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Photosensitive Characteristics of Poly(Methacrylates) Containing Benzylidenephthalimidine Moieties on the Side Chain

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PHOTOSENSITIVE CHARACTERISTICS OF POLY(METHACRYLATES) CONTAINING BENZYLIDENEPHTHALIMIDINE MOJETIES ON THE SIDE CHAIN

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Abstract Photosensitive polymethacrylates having benzylidenephthalimidine(BPI) moiety on the side chains were synthesized. Upon photoirradiation of the polymer film, there occurred two kinds of photoreactions; the E/Z photoisomerization and [2+2] cycloaddition. The cycloaddition of BPI units of polymers resulted in the crosslinking of the polymer chains. The quantum yield for the photocrosslinking reaction was estimated from gelation experiment. Irradiation of the film with linearly polarized UV light induced a dichroism of BPI. Linearly polarized UV light irradiation of a nematic liquid crystals (LCs) cell assembled with a glass plate surface-modified with a Poly[N-(2-methacryloyloxy)ethyl-p-methoxy benzylidenephthalimidine] film brought about the homogeneous alignment.

INTRODUCTION

Many studies have been carried out on various photosensitive polymers because it have numerous technological applications such as photodisplay, photochemical switching devices, information storage devices.¹⁻⁸ Concerning these subjects, several reports described linearly polarized light (LPL) induced alignment regulation of liquid crystals (LCs) by surfaces of photosensitive polymer including poly(vinyl cinnamate)s⁸ or polymers having azobenzenes on the side chains.²⁻⁵ The phenomenon was considered to be brought about by a polarized axis-selective photoreaction, namely, the cycloaddition or

the E/Z - isomerization. However, the mechanism for the LC alignment induction by a polymer surface is not clear, and there is a possibility for another photosensitive polymer to cause the LC alignment regulation.

BPI has a stilbene skeleton, and the rotation around one of the C-C bonds is



E -isomer

Z-isomer

restricted by the condensed ring structure. This compound is known to undergo the E/Z isomerization upon photoirradiation in a solution.⁹ There are no reports on photocycloaddition of BPIs, however.

In this paper, we describe the synthesis and photochemical properties of polymethacrylates having BPI moiety in their side chains. Moreover, we applied the photochemical behavior of the polymer film to the photoregulation of LC alignment by linearly polarized light irradiation.

EXPERIMENTAL

<u>General</u>

Gel permeation chromatography(GPC) was carried out with a Jasco system (860-CO) equipped with UV detectors at a flow rate at 1.0 ml/min with chloroform as an eluent. Differential scanning calorimetory was conducted with a DSC2000 (Seiko Electronics). UV absorption spectra were measured with a Hitachi UV 320 spectrometer. ¹H NMR spectra were recorded on a JEOL FX90Q spectrometer using chloroform-d as a solvent. IR spectra was measured with a JEOL JIR-3050.

Monomer Synthesis

Compounds 2a and 2b were prepared by the reaction of the corresponding 3benzylidenephthalide and 2-aminoethanol according to the method reported byMarshal.^{9,10} 2a: white amorsphous; 84% yield; mp 118-119°C; ¹H NMR, 2.08 (1H, s, OH), 3.8-5.0 (4H, m, CH₂CH₂), 6.50 (1H, s, C=CH), 7.3-7.9 (9H, m, Ar-H); IR (KBr) 3421, 1676, 1645 cm⁻¹; Anal. Calcd for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28 Found: C, 76.88; H, 5.81; N, 5.22.

2b: white amorphous; 61% yield; mp 143-145 °C; ¹H NMR, 2.47 (1H, s, OH), 3.89 (3H, s, O-CH₃), 3.9-4.1 (4H, m, CH₂CH₂), 6.62 (1H, s, C=CH), 6.9-7.9 (8H, m, Ar-H); IR (KBr) 3413, 1698, 1648 cm⁻¹, Anal. Calcd for $C_{18}H_{17}O_3N$: C, 73.2; H, 5.80; N, 4.74 Found: C, 73.12; H, 5.90; N, 4.77

To a mixture of **2a** (1.0 g, 3.8 mmol) and triethylamine (0.50 g, 5.0 mmol) in dry dioxane under N₂ atmosphere at 0°C was added dropwise methacryloyl chloride (4.5 g, 4.3 mmol), and the reaction mixture was stirred for 2 h. The solution was poured into 50 ml water and diluted with Et_2O . The organic layer was washed successively with 2.4 N HCl and brine, dried over MgSO₄ and evaporated. The residue was recrystallized from MeOH to give 0.82 g (66%) of **3a**.

