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Heon Seung Chae [a] & Yun Heum Park [a b]

[a] Department of Organic Materials Engineering, Sungkyunkwan University, Suwon, Korea

[b] Hyperstructured Organic Materials Research Center, Seoul, Korea

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Synthesis and Properties of Novel Photosensitive Copolymers Having Photoreactive Pendant Group

Heon Seung Chae
Department of Organic Materials Engineering, Sungkyunkwan University, Suwon, Korea

Yun Heum Park
Department of Organic Materials Engineering, Sungkyunkwan University, Suwon, Korea; Hyperstructured Organic Materials Research Center, Seoul, Korea

The novel photopolymers having photoreactive pendant group were designed and synthesized through the reaction between precursor, poly(methacrylic acid-co-2-hydroxyethyl methacrylate-co-styrene)(poly(MAA-HEMA-STY)) and photoreactive compounds such as methacryloyl chloride (MAC), cinnamoyl chloride (CC), methacryloyl isocyante (MAI) and 3-isopropenyl-α, α-dimethylbenzyl isocyanate (TMI), respectively. The prepared poly(MAA-HEMA-STY) and novel photopolymers were characterized by ^{1}H-NMR and FT-IR spectroscopy.

The photosensitivity of photopolymers was estimated with the UV exposing time by FT-IR spectra change at 1630 cm^{-1}. The photosensitivity of photoresists was determined by calculating the UV energy at the pattern-remaining step after developing the thin film using gray-scale mask. In connection with the photosensitivity the surface hardness and compression properties of photopolymer films were determined by nano indenter. All prepared photopolymers revealed higher surface hardness than poly(MAA-HEMA-STY). Photopolymers with methacryloyl functional side group showed better photosensitivity than photopolymers with vinyl aromatic and cinnamoyl group. Especially photopolymer prepared from poly-(MAA-HEMA-STY) and MAI showed good potential for the application of negative-working photoresist.

Keywords: film hardness; nano indenter; photosensitivity; photopolymers; photoresist; photoreactive pendant group

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Address correspondence to Yun Heum Park, Department of Organic Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: yhpark@skku.edu

1. INTRODUCTION

Since the introduction of polyvinylcinnamate [1], many photopolymers have been developed in the fields of photolithography, printing technology and biology [2–6]. The photosensitivity studies have been mainly focused on the acrylate photopolymers with cinnamoyl or chalcone functional pendant groups [7–10]. These photopolymers are widely known that they have high photosensitivity, good solubility and ability to form films. Other polymers such as epoxy polymer with acrylic pendant [11] and acryloylmorpholine polymer with acryloyl pendant group [12] have been reported as negative photoresist. In recent photolithography, it becomes to be increasingly important to strengthen the photosensitivity of the photoresist because it is essential to increase the productivity by reducing the UV exposing time. Especially, the photoresists used in LCD panel have been required for improvement of the quality performance, photosensitivity and mechanical strength, *et al*. [13–15]. In this study, the structure effect of side pendant group on the photosensitivity of the novel photopolymers was investigated. The surface hardness and compression recovery properties of photopolymer thin films were also investigated.

