Photocyclomerization of bis(9-anthrylmethyl) ether in solid polymers

Hiroaki Yoshizawa, Kazuo Ashikaga and Masahide Yamamoto*

Department of Polymer Chemistry, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

and Qui Tran-Cong*

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Photocyclomerization of bis(9-anthrylmethyl) ether (BAME) in solid polymers, polystyrene (PS) and poly(vinyl acetate) (PVAc), was observed over a wide range of temperatures. The rates of photocyclomerization in PS and PVAc matrices above T_g followed a temperature dependence of WLF (Williams–Landel–Ferry) type, namely the intramolecular conformational transitions of BAME are governed by the free volume of polymer segments. Below T_g in the PS matrix, the reaction rate is also affected by a secondary relaxation process of the polymer matrix ($T_\beta \simeq 60°C$), and at room temperature the yields of photocyclomerization are determined by the initial distribution of BAME frozen conformations in the PS matrix. Finally, the changes in refractive index involved in this reaction in solid PVAc were measured and the normalized refractive-index difference $n_0 = 0.4 \times 10^{-22}\,\text{cm}^3$ (D line) was obtained for BAME-doped (39 mmol l^{-1}) PVAc film.

INTRODUCTION

The photodimerization of anthracene is one of the oldest known photochemical reactions of aromatic compounds[1]. Studies on photochemical and photophysical aspects of these reactions of anthracene and its derivatives have been extensively carried out in various solvents as well as in glass matrices at 77 K by a number of workers, as reviewed recently[2]. These reactions have been given special attention because of the possibility of using these derivatives as optical recording materials owing to the large changes in refractive index accompanying photodimerization[3]. Since intermolecular photodimerization is only possible when two anthracene rings approach each other within a critical distance, i.e. the radius of the active sphere, a very high concentration of anthracene is required to achieve dimerization. To avoid this shortcoming and to increase the efficiency of the reaction, bichromophoric molecules which have two photodimerizable aromatic rings linked together by a flexible chain have been introduced[4]. By appropriate molecular design, a number of such bichromophoric molecules can be synthesized for particular purposes and the high efficiencies of dimerization can be accessed by taking advantage of Hirayama's C-3 rule[5]. Some of these bichromophoric molecules have been employed as excimer fluorescent probes to investigate the dynamics of concentrated polymer solutions[6] as well as polymer melts[7]. On the other hand, by taking advantage of the photochromicity of anthracene photodimerization, bis(9-anthrylmethyl) ether (BAME) derivatives have recently been used in forced Rayleigh scattering (FRS) for measurement of mass diffusion in polymers as well as self-diffusion of polymer chains in solution[8]. Upon irradiation, BAME cyclomerizes as shown in the following scheme:
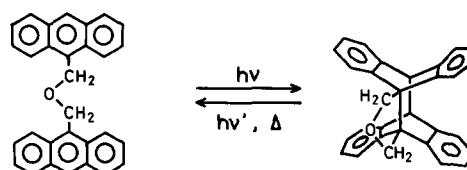
In these experiments, mass diffusion is directly measured by following the relaxation process of a refractive-index grating which is created in the sample by taking advantage of the photocyclomerization reaction of BAME.

However, to obtain such a photoinduced refractive-index grating, intramolecular conformational transitions favouring the photocyclization of BAME are indispensable. Therefore, the effects of environments such as temperature and viscosity on the photocyclization of BAME, especially in high-viscosity media such as solid polymers and polymer blends, must be studied.

These effects, particularly of solid polymers on photocyclomerization, were examined to evaluate the effectiveness of BAME and its derivatives as probes for the forced Rayleigh scattering technique. Also, some of the characteristics required for use as optical recording materials such as thermal reversibility and the magnitude of refractive-index changes of BAME under irradiation in solid polymers were investigated.

