Synthesis and Characterization of Liquid Crystal Photoresist

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SYNOPSIS

A thermotropic liquid crystal polymer with photosensitive groups (liquid crystal photoresist), copoly(4-methoxyphenyl 4'-(2"-acryloyloxy ethoxy)benzoate (MPAEB)-4-vinylbenzyl cinnamate (VBC)) was prepared, and its thermal behavior was characterized by a differential scanning calorimetry. The copolymer exhibited a liquid crystal mesophase between approximately 70°C and 120°C. In the mesophase, poly(MPAEB-VBC) (85/15) had a higher photo-crosslinking ability than that at room temperature and at 140°C, where the copolymer exhibited the isotropic phase. It was found that the liquid crystal photoresist had a high crosslinking ability owing to alignment of its photosensitive groups. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Photosensitive polymers, which can be insolubilized by a photodimerization between functional groups on the polymer chains under UV irradiation, have been extensively applied as a negative type photoresist. For their industrial uses, the activation of crosslinking ability and increase of resolving power are very important. It was reported that the dimerization was activated by aligning the photosensitive groups; it was called "topochemical factors."[1] Therefore, a resolving power of the photoresist may also increase in the anisotropic field constructed by a polymer liquid crystal. Further, the oriented liquid crystal polymer film without photo-sensitive groups was used as a film-matrix for information thermorecording by means of a laser beam.[2]

The polymeric liquid crystals with photosensitive groups were synthesized by Krigbaum et al.[3] Their polymers were polyesters having cinnamate structure in the polymer main chain and their dimerizations were estimated in a liquid crystal state by Ikeda and Tazuke.[4] The polymeric liquid crystals with cinnamate groups as side chains were synthesized, and their photochemistries in the mesophase were also investigated.[5-7] Their application for a photoresist, however, was not discussed in the re-

ports. The side chain type photoresist has the following advantage: (a) it is easily prepared; (b) it may be copolymerized with various monomers and has wide applications.[8]

In this article, we report the syntheses of thermotropic liquid crystal polymers with photosensitive groups as side chains and the photo-crosslinking of these copolymers in the anisotropic mesophase.

EXPERIMENT

Materials

Solvents were purified by distillation just before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol (MeOH). 4-Methoxyphenyl 4'-(2"-acryloyloxyethoxy)benzoate (MPAEB) was synthesized by Ringsdorf's method.[9] The synthesis of 4-chloromethylstyrene (CMS) was followed by a previous method.[10] Other reagents were obtained commercially and used without further purification.

Copolymerization of MPAEB with CMS

Radical copolymerizations of MPAEB with CMS were carried out in the presence of AIBN at 60°C in dimethylsulfoxide (DMSO). The required amount of MPAEB, CMS, AIBN, and DMSO was charged into a Pyrex ampoule. The ampoule was

Table I Copolymerization of MPAEB with CMS[a]

	Monomers			Copolymers[c]		
	[MPAEB] (M)	[CMS] (M)	Time (h)	Yield (%)	[MPAEB] (mol %)	[CMS] (mol %)
MPAEB-CMS (89/11)	0.49	0.01	24	60.0	89.1	10.9
MPAEB-CMS (85/15)	0.45	0.05	40	83.7	84.9	15.1
MPAEB-CMS (77/23)	0.35	0.15	40	79.5	77.3	22.7
HomoPCMS[b]	0.00	3.00	22	60.0	0.0	100.0

[a] Copolymerized at 60°C in DMSO, [AIBN] = $5 \times 10^{-3}M$.
[b] [AIBN] = $3 \times 10^{-3}M$.
[c] Determined by elemental analysis of chlorine.

then degassed by conventional freezing and thawing techniques and sealed off under vacuum. After polymerization, the contents of the ampoule was poured into a large amount of MeOH. The precipitated polymer was purified twice by reprecipitation from the chloroform/MeOH system. The copolymer composition was determined by elemental analysis of chlorine (Table I).

