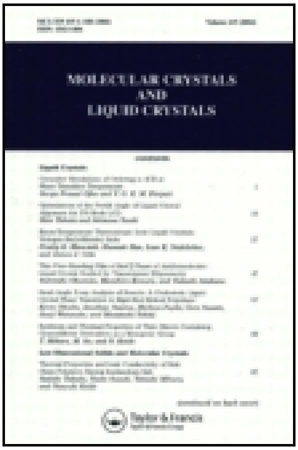

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Intra- and Intermolecular Photodimerization of Mesogenic Triphenylene Derivative having Cinnamate Groups: Effects of Orientation and Mobility of the Mesogenic Molecules on the Photoreaction Behavior

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The photoreactivity of cinnamate groups attached to a triphenylene ring was investigated in terms of formation of oligomers by photodimerization between cinnamate groups. It was found that the triphenylene derivative, 2,3,6,7,10,11-hexa(4′-octadecyloxycinnamate)triphenylene, showed discotic mesophases: a hexagonal disordered columnar phase (D_{hd}) and a nematic columnar phase (N_D) as discotic mesophases and a solid biphase which consisted of a glassy phase and a D_{hd} phase. The photooligomerization was strongly depressed both in the solid biphase and isotropic phase. The less mobility of mesogenic molecules in the solid biphase led to a low conversion of photooligomerization. On the other hand, the intramolecular photodimerization due to less ordering of the mesogenic molecules in the isotropic phase resulted in a low conversion to photooligomers.

Keywords: discotic liquid crystal, cinnamate, photodimerization, photooligomerization

INTRODUCTION

It is well known that cinnamic derivatives undergo photodimerization through cyclobutane formation at the C═C part of the cinnamic acid groups on photoirradiation at >300 nm. Schmidt *et al.*[1] found that the photochemical reactivity and the structure of photoproducts are determined predominantly by spatial orientation of the relevant two chromophores in crystals and termed this sort of photoreaction as a topochemical reaction. The topochemical photoreaction was extended to bifunctional molecules by Hasegawa *et al.*[2] who showed that a photopolymerization takes place in these bifunctional molecules in such a way that the crystalline structure of the resulting oligomers retains its original crystalline structure. Later, they found a number of bifunctional monomers capable of the topochemical polymerization. A few studies have been reported to extend the topochemical reaction to the liquid crystalline system,[3] since the liquid crystals possess the ordered structure of mesogens, though the order is somewhat lower than those of crystals. The different ordering of mesogens in liquid crystals may be expected to provide the different types of topochemical photoreactions.[4]

In addition to the conventional rod-like molecules disc-like flat molecules have been shown to form thermotropic mesophases. The mesophases are generally termed as discotic and may either be nematic (N_D), when the only order is a parallel orientation of the molecular discs, or columnar (D), when the discs are stacked into parallel columns which are located at the vertices of a two-dimensional lattice of a hexagonal, rectangular, oblique, or tetragonal type.[5–7] Billard *et al.*[8] reported on a discotic triphenylene derivative having hexyloxycinnamate groups in side chains, which showed a N_D phase. Mertesdorf *et al.*[9] investigated discotic liquid crystalline properties of a hexacyclene derivative with cinnamoyl groups as side chains and the fixation of the columnar phase through the dimerization of the cinnamoyl groups by UV irradiation. The fixation of the supramolecular arrangement by the discotic mesophases is a current topic of interest in view of application to new functional polymolecular devices.

In this paper we present the thermal phase transition behavior of a discotic triphenylene derivative with octadecyloxycinnamate groups in the side chains and the fixation of the discotic orientation by photodimerization of the cinnamate groups. The effects of the orientation, morphology and mobility of the discotic system on the photochemical reactivity of the cinnamate groups were also investigated.

EXPERIMENTAL

Material

The structure of the compound used in this study, 2,3,6,7,10,11-hexa(4′-octadecyloxycinnamate)triphenylene (TP-18AC), is given in Figure 1. *p*-Hydroxycinnamic acid was followed by alkylating with octadecyl bromide and refluxing with oxalyl chloride to give *p*-octadecyloxycinnamoyl chloride. 2,3,6,7,10,11-Hexahydroxytriphenylene was prepared by heating a corresponding hexamethoxy derivative, 2,3,6,7,10,11-hexamethoxytriphenylene,[10] with pyridinium chlorohydrate.[11] TP-18AC was obtained by reacting 2,3,6,7,10,11-hexahydroxytriphenylene with 6 equiv. of *p*-octadecyloxycinnamoyl chloride in anhydrous pyridine. This material was purified by column chromatography (silica gel; eluent: chloroform). The structure of TP-18AC was confirmed by NMR, IR and elemental analysis.

