NOTES

Synthesis and Photoreaction of Poly[6-(4'-cinnamoylbiphenyloxy)-hexylmethacrylate-co-methylmethacrylate]

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Photocrosslinkable LC materials have attracted attention for their mechanical and thermal stability as well as electro-optical applications because the possibility of locked-in liquid crystalline (LC) structures.^{1–6} Several photocrosslinkable LC polymers using cinnamic esters have been investigated in recent years.^{4–6} We also synthesized new photoreactive LC polymers having cinnamoylbiphenyl mesogen and studied their aggregation behavior.⁷ Photoreaction efficiency of these polymers in solid state would be influenced by the conformation of photoreactive mesogens or reaction temperature since the photoreactivity of the LC materials greatly depend on the reaction conditions.^{5,6}

In this article, LC methacrylate monomer of 6-(4'-cinnamoylbiphenyloxy)-hexyl methacrylate **1**, synthesized previously,⁷ was copolymerized with methyl methacrylate (MMA) to change the degree of aggregation of the LC mesogen. The effect of the reaction temperature on the photoreaction rate was investigated using copolymers with various copolymerization ratios.

EXPERIMENTAL

Polymer Synthesis and Characterization

Copolymers were synthesized by free radical polymerization of **1** and MMA using α, α -azobisisobutyronitrile (AIBN) as initiator in tetrahydrofuran (THF) solution. The chemical structure of the copolymer is given in Figure 1. Homopolymer **2a**⁷ was also used. The molecular weight and molecular weight distribution, differential scanning calorimetry (DSC), FT-IR, UV-VIS spectra, and X-ray diffraction measurements were performed by same procedures as previously described.⁷

Figure 1. Chemical structures and compositions of the synthesized copolymers.

Photoreaction

For the photoreaction of the copolymers, thin films were prepared by casting method on a KBr substrate from a methylene chloride solution. The film was irradiated with a high pressure Hg-UV light. The progress of photoreaction was determined by FT-IR with monitoring the decrease of intensity of the $\text{C}=\text{C}$ vibration (1638 cm^{-1}) of cinnamoyl group in monomer **1**.⁸ The phenyl vibration (1600 cm^{-1}) was used as the initial standard.

RESULTS AND DISCUSSION

Polymer Synthesis and Thermal Properties

Copolymers **2b–2h** were obtained by the free radical polymerization. All synthesized copolymers were completely soluble in organic solvents such as chloroform or THF, indicating no crosslinking occurred during polymerization. The number average molecular weights were in order of $24000\text{--}65000\text{ g mol}^{-1}$ and molecular weight distributions were $2.19\text{--}3.10$. Table I summarizes the composition and thermal properties of the (co)-polymers.

As shown in Table I, homopolymer **2a** and copolymers **2b–2f** exhibited thermotropic LC behavior, while **2g** and **2h** did not. For **2a** and **2b**, a smectic phase was observed

Table I. Composition, thermal properties and spectroscopic data for the copolymers

No.	Composition ^a x	Transitions $^{\circ}\text{C}^b$				λ_{max} ϵ^c	
		T_g	T_m	T_{sn}	T_{ni}	Solution	Film
2a	0	—	144	157	219	282 (47.2)	272
2b	10	—	138	150	209	282 (43.4)	273
2c	28	—	126	—	189	282 (43.4)	273
2d	40	—	109	—	167	282 (54.9)	274
2e	55	—	99	—	144	283 (56.1)	275
2f	65	—	83	—	125	283 (51.7)	277
2g	75	77	—	—	—	282 (57.7)	282
2h	90	71	—	—	—	283 (61.2)	281

^a MMA composition (mol%). Determined by ^1H NMR. ^b Determined by DSC. Heating rate, 10 K min^{-1} ; T_g , glass transition; T_m , melting; T_{sn} , smectic–nematic transition; T_{ni} , clearing point. ^c Solution: in CH_2Cl_2 . ϵ ($\times 10^{-3}$) was calibrated with the composition of LC-monomer **1** in the copolymer. Film, on quartz.

in a small temperature range followed by a nematic phase. The melting and clearing temperatures decreased with increasing MMA composition for the LC (co)polymers **2a**–**2f**. T_g was observed only for the non-LC copolymers (**2g**, **2h**) and strong melting peak was detected for the LC copolymers on the second heating of DSC. This is consequence of high crystallinity of the cinnamoylbiphenyl mesogen in the LC (co)polymers.