Introduction of Cinnamate Group

The CMS copolymers were converted to 4-vinyl-benzyl cinnamate (VBC) copolymers by reaction with potassium cinnamate at 100°C for 24 h in DMSO. The prepared VBC copolymers were purified by reprecipitation from benzene/MeOH system. The copolymer composition was determined by elemental analysis of chlorine (Table II). ^{1}H-NMR and IR spectra of the VBC copolymers supported their cinnamate structures. The resulting copolymers were abbreviated poly (MPAEB-VBC) (x/y), in which x and y represented the mol % of MPAEB and VBC in the copolymer, respectively.

Photo-Crosslinking of Polymers

The photo-crosslinking of the copolymer was investigated as follows: a benzene solution of the copolymer was cast on a glass slide, and then the film was dried standing overnight at room temperature. The thin film obtained (thickness ca. 5–10 μm) was irradiated by a 100 W high pressure mercury lamp (Toshiba SHL-100UV-2) from a distance of 10 cm on a hot stage (Pasorina Hot Plate HP-300). After irradiation, the glass slide was placed in benzene for 5 h to develop the crosslinked film. The degree of photo-crosslinking was estimated by the weight of the film remaining on the glass slide after its development.

Instruments

IR spectra were measured on a JASCO IR-700, and ^{1}H-NMR spectra were obtained on a Hitachi R-600 spectrophotometer. DSC analyses were carried out with a Rigaku PTC-10A at a heating rate of 10°C/min under air.

Table II Preparation of Liquid Crystal Photoresist[a]

	Conv. (%)	[MPAEB] (mol %)	[VBC][b] (mol %)	η sp/C[c] (dL/g)	Tg[d] (°C)	Ti[d] (°C)
MPAEB-VBC (89/9)	86.2	89.1	9.4	0.22	63.0	116.0
MPAEB-VBC (85/15)	97.4	84.9	14.7	0.19	73.2	117.0
MPAEB-VBC (77/22)	96.0	77.3	21.8	0.16	77.7	114.0
HomoPVBC	99.3	0.0	99.3	0.47	73.8	—

[a] Prepared at 100°C in DMSO for 24 h; [CMS] = $0.055M$. [Potassium cinnamate] = $0.11M$.
[b] Determined by elemental analysis of chlorine.
[c] Measured at 30°C in $CHCl_3$, C = 0.3 g/dL.
[d] Measured by DSC.

RESULTS AND DISCUSSION

Preparation and Thermal Behavior of Polymeric Liquid Crystals with Photosensitive Groups

MPAEB was used as a mesogenic monomer because the thermal range of liquid crystal state of its polymer (62–114°C) was preferable to the photo-crosslinking reaction.[9] The cinnamate group was chosen as a photosensitive group owing to its linearity and rigidity. For this reason, the cinnamate group was reported to be used as a mesogenic group of polymeric liquid crystal.[5–7] Further, the functional group was introduced to the liquid crystal prepolymer (MPAEB-CMS) by a polymer reaction because a crosslinked insoluble polymer is easily generated in polymerization of a vinyl monomer with a cinnamate group.[11] Then, MPAEB was copolymerized with CMS with a prefunctional chloromethyl group by ordinary radical polymerization, and the resulting copolymers were reacted with potassium cinnamate in DMSO (Scheme 1). These polymer reactions quantitatively proceeded at 100°C for 24 h without crosslinking.

