

Preparation of Novel Acrylate-Based Liquid Crystalline Polymers and the Photoinduced Alignment Behavior of Their Films

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ABSTRACT: Two acrylate monomers containing both mesogenic biphenyl group and photoreactive cinnamoyl group as well as different length of flexible spacers (i.e., n -[4'-(n -cinnamoyloxyalkoxy)biphenyl-4-yloxy]alkyl acrylate, $n = 4$ (A4OO4C) and 6 (A6OO6C)) were synthesized for the first time. Their corresponding polymers (i.e., PA4OO4C and PA6OO6C) were obtained by free radical polymerization using AIBN as an initiator. The monomer A4OO4C showed smectic liquid crystalline phase and a clear fan texture was observed under optical polarizing microscope. However, no liquid crystalline phase was found for A6OO6C. In contrast, PA4OO4C

showed no liquid crystalline phase while PA6OO6C showed a clear nematic schlieren texture during the cooling process. The optical polarized microscope of E5 cast on the top of the polymer film also showed the alignment. Furthermore, the irradiation of the polymer films by LP-UV light led to the cycloaddition of the cinnamoyl groups, resulting in the simultaneous alignment of the biphenyl groups. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4565–4572, 2006

Key words: liquid-crystalline polymers; films; cyclopolymerization; photoalignment; POM

INTRODUCTION

The photoalignment technique for liquid crystalline display has received much attention in recent years,^{1–6} because it is a clean and photopatternable system with the ability to widen the viewing angle. Many photocrosslinkable side chain liquid-crystalline polymers bearing cinnamic esters and their analogs have been studied recently.^{7–12} These polymers can be photocrosslinked by UV-irradiation through [2 + 2] photocycloaddition reaction of cinnamoyl group, and their crosslinked films show thermal stability of the aligned structures.^{9,10} Nobuhiro has synthesized a series of methacrylate-based polymers containing a mesogenic biphenyl group and a photoreactive cinnamoyl function, i.e., poly[m -[4'-(n -cinnamoyloxyalkoxy)biphenyl-4-yloxy]alkyl methacrylate]s ($m, n = 2, 6$), through five steps.¹⁰ However, to our knowledge, the acrylate-based polymers have never been reported. In this article, two acrylate-based monomers containing a mesogenic biphenyl group and a photo-

reactive cinnamoyl function and their polymers have been prepared in a relatively simple synthetic route as shown in Scheme 1. Their thermal properties and the mesophase structure were studied by differential scanning calorimetry (DSC) and thermal optical polarized microscope (POM). Furthermore, the photoinduced alignment behavior of the polymer film materials was also investigated.

EXPERIMENTAL

Materials

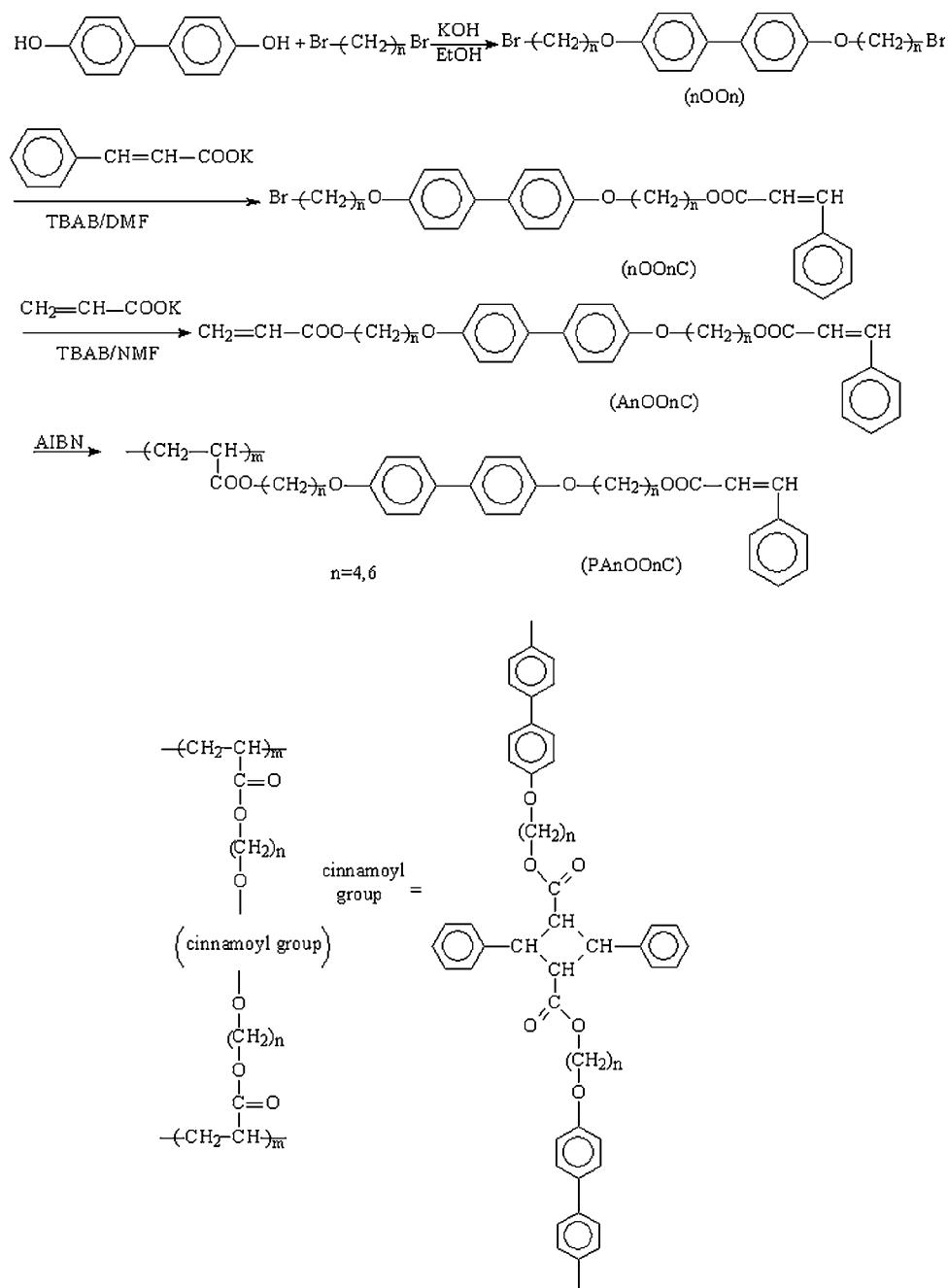
Dimethylformamide (DMF), dried and purified in the usual ways, dichloromethane (CH₂Cl₂), n -hexane, ethanol, acrylic acid 4,4'-biphenyldiol, tetrabutylammonium bromide, triethylamine (TEA), 2,2'-azobis(2-methylpropionate) (AIBN), petroleum ether, 1,6-dibromohexane, and 1,4-dibromobutane were of A.R. grade.