---

*To whom correspondence should be addressed

EXPERIMENTAL

Materials

Bis(9-anthrylmethyl) ether (BAME) and its model compound, 9-methoxymethylanthracene (MMA), were prepared by the Williamson method of synthesis according to the procedure described by Castellan et al.[9] BAME was synthesized as follows: 9-anthracene-methanol (Aldrich, 1.1 g) in dimethylsulphoxide (DMSO) solvent was added dropwise to a DMSO solution of sodium hydride under stirring. Then a DMSO solution of 9-(chloromethyl)anthracene (Tokyo Kasei Co., 1.2 g) was added dropwise to the reaction mixture. The whole solution was heated for 2 h at 80°C with stirring. At the end of the reaction, the product was separated by pouring the reaction mixture into water. By a similar procedure, MMA (An–CH_2–O–CH_3, An = anthracene) was obtained from the reaction of 9-(chloromethyl)anthracene with sodium methylate. The products of these reactions were recrystallized from benzene–petroleum ether mixture and purified by column chromatography on silica gel with benzene as the eluent. All the solvents used in these experiments were purified by conventional methods. Polystyrene (PS; M_w = 300 000, Nakarai Chemicals) and poly(vinyl acetate) (PVAc; M_w = 200 000, Wako Chemicals) were reprecipitated with methanol and petroleum ether, respectively. The porous PVAc was obtained by the freeze–dry method from its benzene solution. Glass transition temperatures T_g of PS and PVAc measured by d.s.c. were 96 and 6°C, respectively.

Photoirradiation

Photoirradiation was carried out in a thermostat with a Toshiba 300 W high-pressure mercury lamp as the excitation source. A spectral line at 365 nm was selected using the combination of two filters, Toshiba UVD-2 and Corning C.S.0-52. The concentrations of BAME and its model compound MMA were kept at ~ 1 mmol l^{-1} in all samples. Molar extinction coefficients ε for BAME in dimethylformamide (DMF) are 19 500 (390 nm) and 11 500 dm^3 mol^{-1} cm^{-1} (365 nm); that for MMA in DMF is 13 300 dm^3 mol^{-1} cm^{-1} (365, 390 nm). The polymer film containing BAME and/or MMA was 0.3 mm thick, and was obtained by the casting method. The film was dried for 3 days under vacuum at ~ 150°C for PS and ~ 60°C for PVAc. The number of photons at 365 nm from the mercury lamp was measured by using potassium ferrioxalate actinometry[10] and was 1.89 × 10^{-9} E cm^{-2} s^{-1}. All the experiments in this study were carried out without deaeration, since the effect of oxygen on photodimerization of the anthryl group is negligibly small even in fluid solutions, as described in the following section.

Analysis of photocyclomerization of BAME in PS below T_g

To estimate the fractions of BAME undergoing intramolecular photodimerization, the following experimental procedures were taken. First, two PS films of the same thickness containing BAME and MMA of the same absorbance at 365 nm were prepared. The variation of absorbances with irradiation times was followed at 390 nm. Then, the time dependence of concentrations of BAME and MMA was obtained using relevant molar extinction coefficients at 390 nm. Although the initial

concentrations of BAME and MMA were different, the initial concentration of MMA was matched to that of BAME at $t = 0$, since the photoreaction of MMA under irradiation seems to be unimolecular. Then, the conversion of intramolecularly photocyclized BAME was estimated by subtracting the photoreacted MMA from the photoreacted BAME after 50 min irradiation. Note that no dimer was detected for the MMA photoproduct within the experimental limit of our analysis with LC.

Product analysis

The product of the photocyclomerization of BAME was identified by using a Jasco HPLC Trirotar-V with a Finepac Sil column. A mixture of n-hexane and dichloromethane (55:45) was used as eluent. U.v. and i.r. spectra of the product were measured by a Shimadzu UV-200S double-beam spectrophotometer and a Jasco IR-810 infra-red spectrometer, respectively. The n.m.r. data of the photoproduct identified by a Jeol FX-90Q spectrometer with tetramethylsilane (TMS) as internal standard are as follows: ^{1}H n.m.r. (DMSO-d_6), δ = 4.6 ppm (s, methine, 2H), δ = 4.8 ppm (s, methylene, 4H), δ = 6.8–7.2 ppm (m, aromatic, 16H).