UV-VIS Spectra

Spectroscopic data of the copolymers in both solution and thin film at r.t. are also listed in Table I. The absorption spectra of all copolymers in solution exhibited the same shapes of homopolymer **2a** in solution with the absorbance maxima at 282–283 nm. On the other hand, the absorption maxima of the LC copolymer films (**2a**–**2f**) shifted to shorter wavelength than the solution with increasing composition of **1** in the copolymer and the spectrum showed tail-stretching to longer wavelength. This blue shift can be attributed to head to head arrangements of the chromophore based on the observation of similar cinnamate mesogen studied by Hoyle *et al.*⁹ Non-LC copolymers **2g** and **2h** did not show blue shift or tail-stretching, suggesting no-aggregation. These results indicate only LC copolymers aggregate and the degree of aggregation decrease with increasing MMA composition. On heating all LC copolymers to the LC state, the absorption intensity decreased and absorption maxima shifted to longer wavelength in the LC state, suggesting change of aggregation from head-head to head-tail. In the isotropic state, the absorption increased again and the spectrum became similar to that in the solution. After cooling from the isotropic state, absorption decreased again and shifted to longer wavelength. These phenomena were also observed for homopolymer **2a** as described previously,⁷ whereas the absorption spectrum scarcely changed in heat treatment for non-LC copolymers.

Photoreaction

On the UV irradiation, all (co)polymers became insoluble in organic solvents due to the photocrosslinking of cinnamoyl group. For example, Figures 2(a) and (b) show the progress of the reaction of LC copolymer **2d** and non-LC one **2h** at various sample conditions.

In the LC state of **2d**, photoreaction was much faster than in other states. Further, higher reactivity was observed in the isotropic state than that at r.t. for both copolymers. For the photoreaction of **2d** at r.t., the reactivity of the film cooled slowly from the isotropic state or quenched from the LC state decreased compared to that of as-casted one, while quenching from the isotropic state or from 100°C (below T_m) scarcely changed the reactivity. On the other hand, the heat treatment did not affect the reaction rate of **2h**. Other LC- and non-LC (co)polymers showed same tendencies.

Fast photoreaction in the isotropic and the LC state would arise from the high mobility of the chromophore for all (co)polymers. Since head-tail aggregation is predominant after cooling slowly from the isotropic state,⁷ conformational change of the chromophore during the photoreaction might be needed for the photoreaction of LC (co)polymers, resulting in slow reac-

Figure 2. Time-conversion plot of photoreaction of the copolymers. (a) **2d**: ●, as casted; ▲, at 150°C (nematic); ■, at 190°C (isotropic); ○, at r.t. cooled from 190°C; △, at r.t. quenched by liq. N₂ from 190°C; □, at r.t. quenched by liq. N₂ from 150°C; ◇, at r.t. quenched by liq. N₂ from 100°C. (b) **2h**: ●, as casted; ○, at r.t. cooled from 160°C; ■, at 120°C (above T_g).

tion. Similar conformation may occur after quenching from the LC state because UV-VIS spectra suggested the head-tail aggregation of the LC chromophore in the LC state. Fast quenching from the isotropic state did not cause this aggregation. X-Ray diffraction suggests high crystallization after cooling the LC (co)polymers from the isotropic state. For example, in case of homopolymer **2a**, a reflection ascribable to the distance between the mesogenic groups at $2\theta = 20.4^\circ$ ($d = 4.3 \text{ \AA}$) in the solid state became very sharp after cooling. This peak became broad ($d = 4.6$ – $4.8 \text{ \AA}$) in the LC state. Quenched sample from the LC state showed similar diffraction as the cooled sample from the isotropic state. In contrast, UV spectra and X-ray suggest no-conformational change for non-LC copolymers, resulting in no-change in the reaction rate after quenching.

In conclusion, we show differences in photoreaction ability for copolymers and effects of the reaction temperature. Conformation and the mobility of the cinnamoylbiphenyl mesogen strongly affect the reaction rate.

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