2. EXPERIMENTAL

Chemicals

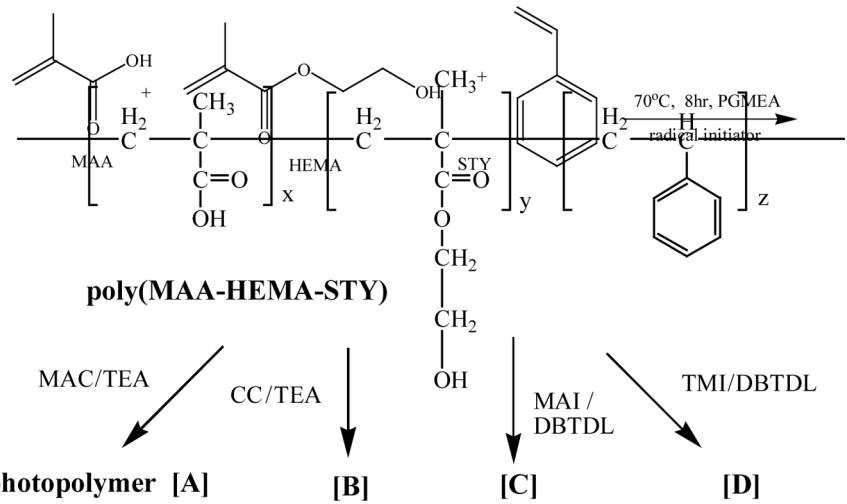
The chemicals used for the preparation of poly(MAA-HEMA-STY) were ACS grade (Aldrich). Methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA) and styrene (STY) were used as comonomers, 2,2′-azobis(2,4-dimethyl-valeronitrile) (ABDV) (WAKO) as radical initiators and propylene glycol monomethyl ether acetate (PGMEA) (Aldrich) as solvent. The other reactants such as methacryloyl chloride (MAC), cinnamoyl chloride (CC), methacryloyl isocyante (MAI), 3-isopropenyl-α, α-dimethyl benzyl isocyanate (TMI) and catalysts, dibutyltindilaurate (DBTDL) and triethylamine (TEA) were purchased from Aldrich and used without further purification. 1,2-octanedione-1[(4-phenylthio)phenyl]-2-o-benzoyl-oxime (ODPB) (Ciba-Geigy) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (BDMB) (Ciba-Geigy) were used as photoinitiators and dipentaerythritol hexaacrylate (DPHA) (Aldrich) was used as photo-curable monomer. 0.04%(w/w) potassium hydroxide aqueous solution was used as developer and distilled water for rinsing.

Synthesis of Poly(MAA-HEMA-STY) and Photopolymers

Poly(MAA-HEMA-STY) was synthesized by polymerization of MAA, HEMA and STY (15/30/55 w/w composition in total monomer content) with ABDV for 8 h at 70°C under N_2 atmosphere in PGMEA. Photoreactive copolymers were prepared by the reaction of synthesized poly(MAA-HEMA-STY) and MAC, CC, MAI and TMI, respectively (Scheme 1). Esterification reactions for the preparation of photopolymer [A] and [B] were carried out at 70°C for 4 hr with catalyst, TEA followed by further purification process such as filtration of the residual salt, neutralization (pH 4), and drying with magnesium sulfate. Urethane reactions for photopolymer [C] and [D] were adopted at 80°C for 5 hr with catalyst, DBTDL.

Characterization

All prepared copolymers were reprecipitated in methanol/hexane solutions and dried in vacuum. The structures of synthesized copolymers were analyzed by FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopy. FT-IR spectra were obtained from KBr pellets.



SCHEME 1 The synthetic route for poly(MAA-HEMA-STY) and photopolymers [A] to [D].

Measurement of the Photosensitivity

In order to prepare films of photopolymer and photoresist, the solutions for spin coating were prepared in advance by mixing the individual copolymers, photoinitiators (ODPB and BDMB) and photocurable monomer (DPHA, for photoresist only) followed by filtration with a 0.45 μm membrane. The films were prepared by spin coating on KBr pellet and pre-baking for 2 min at 100°C on hot plate. The photosensitivity of photopolymers was estimated with the UV exposing time by variation of FT-IR spectrum at 1630 cm^{-1}. The photosensitivity of photoresists was estimated by calculating the UV energy at the pattern-remaining step after three processes such as UV exposing through the gray scale mask (STOUFFER^{TM} Graphic Arts T2115) with the UV intensity of 200 mJ/cm^2 and followed by developing with 0.04% KOH aqueous solution for 60 sec and post-baking for 30 minutes at 220°C. The UV exposure was carried out using Thermo Oriel UV EXPOSURE 6285 with proximity type under the condition of UV power, 28 mW/cm^2.

Evaluation of the Surface Hardness and Compression Property

The film thickness was measured with a surface profiler (Tencor Alpha-Step 200). The surface hardness and compression property of the photopolymer films were determined by nano indenter (Shimadzu Co. DUH-W201S-E) under the condition of the force of 3 gf, the loading speed of 0.45 gf/sec and the holding time of 5 sec with triangular type. The compression recovery (%) was calculated using the following equation [16].

$$\text{Compression recovery}(\%) = \frac{D_1 - D_2}{D_1} \times 100$$

where, D_1 is the indented depth at the force of 3 gf, D_2 is the depth indentation after removing force.