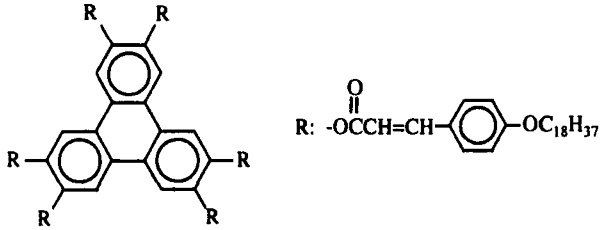

FIGURE 1 Structure of TP-18AC.

Data for TP-18AC: ^{1}H NMR ($CDCl_3$ ppm) δ 0.9 (s, 3H, CH_3 of alkoxy group), 1.2–1.8 (m, 32H, methylene of alkoxy group), 3.9 (t, 2H, CH_2 of alkoxy group), 6.4, 7.8 (d, d, 2H, CH=CH), 6.6, 7.2 (d, d, 4H, phenyl), 8.2 (s, 1H, triphenylene). IR (KBr cm^{-1}); 1730 ($\nu_{C=O}$). Elemental analysis; calcd. for ($C_{180}H_{264}O_{18}$) C, 79.6, H, 9.8; found C, 79.2, H, 9.8.

Thermotropic Properties

The thermal phase transition behavior of TP-18AC was examined by means of differential scanning calorimetry (DSC; SEIKO I&E SSC-5020), X-ray powder measurement and polarized optical microscopic observation (Olympus BHSP; Mettler FP80 and FP82).

Photochemical Reactions

Samples for photoirradiation were prepared by loading 2 mg of an isotropic melt of TP-18AC into two glass plates with ca. 15 μm gap and by gradually cooling to a desired temperature. The sample thus prepared was placed in a thermostatted block and irradiated with a 75 W high pressure mercury lamp through a glass filter ($280 < \lambda < 370$). After photoirradiation, the sample irradiated was removed from the glass plates and was subjected to various measurements: gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF-80M + KF-80M; eluent tetrahydrofuran), IR (JASCO A-702) and NMR (JEOL EX400M).

RESULTS AND DISCUSSION

DSC thermograms of TP-18AC were measured on heating or cooling at a rate of 2°C/min. In some cases, the second heating scan resulted in a different thermal behavior from the first scan because of thermal histories. The second heating (a) and cooling (b) thermograms are shown in Figure 2. Solid to mesophase and mesophase to isotropic phase transition temperatures were determined to be 83 and 206°C on the second heating scan (Figure 2a). The mesophase in the range of 83 to 206°C is assigned as the N_D phase on the basis of the observation of the shlieren texture, its high fluidity and the X-ray powder pattern. The transformation of the solid phase to other phase was brought about by heating up to 65°C, following the appearance of both the endothermic peak at 33°C due to a segmental motion of TP-18AC and the exothermic peak at 50°C (Figure 2c). The phase obtained by heating up to 65°C is a hexagonal disordered columnar phase (D_{hd} phase) based on the X-ray powder pattern. The phase transition from the D_{hd} phase to N_D phase occurred at 83°C on the heating scan. On the other hand, the solid phase observed below 65°C seems to consist of the glassy phase and the D_{hd} phase. In fact, the gradual endothermic change below 100°C due to the formation of the glassy phase and the exothermic transition to the D_{hd} phase at 43°C were observed on the second cooling scan (Figure 2b). The formation of the glassy phase may have resulted from the hinderance of phase transition from the N_D phase to the D_{hd} phase due to the long and bulky side chains of TP-18AC. The thermal phase transition behavior of TP-18AC is summarized in Figure 3.

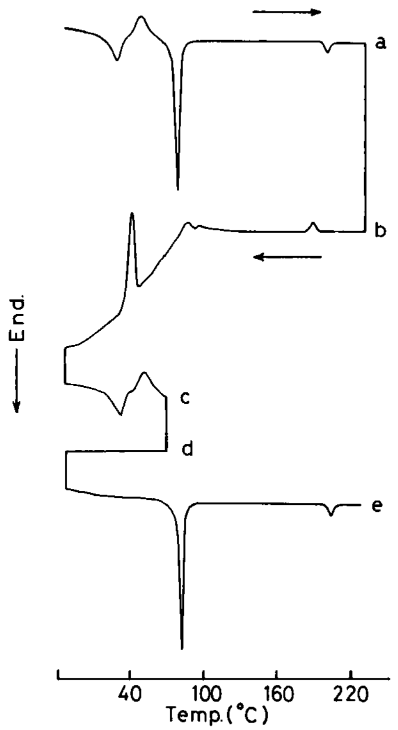

FIGURE 2 DSC thermograms of TP-18AC. The DSC thermograms were obtained on second and successive scans.