Table II summarizes the thermal transition temperatures of the polymers measured by means of DSC. HomoPMPAEB had two endothermic peaks at 68°C and 114°C (lit: 62–114°C),[9] and in the range between these temperatures the liquid crystal mesophase was observed by thermo-optic observation. Further, poly(MPAEB-VBC) (85/15) showed the glass transition temperature (T_g) and the isotropization temperature (T_i) at 73°C and 117°C, respectively. HomoPVBC, however, showed only one

endothermic peak at 74°C (T_g), and the polymer did not exhibit a liquid crystal mesophase because VBC polymer did not have a long alkyl spacer chain between the polymer main chain and mesogenic group (cinnamate group). By considering their thermal transition behavior, the photo-irradiation to these polymers was carried out at three temperatures, that is, at room temperature where the polymers were in a glassy state, at 85°C where the polymers showed the liquid crystal mesophase, and at 140°C where the polymers exhibited the isotropic phase.

Photo-Crosslinking

The yield of photo-crosslinking of homoPVBC (□) and poly(MPAEB-VBC) (85/15) (○) at each temperature is shown in Figure 1. The reactivity of homoPVBC was not affected by the irradiation temperature, although the copolymer had a higher reactivity at 85°C than that at room temperature and at 140°C. Further, they did not crosslink at each temperature in the absence of UV irradiation.

It was reported that homoPMPAEB exhibited a nematic mesophase between T_g and T_i.[7] Thus it is assumed that, in the nematic mesophase, the photo-crosslinking proceeds easily, owing to the alignment of the photosensitive side chain groups. The assumption that the high reactivity at 85°C was not owing to the increase of the reactivity at high temperature was proved by the results of homoPVBC at each temperature, the results of poly(MPAEB-VBC)(85/15) at 140°C, and the results without UV

$$\text{MPAEB-CMS}(x/y) \xrightarrow{\text{PhCH=CHCO}_2\text{K}} \text{MPAEB-VBC}(x/y)$$
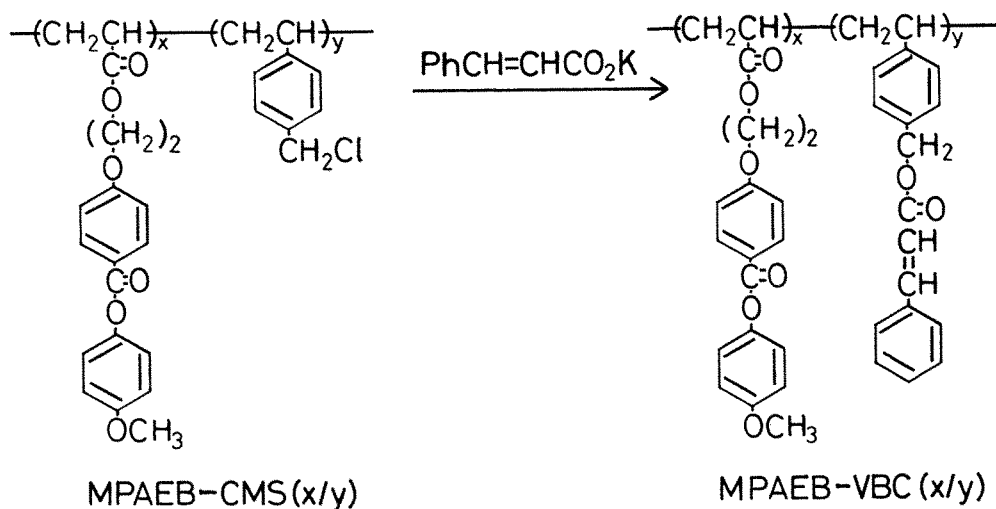
Scheme 1

irradiation. The irradiation temperature would scarcely influence the crosslinking. Because the copolymer underwent isotropization and the functional side chain groups could no longer be aligning at 140°C, the yield of the insoluble copolymer was lower than that at 85°C.

Further, the copolymer that was quenched to room temperature from 140°C (●), interestingly, had the highest reactivity at room temperature, but the quenched homoPVBC (■) had similar reactivity to the original homoPVBC. It was observed that the quenched copolymer had an anisotropic phase even in the solid state at room temperature. Because the cinnamate group of this copolymer was fixed in the aligning state even at room temperature, the quenched copolymer had a higher reactivity than that of the original copolymer, even at room temperature.