Instruments and measurements

¹H NMR analyses were performed on a Mercury-Vx 300 spectrometer, using TMS as the internal standard. FTIR spectra ranging from 400 to 4000 cm⁻¹ were obtained on a Bio-Rad FTS 135 spectroscopy. Gel permeation chromatography (GPC) analyses were performed at 25°C on Water's liquid chromatograph

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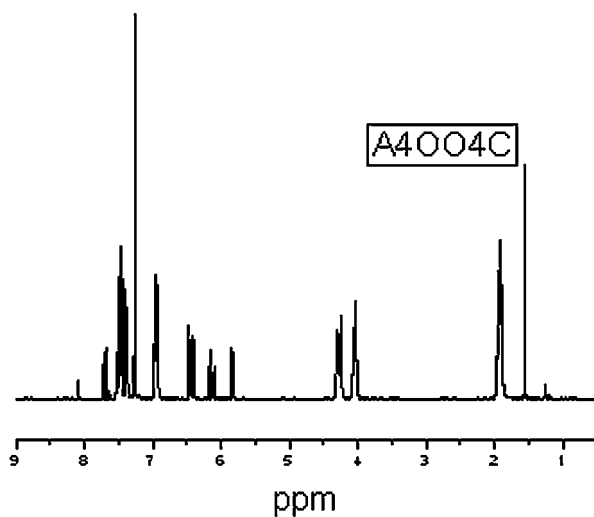
Scheme 1

equipped with Waters 510 pump, Waters 410 refractive index detector, and three poly(divinylbenzene) columns of 10^6 , 10^4 , 10^3 , and 10^2 . Tetrahydrofuran was used as the mobile phase (1 mL/min), and the column was calibrated with polystyrene standards. Netzsch DSC 204 differential scanning calorimeter was used for the assessment of thermal transitions. In all cases, heating and cooling rates were $10^\circ\text{C}/\text{min}$. Liquid crystalline textures and morphologies were determined by an Olympus BX51 thermal optical polarized microscope (POM). The polymer films were prepared by dissolving polymers in DMF and then coating

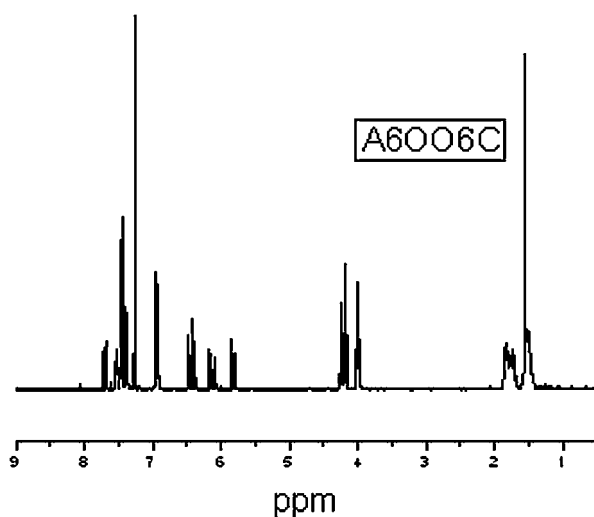
them onto quartz plate, followed by drying at 40°C in vacuum oven for 6 h. The photoinduced alignment behavior of the polymer films was investigated under a linearly polarized light irradiation (Coherent Innova 90C-A6, Ne laser, $\lambda = 351 \text{ nm}$, $I = 38 \text{ mW}/\text{cm}^2$).