RESULTS AND DISCUSSION

Photocyclomerization of BAME in solution

Figure 1 shows the irradiation-time dependence of absorption spectra of BAME in benzene at 20°C. The characteristic absorption spectra of BAME decreased with increasing irradiation time and finally disappeared completely after 15 min. Since the reaction takes place very fast under the experimental conditions, the light intensity was attenuated to 14.8 % of the original intensity by using a combination of three filters, UV-36A, UV-36B and UV-36C (Toshiba). It is clear that the photocyclomerization of BAME takes place efficiently in
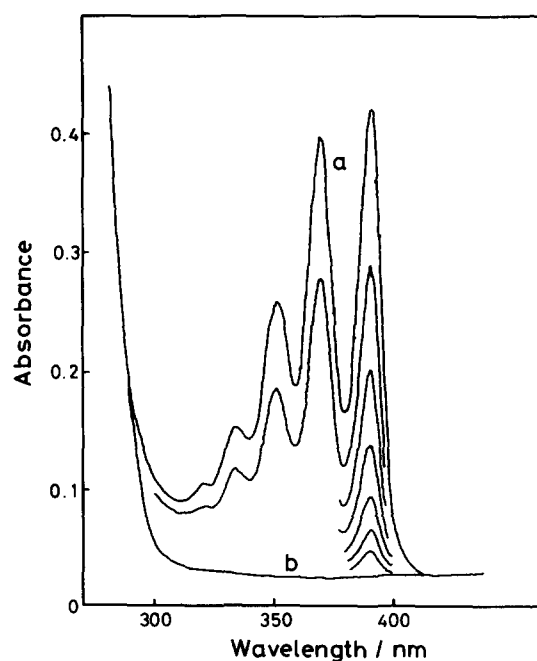
Figure 1 Change of the absorption spectra of BAME in benzene at 20°C upon photoirradiation: (a) before irradiation; (b) 15 min after irradiation
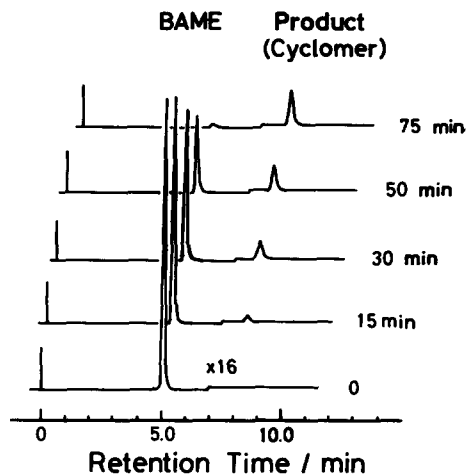
BAME   Product
(Cyclomer)

Figure 2 Chromatograms of BAME and its product, the photocyclomer, after various photoirradiation times: eluent, CH_2Cl_2/n-hexane=45/55; monitored at 255 nm
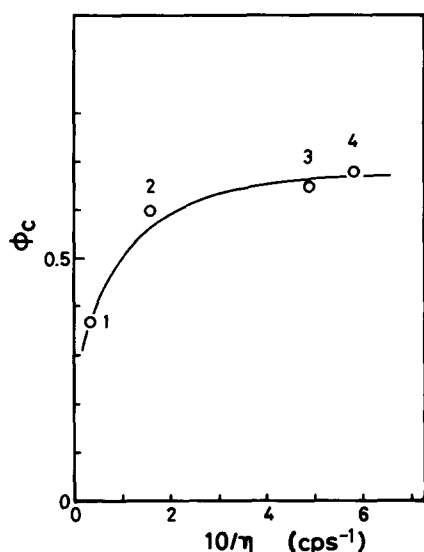

Figure 3 Effects of viscosity on the quantum yield ϕ_c of photocyclomerization of BAME in a series of Cellosolves at 25°C: 1, phenyl cellosolve; 2, butyl cellosolve; 3, ethyl cellosolve; 4, methyl cellosolve

solution due to high flexibility of the C–O–C bond. Actually, the quantum yield of the reaction measured by actinometry was 0.67.

The photoproduct in benzene under different irradiation times was subsequently analysed by h.p.l.c. (*Figure 2*). As the reaction proceeds, the amount of photoproduct increases, accompanied by a decrease in the amount of BAME. As indicated in *Figure 2*, it is obvious that, for the photocyclomerization of BAME, there is only one photoproduct, which is identified as the intramolecular cyclomer of BAME. On the other hand, the effect of oxygen on this photoreaction was checked by using MMA. The fluorescence lifetime of MMA in ethylbenzene with and without deaeration was measured by a single-photon-counting method at room temperature. Almost no difference of the lifetime ($\simeq 2.1$ ns) was recognized in either case, that is, the fluorescence of the anthryl group was scarcely quenched by oxygen owing to the short lifetime of MMA. Furthermore, photoirradiation of MMA in ethylbenzene with and without deaeration was carried out at room

temperature. The absorption spectra of these two solutions were almost unchanged after a long period of irradiation (600 min). From these results, it is concluded that the effect of oxygen on this photodimerization is negligibly small. Therefore, in the subsequent experiments, the photocyclization reaction of BAME was followed by monitoring the change of the absorbance at the first maximum peak (390 nm) of absorption spectra.