Next, a dependence of the copolymer composition on the photo-crosslinking ability was investigated at each temperature. Figure 2 shows the yield of the insoluble copolymer at room temperature (○) and at 85°C (●), and the yield of the quenched copolymers at room temperature (□) after UV irradiation for 20 min. Although homoPVBC exhibited similar conversion at each temperature, the difference of the conversions increased with the increase of a content of the mesogen units in the copolymer. Then, poly(MPAEB-VBC) (85/15) had the largest difference, although poly(MPAEB-VBC) (89/9)
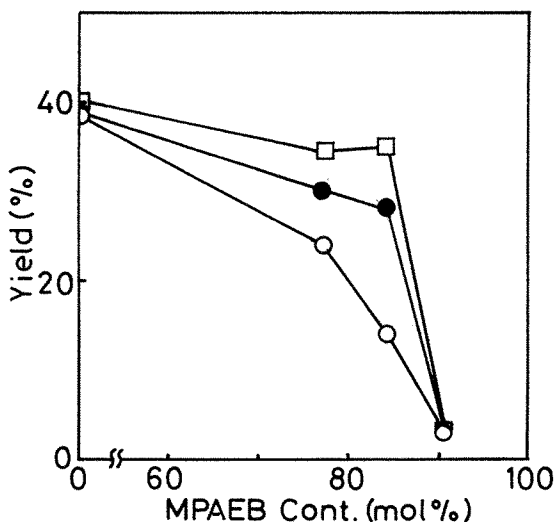

Figure 2 Dependence of copolymer composition of poly(MPAEB-VBC) on the photo-crosslinking ability. Photo-irradiated to original copolymer at r.t. (○) and 85°C (●), and to quenched copolymer at r.t. (□) for 20 min.

almost lost its crosslinking ability under each condition. Because the anisotropic mesophase was stabilized by the existence of many mesogenic groups in the copolymer, poly(MPAEB-VBC) (85/15) had much difference of the conversion between at 85°C and at room temperature. The copolymer, however, no longer acted as a photoresist; when the copolymer had too much of mesogenic groups, that is, it had only a small photo-sensitive group, poly(MPAEB-VBC) (89/9). It was found that the copolymer needed a sufficient anisotropic mesophase to align the photosensitive group and some crosslinking point to insolubilize the polymer in order to exhibit the specificity of the liquid crystal photoresist.

In conclusion, poly(MPAEB-VBC) had a high photo-crosslinking ability in the anisotropic liquid crystal state. The copolymer composition largely affected their crosslinking ability. It would be possible to increase the resolving power by controlling the anisotropy of aligned mesophase magnetically and/or electrically.

Figure 1 Dependence of temperature on the photo-crosslinking ability. Photo-irradiation were carried out for 20 min to poly(MPAEB-VBC)(85/15) (○), quenched poly(MPAEB-VBC) (85/15) (●), homoPVBC (□), quenched homoPVBC (■).
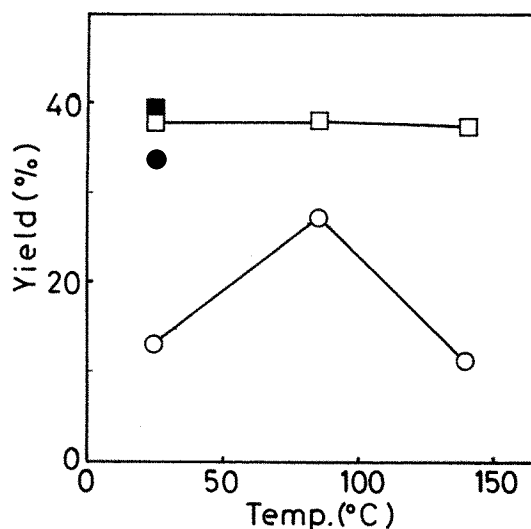
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