Synthesis of the monomers

The detailed synthetic procedure for A4OO4C was described as follows, and A6OO6C was prepared similarly.



(a)



(b)

Figure 1 (a) ^1H NMR spectrum of A4OO4C; (b) ^1H NMR spectrum of A6OO6C.

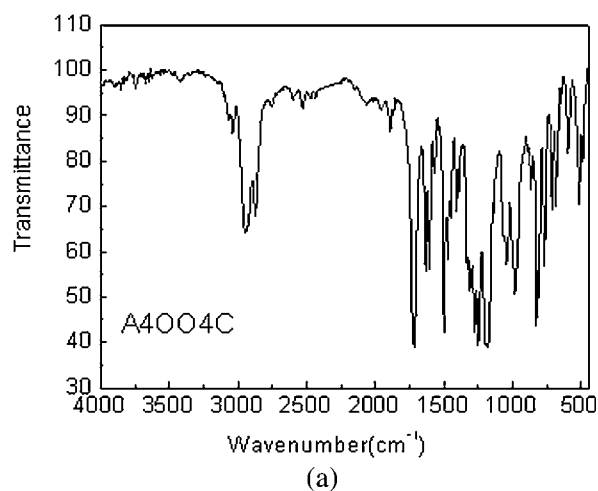
4,4'-di(4-Bromobutyloxy)biphenyl (4OO4)

4,4'-Biphenyldiol (18.6 g, 0.1 mol) and 1,4-dibromobutane (45 g, 0.2 mol) were dissolved in a mixture of H_2O and ethanol (1/1, v/v, 260 mL), and then was heated to the refluxing temperature. A solution of KOH (14.0 g, 0.25 mol) in a mixture of H_2O and ethanol (1/1, v/v, 40 mL) was added dropwise into the above-stirred solution. Afterward, the reaction was maintained at reflux for 4 h. The white precipitate produced during the reaction was collected by filtration, recrystallized twice from 1,2-dichloroethane, and then dried at 60°C in a vacuum oven for 24 h to provide the desired product. Yield 15.0 g (33%), mp 136.9°C , ^1H NMR (CDCl_3): $\delta = 1.98$ (m, 4H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 2.07 (m, 4H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 4.03 (t, 4H, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 6.93 (d, 4H, aromatic

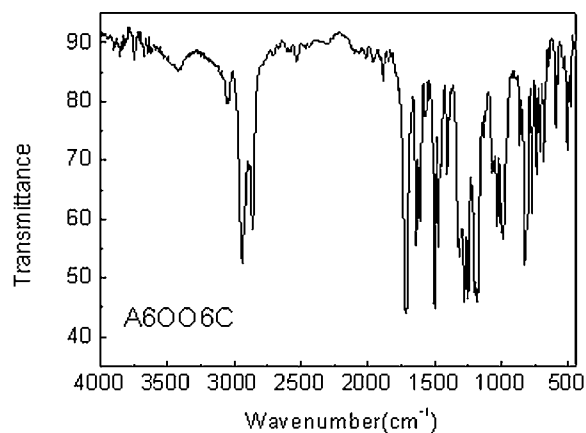
protons), 7.45 (d, 2H, aromatic protons). IR (KBr, cm^{-1}): 2945, 2873, 1607, 1569, 1500, 1273, 1249, 1178, 1004, 825, 655, 585, 516.

4-(4-Bromobutyloxy)-4'-(4-cinnamyl butyloxy)biphenyl (4OO4C)

4OO4 (22.8 g, 0.05 mol), potassium cinnamate (9.2 g, 0.05 mol), and tetrabutylammonium bromide (TBAB, 0.2 g) were dissolved in dried DMF (150 mL) under nitrogen atmosphere and the solution was heated to 60°C . Afterward, hydroquinone (0.3 g) was added and the reaction was stirred for 30 min under nitrogen and then sealed. The reaction was stirred at 40°C for 48 h and a peach color is obtained. After being cooled down to room temperature, the reaction mixture was filtered to remove the produced KBr generated during the reaction. The obtained filtrate was then concentrated on a rotary evaporator to about one-eighth of the original volume and then poured into H_2O (300 mL). The precipitate was collected by filtration, washed with water (100 mL), and then recrystallized



(a)



(b)

Figure 2 (a) IR spectrum of the A4OO4C; (b) IR spectrum of the A6OO6C.