The effect of solvent viscosity on the photocyclomerization of BAME was examined using a series of Cellosolve derivatives. As shown in *Figure 3*, the quantum yield ϕ_c of this cyclomerization depends strongly on solvent viscosity. The more the viscosity increases, the more the quantum yield decreases. This indicates that, to achieve the intramolecular cyclomer, the two anthracene rings of BAME are required to overcome a certain barrier determined by the viscosity of the solvent. These results are consistent with those previously obtained for the intermolecular photodimerization of 9-methylanthracene in solvent mixtures where the dimerization was assigned as a diffusion-controlled reaction[11].

Photocyclomerization of BAME in solid polymers

In solid polymers, polymer segments could suppress the conformational transitions of BAME, such as the rotation of anthracene rings about the ether linkage, and consequently limit the encounter probability suitable for the cyclomerization of BAME. Therefore, it is important to elucidate the effects of the polymer matrix on the photocyclomerization of BAME. In this study, polystyrene (PS) and poly(vinyl acetate) (PVAc) were used as matrices. The changes of absorbance with irradiation time for BAME in these two polymers were measured over a wide range of temperatures above as well as below T_g. As expected, the reaction yields of BAME depended strongly on temperature. *Figure 4* shows the result in PS matrix. With T_g as a boundary, the reaction
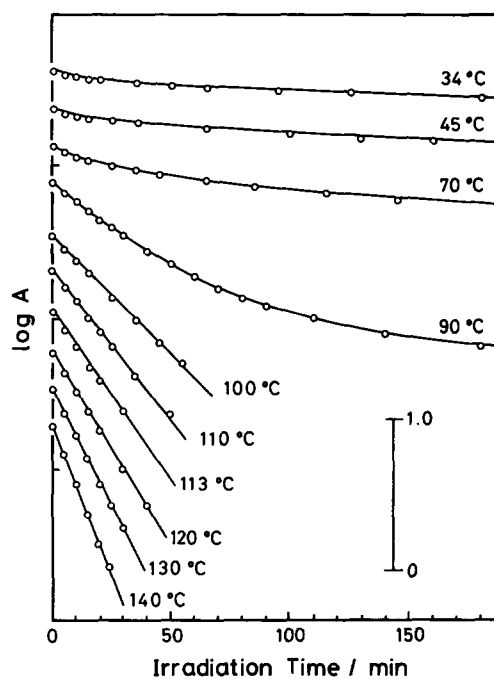

Figure 4 Time dependence of absorbances monitored at 390 nm in bulk PS at various temperatures. The initial absorbance of anthryl group of all samples is 0.35 and the scale for log $A = 1.0$ is also shown
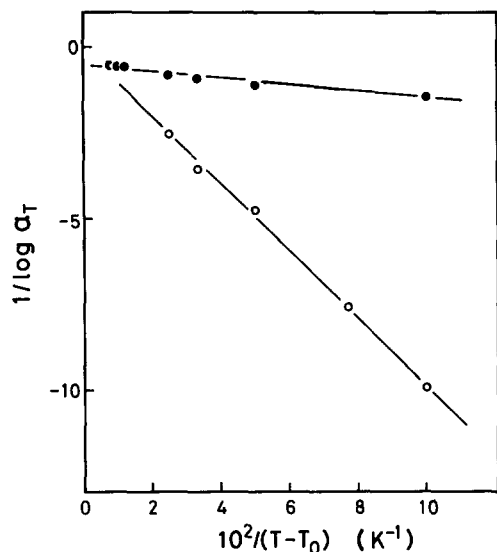
Figure 5 Relation between $1/(\log a_T)$ and $1/(T - T_0)$ for photocyclomerization reaction of BAME in PS ($\bigcirc$), $T_0 = 373$ K and PVAc ($\bullet$), $T_0 = 293$ K

behaved in two distinct ways: above T_g of PS, the absorbance of BAME decreased exponentially with irradiation time; whereas, below T_g, these decay curves appeared non-exponentially with a long tail.