3. RESULTS AND DISCUSSION

Structural Analysis of Synthesized Photopolymers

The chemical structure of the designed and synthesized poly(MAA-HEMA-STY) and photoreactive copolymers was confirmed by ^{1}H-NMR and FT-IR spectra. The ^{1}H-NMR peaks of poly(MAA-HEMA-STY) were appeared at 5.05 ppm corresponding to the HEMA methylene ($-CH_2-$) protons, 6.5–7.5 ppm, aromatic STY protons and 11.9 ppm, hydroxyl

proton, −OH. The characteristic signals appeared at 5.5–6.0 corresponding to methacryloyl protons (−CH=CH−) of the photopolymers [A] and [C], 7.0–8.0 ppm, cinnamoyl protons (−CH=CH−Ph) of the photopolymer [B], 5.0–5.5 ppm, terminal vinyl protons (CH_2=C(CH_3)C−) of the photopolymer [D] respectively. As a result of FT-IR analysis, carbonyl (C=O) absorption peak at about 1720 cm^{-1} and characteristic pendant double bond (C=C) absorption peak at 1630 cm^{-1} were observed at each spectra of photopolymers. From the analyses of ^{1}H-NMR and FT-IR spectra it is assumed that the designed photopolymers have been synthesized.

Photosensitivity of Photopolymers and their Photoresists

The photosensitivity of synthesized polymers was investigated by monitoring the change of the absorbance peak at 1630 cm^{-1} corresponding to pendant double bond stretching. Figure 1 shows

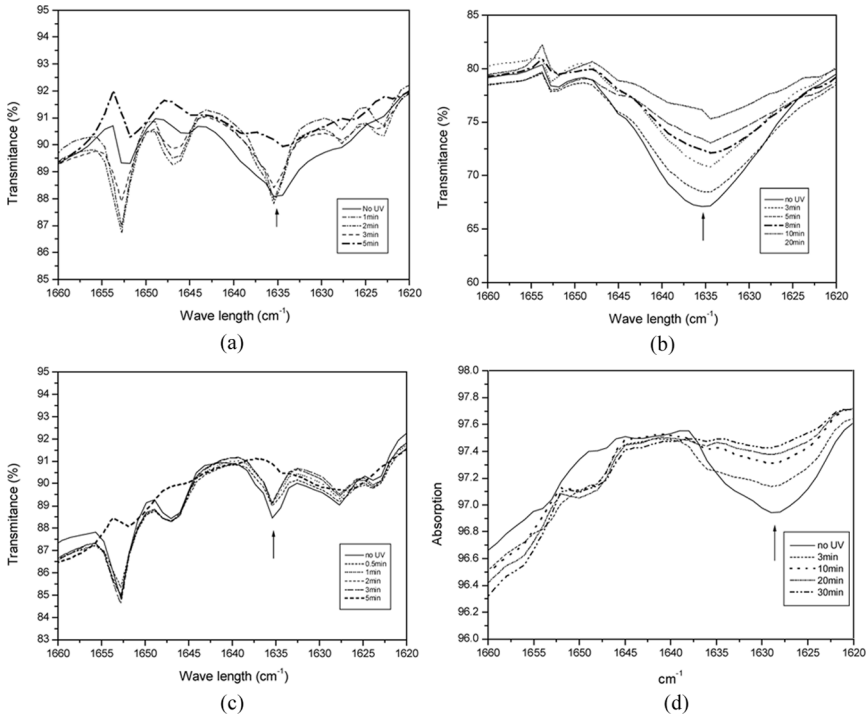


FIGURE 1 IR spectra change of photopolymers with the UV exposure time at 1630 cm^{-1}(C=C stretching), (a) photopolymer [A], (b) photopolymer [B], (c) photopolymer [C] and (d) photopolymer [D].

the FT-IR spectra change of photopolymer thin films with the time intervals of UV irradiation. All photopolymers showed the absorbance at 1630 cm^{-1} and its intensity decreased with the UV exposure time, which indicates that the photocuring is progressed. In case of photopolymer [A] and [C], about 5 min exposure was needed to get the spectrum peak with half intensity. On the other hand at least 8 min and 10 min were needed in the photopolymer [B] and [D], respectively. These results imply that the photocuring speed is dependant on the structure of pendant side chain. Photopolymers having shorter side chain with double bond such as photopolymer [A] and [C] showed the higher photocuring reaction rate.