TABLE I
The Yields and Molecular Weights of Polymers

Polymer	Yield (%)	M_n	M_w	M_w/M_n
PA4OO4C	73	13693	14359	1.78
PA6OO6C	65	25261	57233	2.26

twice from ethanol. The obtained white solid product was further purified by column chromatography (silica gel, dichloromethane), and then dried at 40°C in a vacuum oven for 24 h. Yield 9.1 g (34.8%), mp 97.9°C, $^1\text{H NMR}$ (CDCl_3), δ : 1.55–2.12 (m, 8H, $\text{COO}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}$), 3.52 (t, 2H, $-\text{CH}_2-\text{Br}$), 4.02 (t, 2H, $-\text{CH}_2-\text{O}$), 4.28 (t, 2H, $\text{COO}-\text{CH}_2-$), 6.41 (d, 1H, $\text{CH}=\text{CH}-\text{COO}$), 6.93–7.53 (m, 13H, aromatic protons), 7.66 (d, 1H, $\text{CH}=\text{CH}-\text{COO}$). IR (KBr, cm^{-1}): 2945, 2873, 1715, 1637, 1606, 1499, 1274, 1248, 1175, 981, 824, 766, 708, 652, 596, 516.

4-(4-Acryl butyloxy)-4'-(4-cinnamyl butyloxy) biphenyl (A4OO4C)

4OO4C (8.6 g, 0.015 mol), potassium acrylate (3.4 g, 0.03 mol), and tetrabutylammonium bromide (TBAB, 0.2 g) were dissolved in dried DMF (160 mL) under nitrogen atmosphere. The solution was heated to 40°C and hydroquinone (0.3 g) was added. The reaction was allowed to stir for 30 min while still under nitrogen and then sealed. The reaction was stirred at 40°C for 48 h, and when it became peach in color cooled to room temperature. White precipitate (KBr) generated from the reaction was separated through filtration. The filtrate was then concentrated on a rotary evaporator to about one-eighth of the original volume and poured into 300 mL H_2O . The precipitate was collected by filtration, washed with water (100 mL), and then recrystallized twice from ethanol. The obtained white solid product was then dried at 40°C in a