To elucidate the roles of polymer segments on the cyclomerization of BAME above T_g, we define a_T as the characteristic ratio of reaction rate constants $k_c(T_0)$ and $k_c(T)$ at two different temperatures T_0 and T:

$$a_T = k_c(T_0)/k_c(T) \tag{1}$$

where T_0 is an arbitrarily chosen temperature.

Since the photocyclomerization reaction of BAME depends on viscosity, it is reasonable to assume that the rate constant of the reaction is inversely proportional to the relaxation time τ of conformational transitions:

$$k_c(T) \sim 1/\tau(T) \tag{2}$$

Using equation (1), the characteristic ratio a_T at an arbitrary temperature can be rewritten as follows:

$$a_T(T) \sim k_c(T_0)/k_c(T) \sim \tau(T)/\tau(T_0) \tag{3}$$

Provided that the intramolecular conformational transition of BAME follows the Williams–Landel–Ferry (WLF) relationship:

$$\log[a_T(T)] = -\{C_1(T - T_0)/[C_2 + (T - T_0)]\} \tag{4}$$

the temperature dependence of the rate constants of the photocyclomerization of BAME can then be expressed as:

$$1/\log[k_c(T_0)/k_c(T)] = A/(T - T_0) + B \tag{5}$$

where A and B are constants.

Figure 5 shows the plots of $1/\log(a_T)$ vs. $1/(T - T_0)$ for both PS and PVAc matrices above T_g. They show a good linear relationship with $T_0 = 373$ and 293 K as reference temperatures for PS and PVAc matrices, respectively. This fact implies that the temperature dependence of the

photocyclization of BAME in solid PS and PVAc polymers follows the WLF-type relationship as indicated in equation (5). Consequently, the conformational transitions of BAME favouring the photocyclomerization process in BAME are controlled by the free volume of polymer segments. This finding is also consistent with those previously obtained by fluorescence depolarization experiments[12] and excimer formation of small molecules in polymer melts[13]. In this treatment, the contribution of the side reaction, which will be described below, is neglected. By a rough estimate from the temperature dependence of the side reaction measured below T_g, the error for $k_c(T_0)/k_c(T)$ is $\sim 15\%$ at maximum in the range of temperatures above T_g. From the slopes and intercepts of the two straight lines shown in *Figure 5*, the WLF constants C_1^0 and C_2^0 are estimated. It is found that these constants are different from those obtained by rheological experiments[14]. Besides the differences in such as molecular weights, polydispersity of molecular weights and standard temperatures T_0, the main reason for these differences probably comes from the difference in the time scale (frequency) of observation in these two experiments. Therefore, at this moment, we conclude that the temperature dependence of photocyclization processes of BAME in bulk polymers qualitatively follows the WLF-type relationship. Further systematic experiments will be necessary to elucidate these differences.

On the other hand, the rate of disappearance of BAME with irradiation time below T_g was non-exponential with a long tail. To estimate the fraction of BAME undergoing photocyclomerization, similar experiments were performed for the model compound, 9-methoxymethyl-anthracene (MMA), doped in the same polystyrene at various temperatures. The variations of concentrations of BAME and MMA with irradiation times observed at different temperatures below T_g are shown in *Figure 6*. The long tail of the decay of absorbance was also observed for the model compound MMA over a long irradiation time (10 h).

Note that the effect of oxygen on photocyclomerization of BAME was not observed; the decay of the absorbance of BAME in deaerated ethylbenzene was the same as that obtained in ethylbenzene without degassing. Therefore, the slow decay might come from the degradation of the molecules over a long period of irradiation (~ 10 h). The fluorescence decay of BAME is a single-exponential function of time in solution as well as in a glass matrix (benzene:ethanol = 3:100) at 77 K, whereas the decay is completely non-exponential in solid polymers, especially at room temperature. This phenomenon seems to be due to the inhomogeneity of the matrix. Anthryl groups of BAME in solid polymers have many different sites intramolecularly and the extent of the intramolecular interaction or coupling between a pair of anthryl groups varies in polymer solids, compared with fluid solutions. This exerts various influences upon the fluorescence lifetime. As a result of this, the decay showed the non-exponential curve in solid polymers. In the present work, we believe that the subtraction, using the model compound MMA, though approximate, is an adequate procedure to obtain the pure contribution of photocylomerization.

