the intramolecular excimer of BAME, an intermediate of this photodimerization reaction, is of the order of nanoseconds[13]. Also the large change of refractive index and the thermal stability of anthracene photodimers render a good sensitivity as well as a long lifetime for measurements of slow diffusion, especially those of polymer chains in bulk as well as in polymer mixtures at high temperatures, which are currently in progress. Furthermore, because of the properties mentioned above, polymers labelled with the BAME probe also have the potential of being used as optical recording materials.

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