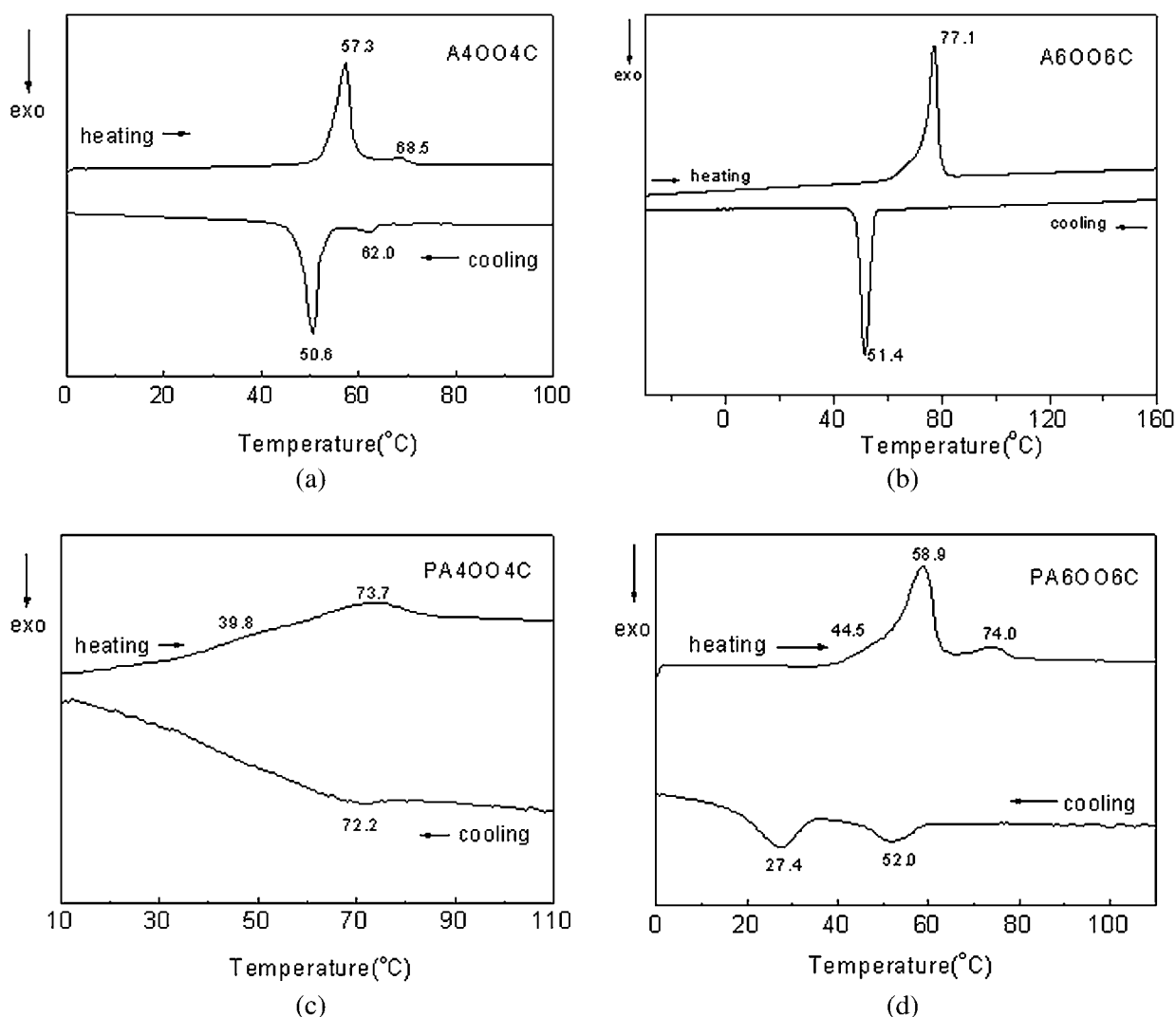


Figure 3 (a) DSC measurement of A4OO4C at heating and cooling rate of 10°C/min; (b) DSC measurement of A6OO6C at heating and cooling rate of 10°C/min; (c) DSC measurement of PA4OO4C at heating and cooling rate of 10°C/min; (d) DSC measurement of PA6OO6C at heating and cooling rate of 10°C/min.

vacuum oven for 24 h. Yield 7.2 g (69.5%), mp 70.6°C, $^1\text{H NMR}$ (CDCl_3), δ : 1.90–1.96 (m, 8H, $\text{COO}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2\text{O}$), 4.04 (t, 4H, $-\text{CH}_2-\text{O}$), 4.24 (t, 4H, $\text{COO}-\text{CH}_2-$), 5.81 (d, 1H, $\text{CH}_2=\text{CH}-$, cis), 6.09 (q, 1H, $\text{CH}_2=\text{CH}-$), 6.39 (d, 1H, $\text{CH}_2=\text{CH}-\text{C}$, trans), 6.44 (d, 1H, $\text{Ph}-\text{CH}=\text{CH}-$), 6.92–6.97 (m, 4H, aromatic protons), 7.37–7.53 (m, 9H, aromatic protons), 7.66 (d, 1H, $\text{Ph}-\text{CH}=\text{CH}-$). IR (KBr, cm^{-1}): 2944, 2872, 1718, 1637, 1605, 1499, 1274, 1248, 1044, 982, 824, 769, 712.

4-(6-Acryl hexyloxy)-4'-(6-cinnamyl hexyloxy) biphenyl (A6OO6C)

The preparation of A6OO6C was similar with A4OO4C. Yield 65%, $^1\text{H NMR}$ (CDCl_3), δ : 1.46–1.86 (m, 16H, $\text{COO}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-\text{O}$), 3.97–4.03 (m, 4H, $-\text{CH}_2-\text{O}$), 4.17–4.25 (m, 4H, $\text{COO}-\text{CH}_2-$), 5.80 (d, 1H, $\text{CH}_2=\text{CH}-$, cis), 6.06 (q, 1H, $\text{CH}_2=\text{CH}-$), 6.38 (d, 1H, $\text{CH}_2=\text{CH}-\text{C}$, trans), 6.42 (d, 1H, $\text{Ph}-\text{CH}=\text{CH}-$), 6.92–6.97 (m, 4H, aromatic protons), 7.37–7.53 (m, 9H, aromatic protons), 7.67 (d, 1H, $\text{Ph}-\text{CH}=\text{CH}-$). IR (KBr, cm^{-1}): 2940, 2863, 1709, 1636, 1610, 1502, 1275, 1249, 1067, 1034, 990, 824, 770, 712.

Polymerization

The polymers were synthesized by a free radical solution polymerization in dried DMF at 65°C for 24 h. The concentrations of monomer and 2,2'-azoisobutyronitrile (AIBN) were 1 g/mL and 1 mg/mL. After the reaction, the polymer was obtained by pouring into excessive methanol. The polymer was further purified by reprecipitations from CH_2Cl_2 solution into methanol. The polymer was then dried *in vacuo* at 60°C for 24 h. Yield: 73%.

RESULTS AND DISCUSSION

Monomer synthesis

The synthetic route for the acrylate-based monomers (A4OO4C and A6OO6C) containing both mesogenic biphenyl group and photoreactive cinnamoyl function was shown in Scheme 1. The monomers were prepared in steps in reasonable yields and their structures were confirmed with $^1\text{H NMR}$ [Fig. 1(a,b)] and FTIR [Fig. 2(a,b)] techniques.

Polymer synthesis

A4OO4C and A6OO6C were polymerized by free radical polymerization in dried DMF at 65°C for 24 h using AIBN as the initiator (Scheme 1). The polymers were obtained by precipitating the reaction mixture into methanol and further purified by reprecipitations from

their dichloromethane solutions into methanol. The polymers are completely soluble in organic solvents such as chloroform and DMF, indicating that no cross-linking occurs during polymerization. The molecular weights and polydispersity indices of the obtained polymers were determined by GPC using polystyrene as a reference. The results are listed in Table I.