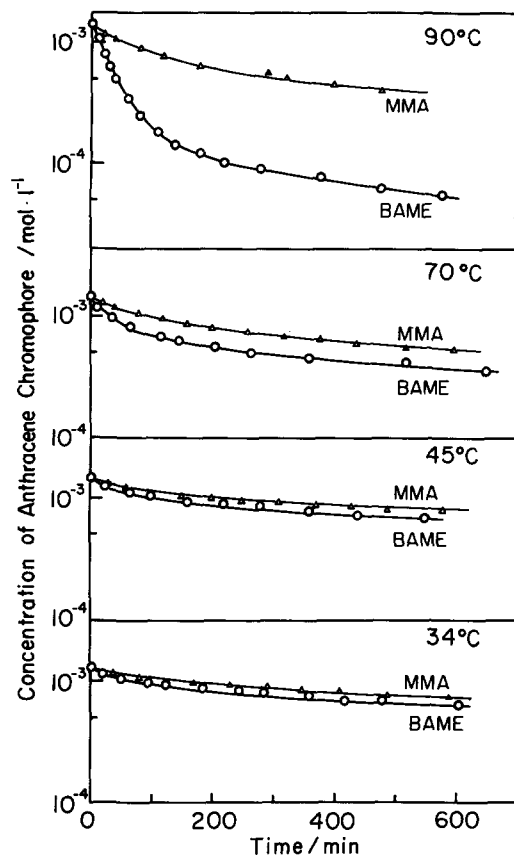*Figure 7* shows the temperature dependence of the conversion of photocyclomerization for BAME after

Figure 6 Time dependence of concentrations of anthracene chromophores in BAME (○) and in MMA (△) at various temperatures below T_g in PS matrix

50 min of irradiation at temperatures lower than T_g in bulk PS. From room temperature up to $\sim 60^\circ$C, the fraction of photoreacted BAME is 5–10% and is almost unaffected by temperature. This shows that BAME cyclomerizes in polymer solids even at temperatures lower than T_g, which is consistent with the fact that the diffraction signals could be observed even at 22°C in the forced Rayleigh scattering experiments carried out with the same sample[15]. Therefore, it is reasonable to assume that the photocyclomerization of BAME in this range of temperatures is determined by the conformational distributions of the two anthracene rings in BAME. This initial distribution of anthracene rings is probably determined at the time of sample annealing prior to irradiation. It turns out that in PS at room temperature, 90–95% of the equilibrium conformations of anthracenes in BAME are not suitable for cyclomer formation. As the temperature increases, the fractions of photoreacted BAME start to increase at $\sim 60^\circ$C, which is close to the temperature of the β-relaxation process in polystyrene previously reported by Yano and Wada[16]. Therefore, we conclude that the local motions of polymer segments below T_g also affect the intramolecular conformation of BAME. Finally, above T_g, as described above, the rates of the reaction are determined by the free volume of polymer segments for both PS and PVAc matrices.

It is worth noting that there are two possible ways of estimating the fractions of BAME photocyclizing in polymer matrices below T_g: (i) If the photocyclomerization and the side reaction occur competitively for the excited BAME, the fraction of pure photocyclomerization should be estimated by subtracting

the photoreacted MMA from the photoreacted BAME at the same initial concentration as described in the experimental section. The result is shown by curve a in *Figure 7*. (ii) There is the other situation. Below T_g, only BAME with conformations favourable to photocyclomerization photocyclizes and the rest of the BAME remains unchanged, but under irradiation over very long times the unphotocyclizable BAME may degrade. If this is the case, the photocyclomerization and the photodegradation reaction are considered to be independent. Then, the pure contribution of photocyclomerization reaction to the decay of absorbance of BAME below T_g can be estimated by subtracting the decay of MMA concentration from that of BAME concentration after matching these two decays at the later parts. The result is shown by curve b in *Figure 7*. As shown in *Figure 7*, the fractions estimated by these two different methods are not much different at temperatures below T_β, but deviate at temperatures above T_β, especially close to T_g. Therefore, we think that the fractions of BAME purely undergoing photocyclomerization in PS below T_g probably follow curve b at temperatures below T_β where no considerable mobilities of polymer segments take place and these fractions probably approach curve a above T_β, especially at temperatures close to T_g. The exchangeability of void sizes in polymer solids below T_g is strongly related not only to the physical ageing phenomena of glassy materials but also to the percolation problems proposed recently by Cohen and Grest[17] in an attempt to explain the nature of glass transition. More experiments are necessary to elucidate these problems.