3a: white amorphous; ¹H NMR, 1.89 (3H, s, C=C-CH₃), 4.1-4.5 (4H, m, CH₂CH₂), 5.57 (1H, s, C=C-H), 6.10 (1H, s, C=C-H), 6.65 (1H, s, C=CH), 7.3-7.9 (8H, m, Ar-H); UV-vis, λ_{max} (ε) in CHCl₃:328 nm (1.13 ×10⁴)

3b: white amorphous; 68% yield; ¹H NMR, 1.87 (3H, s, C=C-CH₃), 3.89 (3H, s, Ar-CH₃), 4.1-4.5 (4H, m, CH₂CH₂), 5.59 (1H, s, C=C-H), 6.15 (1H, s, C=C-H), 6.64 (1H, s, C=CH), 6.9-7.9 (8H, m, Ar-H); UV-vis, λ_{max} (ϵ) in dioxanc: 338 nm (1.01

× 10⁴)

The monomer 3 become insoluble readily in a crystalline state. Therefore, it was immediately used for the polymerization after the recrystallization.

Polymerization

To a 20 ml ampoule was introduced monomer 3, methy methacrylate (1:4 by mol) and AIBN in dioxane. Concentration was 20 wt% for monomer and 0.5 wt% for AIBN. The solution was degassed by several freeze-pump-thaw cycles. After scaling, the mixture was heated at 55° C for 15 h. The resulting viscous solution was cooled down to room temperature and added dropwise into methanol to precipitate polymeric materials. Polymers were repeatedly purified by centrifugal separation from McOH. The results for the polymerization is shown in Table 1.

Sample preparation and photoirradiation

A benzene solution (20 wt%) of the polymer was spin-coated on quartz plates(1 cm x 3 cm). After the films were dried in vacuo, they were annealed for 1 h at 60°C. The thickness of the films was 240 nm. Then, the samples were exposed to UV light (365 nm) from a 500-W high-pressure Hg lamp through glass filters (UV-36A+UV-35).

The LC cell fabrication and photoinduced birefringence measurements were made according to our previous paper.^{11, 12}



Scheme 1

RESULTS AND DISCUSSION

1. Synthesis

Monomers 3a and 3b were synthesized through a combination of known benzylidenephthalimidine preparation and the usual esterification as shown in Scheme 1. The copolymers were prepared by a conventional radical polymerization procedure. For common organic solvents such as benzene, THF, DMSO, the copolymer contained an insoluble particles, probably due to the partial crosslinking through exocylic double bond of BPI. The content of BPI moieties was determined by UV spectra, using molar

R R R R	TAE	TABLE 1 Characterization of the copolymers					
, CH3 0 0 >0 >0	Polymer	Copolymerization ratio (p:q)	Molecular Mw X 10 ⁻⁵	weight Mw / Mn	Tg (°C)	Yield (%)	
* topt	CpBPI-H	1 : 5.9	1.5	1.9	117	35	
R = H · CoBPI-H	CpBPI-Me0	D 1:4.1	1.6	1.9	109	39	

R = MeO : CpBPI-MeO

2. Photochemical behavior





FIGURE 1 Absorption spectral change of CpBPI-MeO film upon irradiation of UV light.



Figure 1 shows the UV spectral change during the photoirradiation of CpBPI-McO film at room temperature. Before irradiation, there was an absorption maximum at 344 nm. After 20 sec of irradiation, there observed an increase in the intensity accompanied by slight blue shift of λ_{max} to 342 nm. Until this time, there was an isosbestic point at 362 nm. Upon prolonged exposure, the intensity of the peak at 342 nm decreased. After 8 h irradiation, no additional change in the spectrum was observed. The polymer film was insoluble at this stage, indicating the occurrence of photocrosslinking of the polymer chains.