Thermal properties

Differential scanning calorimetry and thermal POM were utilized to investigate the thermal properties

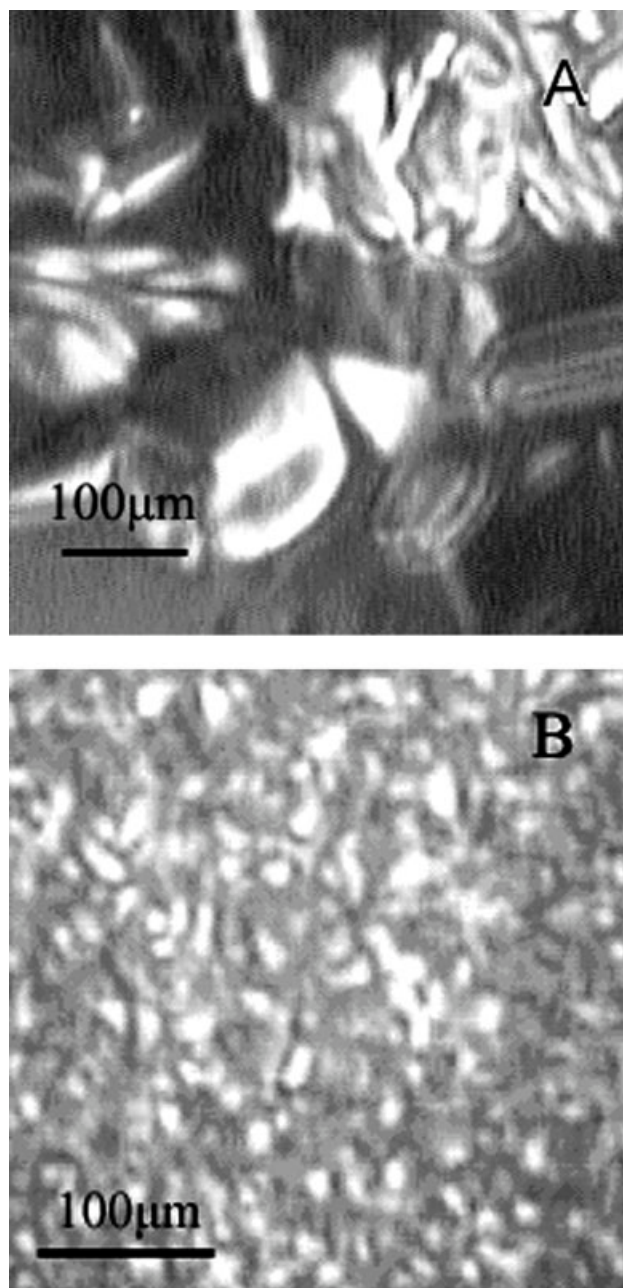


Figure 4 (A) Representative optical polarization micrographics of A4OO4C at 56.1°C; (B) Representative optical polarization micrographics of PA6OO6C at 55°C.

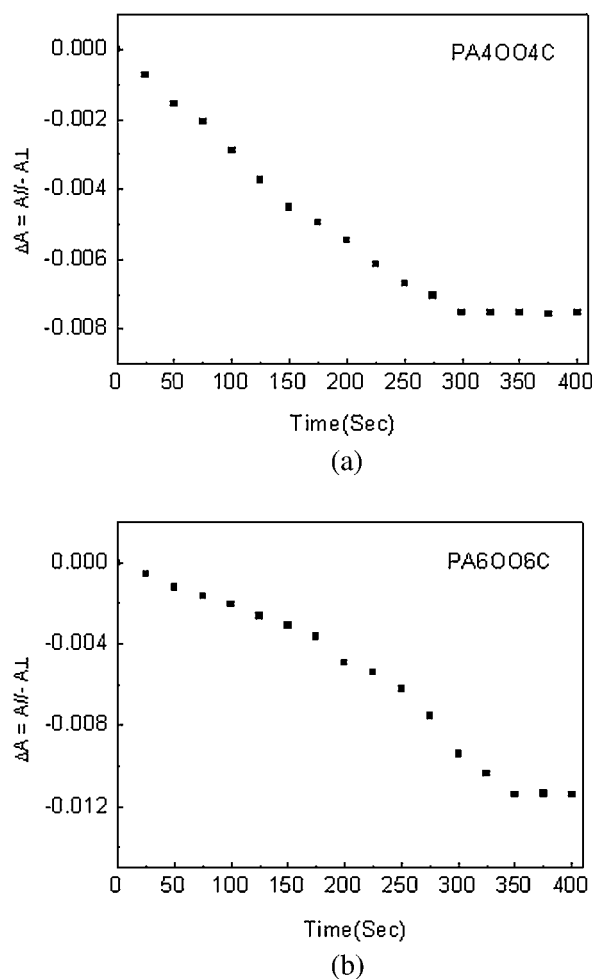


Figure 5 (a) Difference of the absorbance (ΔA) dependence of exposure time of PA4004C; (b) Difference of the absorbance (ΔA) dependence of exposure time of PA6006C.

and mesophase morphologies of the obtained monomers and polymers. The second heating and cooling DSC curves of the monomers and polymers are utilized. It could be seen from Figure 3(a,b) that two exothermal peaks around 62 and 50.6°C were found on the DSC cooling curve of A4004C while A6006C showed only one exothermal peak around 51.4°C. The mesophase structures of the monomers were investigated with an optical polarization micrograph. A fan-shaped texture was observed for A4004C between 62 and 50.6°C in the cooling process at 2°C/min [Fig. 4(A)], indicating the existence of a smectic liquid crystalline phase. In contrast with A4004C, A6006C only shows a phase transition from a crystalline phase to an isotropic phase and no liquid-crystalline texture was observed.