Many years ago, Tomlinson and coworkers suggested that anthracene and its derivatives can be used as refractive-index image recording systems. Diffraction efficiencies of some polycyclic aromatic compounds photodimerizing in crystalline states have been directly measured. To evaluate the capability of BAME, the change in refractive index accompanied by photocyclomerization of BAME (39 mmol l^{-1}) doped in a PVAc matrix was measured. After complete disappearance of the absorbance of BAME on photo-irradiation, the refractive index of the samples was
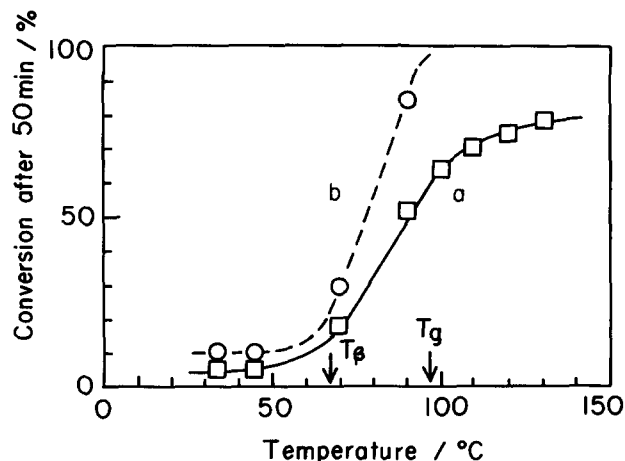

Figure 7 Conversion of intramolecularly photocyclized BAME in bulk PS matrix below T_g after 50 min of irradiation: (a) obtained by subtracting photoreacted MMA from photoreacted BAME; (b) estimated by subtracting the long-tail part of MMA from that of BAME in *Figure 6*
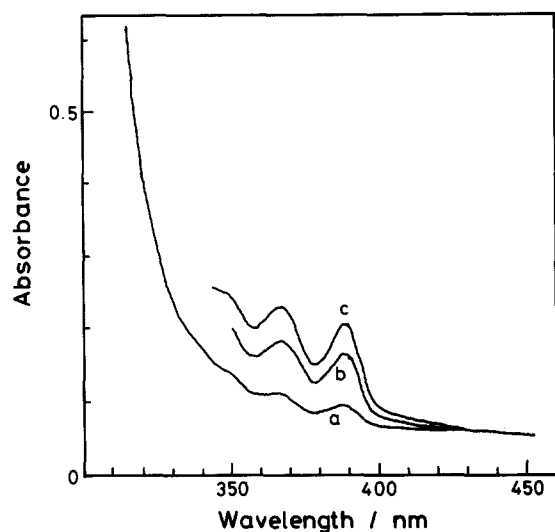
Figure 8 Thermal dissociation of photocyclomers of BAME in PS matrix at 240°C: (a) before heating; (b) after 30 min of heating; and (c) after 60 min of heating

measured at the D line of sodium (589.3 nm). The normalized refractive-index difference n_0 between BAME and its photocyclomer was 0.4×10^{-22} cm^3. Here n_0 is defined as[3]:

$$n_0 = (n_i - n_f)/N_0 \qquad (6)$$

where n_i is the refractive index of PVAc doped with BAME before irradiation, n_f is the refractive index after irradiation and N_0 is the number of molecules per unit volume converted by photocyclomerization. This value is still much smaller than the estimated upper limiting value $n_0 = 10^{-21}$ cm^3 for organic molecules: it is about one-half of the theoretical value 0.7×10^{-22} cm^3 calculated from the bond refraction theory in photocyclomerization reaction of anthracene[3]. Furthermore, the thermal stability of BAME was quite high: the photocyclomer of BAME in PVAc matrix obtained after irradiation was not dissociated (backward reaction) to BAME at 140°C. However, upon heating at 240°C for several hours, the photocyclomer of BAME slowly underwent thermal dissociation to give BAME. This thermal dissociation reaction can be monitored by following the recovery of the absorption spectra of BAME during heating. This backward reaction is somewhat slow at 240°C as shown in *Figure 8*. This result is consistent with the result reported previously by Chandross on the high thermal stability of the intermolecular photodimer of anthracene[18]. This result also indicates that the changes in absorption spectra of BAME under photoirradiation are due to the photocyclomerization process.