FIGURE 3 Thermal phase transition behavior of TP-18AC.

Figure 4 shows GPC chromatograms of TP-18AC before (A), after photoirradiation for 2 h (B) and 10 h (C) at 68°C. The molecular weight was calculated using a polystyrene calibration curve. Before photoirradiation, a sharp peak for monomeric TP-18AC was observed at a retention time of 20.6 min, while the formation of a dimer and oligomers of TP-18AC was induced by photoirradiation; i.e., the dimer of TP-18AC at 19.7 min and the oligomers in the range of shorter than 19 min were observed. IR spectra were found to decrease both peaks at 1635 cm^{-1} due to stretching of the C=C bond adjacent to the carbonyl group and at 980 cm^{-1} due to out-of-plane bending of C=C—H on photoirradiation. In addition, the formation of the cyclobutane ring by photoirradiation was ascertained by the

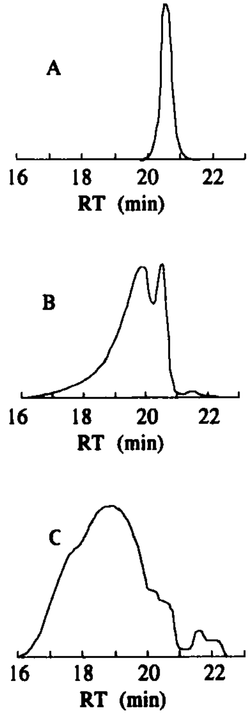

FIGURE 4 GPC chromatograms of TP-18AC before and after photoirradiation: Before irradiation (A) and after irradiation at >300 nm for 2 h (B) and for 5 h (C).

peak at about 4 ppm in NMR spectrum. It is recognized, therefore, that the formation of the dimer and oligomers of TP-18AC is brought about by intermolecular photodimerization of cinnamate groups forming the cyclobutane ring.

To evaluate the efficiency of the photooligomerization, the conversion from monomeric TP-18AC to oligomers was defined as $P/(P + M)$, where P and M are the amounts of oligomers and monomer determined by GPC measurements, respectively. The photoirradiation was performed for 4 h at various temperatures. Figure 5 shows the value of $P/(P + M)$ as a function of irradiation temperature. In addition, the value of $P/(P + M)$ of D_{hd} obtained at 65°C is plotted in Figure 5. It is clearly seen that the conversion is strongly dependent on the irradiation temperature. The conversions in the N_D phase were more than 80%, while the conversions in the solid, D_{hd} and the isotropic phases were much lower than those in the N_D phase. Figure 6 shows the relative photochemical reactivity, A_{980}/A_{1510}, by measuring the decrease in peak intensity at 980 cm^{-1} (A_{980}) relative to 1510 cm^{-1} (A_{1510}) which remained unchanged on photoirradiation. It was found that the relative photochemical reactivity was depressed considerably in the solid biphase compared to that in the N_D phase. In the N_D phase, TP-18AC is expected to be aligned in the appropriate direction for intermolecular photodimerization and the mobility of the TP-18AC chromophores is high enough to enable them to approach each other for dimerization. The intermolecular spacing along the column of TP-18AC in the D_{hd} phase is the order of 4 Å by X-ray diffraction parameter.

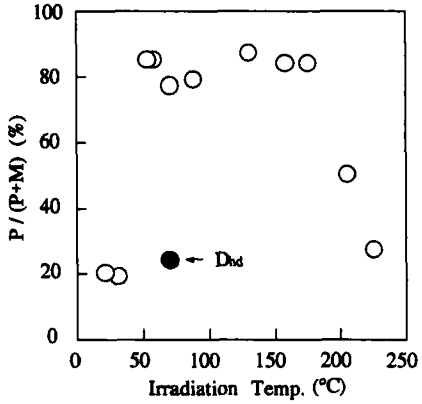

FIGURE 5 Temperature dependence of conversion to oligomers of TP-18AC.

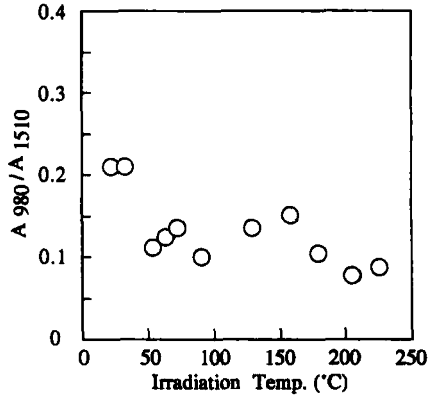

FIGURE 6 Temperature dependence of photochemical reactivity of TP-18AC.