The DSC traces of the corresponding polymers are shown in Figure 3(c,d). The results showed that PA4004C showed only one endothermic peak around 72.2°C in the cooling process at 2°C/min [Fig. 3(c)], while two exothermal peaks were observed for

PA6006C around 52 and 27.4°C, respectively, [Fig. 3(d)]. A schlieren texture was observed at 55°C for PO6H6C upon cooling from the isotropic melt [Fig. 4(B)], which is the characteristic of a typical nematic texture. But no LC texture was found in PA4004C.

Polarized visible light absorption spectroscopy under the irradiation of a linearly polarized light

The polarized visible spectra of the polymer films ($\lambda = 632.8$ nm) were recorded for every 25 s during the

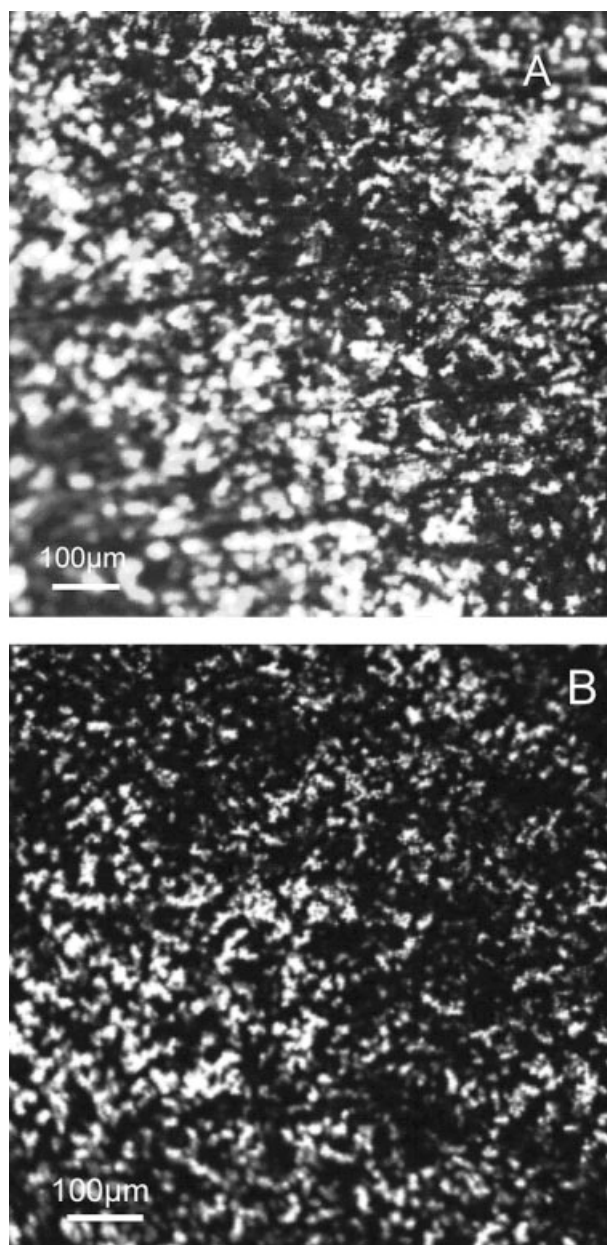


Figure 6 (A) Polarized optical micrographics of E5 cast on the top of PA6006C film initiated by linearly polarized UV-irradiation; (B) Polarized optical micrographics of E5 cast on the top of PA6006C film initiated by unpolarized UV-irradiation.

irradiation of a linearly polarized Ne laser ($\lambda = 351 \text{ nm}$, $I = 38 \text{ mW/cm}^2$). The optical anisotropy and the dichroism of the thin films could be evaluated in terms of the absorbance difference ($\Delta A = A_{\parallel} - A_{\perp}$), where A_{\parallel} denotes the parallel absorption, and A_{\perp} perpendicular absorption with respect to the electric field of the incident linearly polarized UV (LP-UV) pump light. Figure 5(A, B) showed the dependence of the absorbance difference (ΔA) for PA4OO4C and P6OO6C, respectively, on the irradiation time. It could

be seen that ΔA decreased in the initial irradiation period and then leveled off after 300 and 350 s for PA4OO4C and P6OO6C, respectively. The ΔA decrease under the LP-UV irradiation was due to the anisotropic [2 + 2] cycloadditions of the cinnamoyl groups, which induced the alignment of more and more biphenyl groups in the direction paralleling polarization direction of LP-UV light. Furthermore, it was found that the maximum of ΔA for P6OO6C was larger than that of PA4OO4C. This is understandable because the flexible spacer in the side chain of P6OO6C is longer than that of PA4OO4C, resulting in less restricted movement of liquid crystalline groups in PA6OO6C.