Finally, photocyclomerization of BAME is a one-product photochemical reaction. The cyclomer has high thermal stability. These results indicate that BAME can be used as an effective photochromic probe for forced Rayleigh scattering. Therefore, problems encountered in forced Rayleigh scattering, such as short lifetime of photochromic probes at high temperatures as well as the multiple refractive-index grating caused by multiproduct photochromic reactions, can be avoided in this case.

CONCLUSIONS

The following results were obtained for the photocyclomerization of bis(9-anthrylmethyl) ether (BAME) in polymer solids.

Above T_g, for both polystyrene and poly(vinyl acetate) matrices, the temperature dependence of the reaction yields follows the WLF-type relationship. This shows that the conformational transitions of BAME favouring the cyclomerization process are governed by the free volume of polymer segments. This result is consistent with those obtained previously in other types of chromophores[7,12,13].

Below T_g, in polystyrene, from room temperature up to $\sim 60°$C, the yield of this reaction is independent of temperature and is determined by the conformational distribution of the two anthracene rings initially frozen in the polymer matrix. Between $\sim 60°$C and T_g, BAME undergoes photocyclomerization and the yield of the reaction is determined by the local motions of polymer.

The refractive-index change between the two states of BAME in the polymer matrix was directly measured and found to be large enough for optical recording purposes.

REFERENCES

1 Fritzche, J. J. *Prakt. Chem.* 1867, **101**, 333; 1869, **106**, 274; Cowan, D. C. and Drisko, R. L. 'Elements of Photochemistry'. Plenum, New York, 1976, p. 19
2 Bouas-Laurent, H., Castellan, A. and Desvergne, J. P. *Pure Appl. Chem.* 1980, **52**, 2633; Castellan, A., Desvergne, J. P. and Bouas-Laurent, H. *Chem. Phys. Lett.* 1980, **76**, 390; Ferguson, J. *Chem. Rev.* 1986, **86**, 957; and references cited in these works
3 Tomlinson, W. J., Chandross, E. A., Fork, R. L., Pryde, C. A. and Lamola, A. A. *Appl. Opt.* 1972, **11**, 533; Tomlinson, W. J. and Chandross, E. A. *Adv. Photochem.* 1980, **12**, 201
4 Boens, N., De Brackeleire, M., Huybrechts, J. and De Schryver, F. C. *Z. Phys. Chem., NF* 1976, **101**, S. 417
5 Hirayama, F. *J. Chem. Phys.* 1965, **42**, 3163
6 Maruta, M., Kanaya, T., Yamamoto, M. and Nishijima, Y. *Rep. Prog. Polym. Phys. Japan* 1981, **24**, 477
7 Pajot-Augy, E., Bokobza, L., Monnerie, L., Castellan, A. and Bouas-Laurent, H. *Macromolecules* 1984, **17**, 1490
8 Tran-Cong, Q., Chang, T., Nishijima, Y. and Han, C. C. *Polymer* 1986, **27**, 1705; Han, C. C., Tran-Cong, Q. and Chang, T. *ACS Polym. Prep., Div. Polym. Chem.* 1987, **28** (1), 371
9 Castellan, A., Lacoste, J. M. and Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. II* 1979, 411
10 Hatchard, C. G. and Parker, C. A. *Proc. R. Soc. Lond. (A)* 1956, **253**, 518
11 Ushiki, H., Hirayanagi, K., Sindo, S., Horie, K. and Mita, I. *Polym. J.* 1985, **17**, 671
12 Jarry, J. P. and Monnerie, L. *Macromolecules* 1979, **12**, 927; Tran-Cong, Q. and Nishijima, Y. *Rep. Prog. Polym. Phys. Japan* 1982, **25**, 557
13 Monnerie, L. and Bokobza, L. *ACS Polym. Prep., Div. Polym. Chem.* 1986, **27** (1), 69
14 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980, Ch. 11
15 Tran-Cong, Q. and Han, C. C., unpublished results
16 Yano, O. and Wada, Y. *J. Polym. Sci. (A-2)*, 1971, **9**, 669
17 Cohen, M. H. and Grest, G. S. *Ann. NY Acad. Sci.* 1981, **371**, 199
18 Chandross, E. A. *J. Chem. Phys.* 1965, **43**, 4175