Schmidt revealed that the dimerization of cinnamic acid took place at C═C separation of 3.6 ~ 4.1 Å.[12] In the solid biphase and D_{hd} phase, however, unfavorable orientation and the less mobility of TP-18AC may result in the low conversion to oligomers as well as the low photoreactivity of cinnamate groups. It should be noted that the conversions in the isotropic phase were lower than those in the N_D phase, though photodimerization took place sufficiently as can be seen in Figure 6. In the isotropic phase, the orientation is random while the mobility is high. The low conversion in the isotropic phase may be explained in terms of the lower ordering of molecules in the isotropic phase. Figure 7 shows the relative amounts of octamer to dimer (8mer/dimer) in the irradiated sample determined by GPC analysis. It is evident that the ratio of 8mer/dimer decreased with increasing the irradiation temperature. The ratios of 4mer/dimer and 16mer/dimer also showed a similar temperature dependence. These results imply that the propagation of photooligomerization was influenced by the irradiation temperature. It is assumed that the ordering of the molecules changes as a function of temperature even in the identical mesophase; i.e., the orientation of the N_D phase near the isotropic phase is considerably lower compared to that of the N_D phase just above the phase

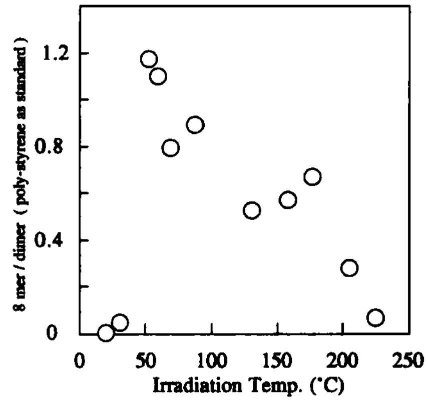

FIGURE 7 Temperature dependence of relative content of octamer to dimer (8mer/dimer) in photoproducts.

transition from the D_{hd} phase to the N_D phase. The propagation of the photooligomerization is essentially based on intermolecular photodimerization. The decrease of the propagation with temperature and, in particular, the extremely low conversion in the isotropic phase are considered to be related to the ordering of the mesogenic molecules. Namely, intermolecular photodimerization is depressed with temperature, while intramolecular photodimerization is facilitated on photoirradiation in the isotropic phase.

The photochemical reactivity of cinnamate groups was influenced by the mobility as well as the ordering of the molecules. The conversion to oligomers in both the solid biphase and the N_{hd} phase was strongly depressed compared to that in the N_D phase. The synthesis of triphenylene derivatives having various alkoxycinnamate groups and other types of photopolymerizable groups is now in progress and will be reported later.

References

1. M. D. Cohen and G. M. Schmidt, *J. Chem. Soc.*, 1969 (1964); G. M. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971).
2. M. Hasegawa and Y. Suzuki, *J. Polym. Sci.*, **85**, 2535 (1967); M. Hasegawa, *Chem. Rev.*, **83**, 507 (1983).
3. T. Ikeda, H. Itakura, C-H. Lee, F. M. Winnik and S. Tazuke, *Macromolecules*, **21**, 3535 (1988), T. Ikeda, T. Ikeda, T. Sasaki, B. Lee and S. Kurihara, *Liq. Cryst.*, **9**, 457 (1991).
4. V. Ramesh and R. G. Weiss, *J. Org. Chem.*, **514**, 2535 (1986).
5. C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
6. A. M. Levelut, *J. Chim. Phys.*, **80**, 149 (1983).
7. K. Ohta, T. Watanabe, H. Hasebe, Y. Morizumi, T. Fujimoto, I. Yamamoto, D. Lelievre and J. Simon, *Mol. Cryst. Liq. Cryst.*, **196**, 13 (1991).
8. P. Le Barny, J. Billard and J. C. Dubois, *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffine and J. F. Johnson, Plenum Press, **57**, 1043 (1987).
9. C. Mertesdorf and H. Ringsdorf, *Liq. Cryst.*, **5**, 1757 (1989), C. Mertesdorf, H. Ringsdorf and J. Stumpe, *Liq. Cryst.*, **9**, 337 (1991).
10. O. C. Musgrave and C. J. Webster, *J. Chem. Soc.*, C 1397 (1971).
11. N. H. Tinh, H. Gasparoux and C. Destrade, *Mol. Cryst. Liq. Cryst.*, **68**, 101 (1981).
12. G. M. Schmidt, *J. Chem. Soc.*, 2014 (1964).