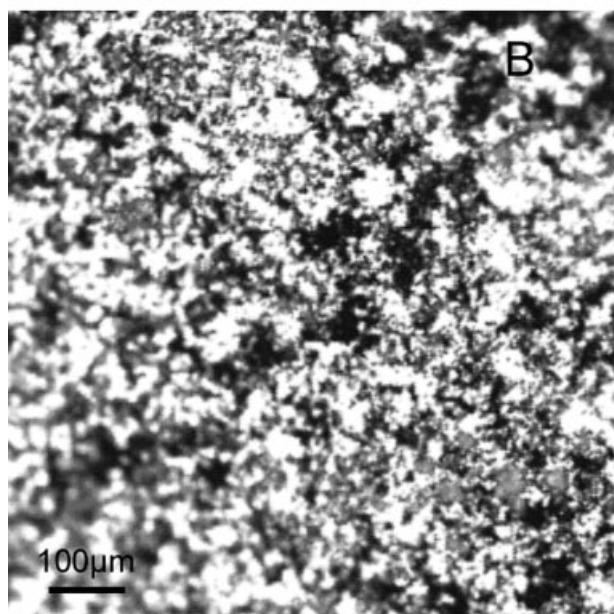
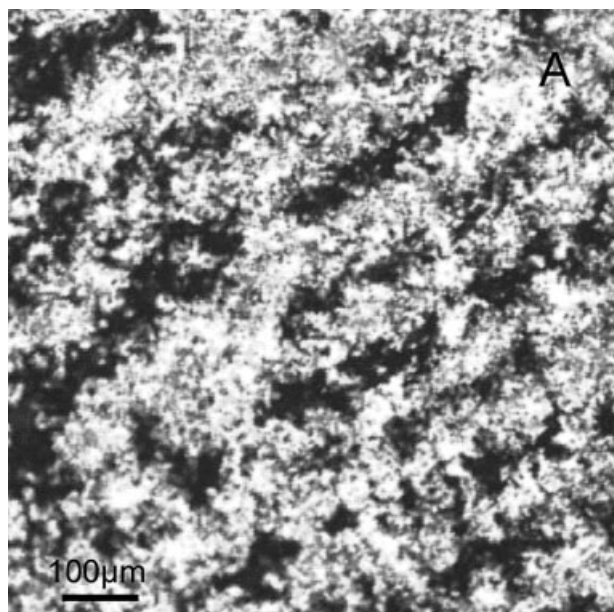


Figure 7 (A) Polarized optical micrographics of E5 cast on the top of PA4OO4C film initiated by linearly polarized UV-irradiation; (B) Polarized optical micrographics of E5 cast on the top of PA4OO4C film initiated by unpolarized UV-irradiation.

Alignment experiment of polymers and nematic crystal

The polymers were dissolved in DMF (0.5%) and cast onto quartz plate followed by drying in vacuum at 40°C for 6 h. Then a nematic mixture E5 (the mixture of 3CB and 5CT) was dissolved in DMF and cast on the top of the polymer films.

By POM observation, we found that E5 aligned regularly on the polymer films initiated by linearly polarized UV-irradiation [Figs. 6(A) and 7(A)]. Comparatively, the alignment of E5 was not observed on the polymer films initiated by unpolarized UV-irradiation [Figs. 6(B) and 7(B)]. These showed that the polymer film could be aligned regularly initiated by linearly polarized UV-irradiation.

CONCLUSIONS

A series of acrylate monomers containing both mesogenic biphenyl group and photoreactive cinnamoyl group as well as different length of flexible spacers (i.e., n -[4'-(n -cinnamoyloxyalkoxy)biphenyl-4-yloxy]alkyl acrylate, $n = 4$ (A4OO4C) and 6 (A6OO6C)) have been synthesized for the first time. Their corresponding polymers (i.e., PA4OO4C and PA6OO6C) were obtained by free radical polymerization using AIBN as an initiator. A4OO4C showed smectic liquid crystalline phase, and a clear fan texture was observed under optical polarizing microscope. However, no liquid crystalline phase was observed for A6OO6C. In contrast, PA4OO4C showed no liquid crystalline phase while PA6OO6C exhibited a clear nematic schlieren texture during the cooling process. Furthermore, the irradiation of the polymer films by LP-UV light resulted in the simultaneous alignment of the biphenyl groups due to the cycloaddition of the cinnamoyl groups and the longer flexible spacer in the side chain of the polymers could induce more significant alignment. Also the polarized optical micrographics of E5 cast on the top of the polymer film initiated by linearly polarized UV-irradiation or not could also approve hereinbefore standpoint.

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