We have previously investigated on the photochemical behavior of several *N*-alkylated BPIs.¹³ In every case studied, λ_{max} of *Z*-isomer is 2 to 4 nm shorter than that of *E*-isomer, and ε_{max} is slightly larger for *Z*-isomer. The increase in the absorbance at the initial stage of photoirradiation was also observed for a solution of *N*-alkylated BPIs upon photoirradiation and is due to the *E/Z* photoisomerization of the BPI moiety in the side chains. The decrease in the absorbance at the latter stages of the photolysis, which is not observed in the solution state photoreaction, was attributed to the photocrosslinking of the polymer chains via [2+2] cycloaddition. In a polymer film, an average distance of the chromophores is sufficiently small to undergo cycloaddition than in solution. However, the unimolecular *E/Z* photoisomerization predominates over bimolecular photocrosslinking reaction even in film state.

photocrosslinking reaction even in film state.

Next, the photoreactivity of the crosslinking reaction was compared for two polymers, CpBPI-H and CpBPI-MeO, by monitoring the change of absorbance at the initial isosbestic point in the UV spectra of the polymer films. The result is shown in figure 2. The sensitivity of CpBPI-MeO was higher than that of CpBPI-H in one order. This fact suggests that the photodimerization has charge transfer character.¹⁴

In order to obtain direct information on the photocrosslinking of polymers, a gelation experiment was carried out. After irradiation with 365 nm light, a film was washed with a solvent (benzene:MeOH=1:1) and the thickness of the remaining film was measured. The irradiation energy-thickness curve shown in Figure 3 indicates that the photocrosslinking occurred in a stepwise manner. The extrapolated point of the curve, Eg, is related to the quantum yield of photocrosslinking, Φ , by the equation (1)

$$\Phi = \frac{rd}{Eg(1-T)Mw} \quad -----(1)$$

where Mw, r, d and T denotes a weight average molecular weight, the film thickness, the specific gravity of the material and the optical transmittance, respectively.^{15, 16} Table 2 shows that the quantum yield for the crosslinking of CpBPI-MeO was much higher than that for CpBPI-H. This result is in good agreement with the UV spectral change mentioned above.



TABLE 2 Quantum yield of photocrosslinking reaction

Polymer	(J/cm ²)	Φ		
CpBPI-H	1.2	2.5 x 10 ⁻⁴		
CpBPI-MeO	0.060	1.9 x 10 ⁻²		

FIGURE 3 Gelation Curve of CpBPI-McO([]) and CpBPI-H(())

3. Photocontrol of LC alignment

It is known that the dichroic polymer film can bring about an in-plane alignment regulation of nematic LCs. Photoinduced dichroic property was also investigated. A film of CpBPI-McO was irradiated with linearly polarized 365 nm light at an exposure energy of 270mJ/cm², and the polarized absorption spectrum was measured. At 342 nm, the absorbance of probe light with an electric vector is parallel to that of actinic light(A_I) was 2.69×10^{-2} while that perpendicular to the actinic light(A_{.t}) was 2.97×10^{-2} . This fact means that the direction of the long axis of BPI is predominantly perpendicular to the incident polarized light. An LC cell was fabricated by sandwiching NPC-02, a nematic LC of Tni=35.0°C, between a glass plate covered with a 40 nm- thick- film of the CpBPI-MeO and a glass plate modified with lecithin. After heating the cell to 45° °C for 20 min, the cell was exposed to linearly polarized UV light (365 nm). Then, the LC cell was set in front of a polarized He-Ne laser (633 nm), and a transmittance through the cell and a crossed polarizer was monitored as a function of the rotation angle of the cell around a optical axis. As shown in figure 4, the transmittance changed periodically in every 90 degrees. This result means that the homogeneous alignment of LC was induced by the surface of a dichroic CpBPI-MeO film. A detailed study on the LC alignment regulation experiment is now under way and will be published elsewhere.



FIGURE 4 Anguar dependence of transmittance of a monitoring He-Ne laser through the LC cell exposed to linearly polarized light at room temperature; $\bigcirc :0 \text{ mJ/cm}^2$, $\bigcirc :270 \text{ mJ/cm}^2$.

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