The photosensitivity of photoresists prepared with corresponding photopolymers and poly(MAA-HEMA-STY) was also investigated by observing the residual film step with 200 mJ/cm^2 through photolithographic procedure and the results are shown in Table 1. All photoresists prepared from photopolymers showed better photosensitivity than that of poly(MAA-HEMA-STY). The photoresist thin films of photopolymer [A] and [C] were observed at the 12th and 14th step of gray-scale mask tablet (Stouffer^{TM}), respectively, while the photoresist film of poly(MAA-HEMA-STY) remained at the 9th step. Those numerical step values such as 12th, 14th and 9th steps correspond to the dosing UV intensity of 0.72 mJ/cm^2, 0.26 mJ/cm^2 and 2.76 mJ/cm^2 respectively. This implies that less UV energy was needed to form the pattern of photopolymers than that of poly(MAA-HEMA-STY). As for the photoresist of photopolymer [B] and [D], similar results were obtained. It is assumed that the photosensitivity order of photopolymers is [C] > [A] > [B] = [D].

TABLE 1 The Photosensitivity Results of Copolymers and their Photoresist Films

	Photosensitivity of thin films	
Copolymer	Method-A[1)]	Method-B[2)]
poly(MAA-HEMA-STY)	–	step 9 (2.76 mJ/cm^2)
Photopolymer [A]	5 min	step 12 (0.72 mJ/cm^2)
Photopolymer [B]	8 min	step 11 (1.08 mJ/cm^2)
Photopolymer [C]	5 min	step 14 (0.26 mJ/cm^2)
Photopolymer [D]	10 min	step 11 (1.08 mJ/cm^2)

[1)]For photopolymer.
[2)]For photoresist.

TABLE 2 The Surface Hardness and Compression Recovery Properties of Poly(MAA-HEMA-STY) and Photopolymers [A] to [D]

Copolymer	Film thickness (μm)	Surface hardness & compression recovery		
		D_1 (μm)	D_2 (μm)	$[(D_1 - D_2)/D_1] \times 100$
poly(MAA-HEMA-STY)	3.645	1.873	1.573	16
Photopolymer [A]	3.411	1.557	1.263	19
Photopolymer [B]	3.209	1.642	1.370	17
Photopolymer [C]	3.512	1.725	1.418	18
Photopolymer [D]	3.540	1.795	1.422	21

Surface Hardness and Compression Properties of Photopolymers

In connection with the photosensitivity, surface hardness and compression properties of photopolymers were also investigated by nano indenter. In order to experimental accuracy, the thickness of films was adjusted to be within the narrow range of 3.20 μm-3.65 μm by spin coating because the results of deformation and recovery in thin film are somewhat variable with the thickness. As shown in Table 2, all photopolymers [A] to [D] showed lower deformation (D_1) and recovery value than those of poly(MAA-HEMA-STY). This result indicates that the film surfaces of synthesized photopolymers are harder than that of poly(MAA-HEMA-STY) and photocrosslinking reaction takes place in the pendant double bonds between each neighboring polymer in the process of UV exposure. Photopolymer [C] and [D] showed relatively lower hardness value than photopolymer [A] and [B] while the photopolymer [D] showed the highest compression recovery.

4. CONCLUSION

For the purpose of investigating the photosensitivity of photopolymers, poly(MAA-HEMA-STY) and photopolymers [A] to [D] were designed, synthesized, and characterized. Photopolymers [A] to [D] showed better photosensitivity in comparison with poly(MAA-HEMA-STY) having no pendant group. The photosensitivity order for photopolymers [A] to [D] was [C] > [A] > [B] = [D]. This result indicates that photopolymers with short pendant photoreactive group showed better photosensitivity compared with photopolymers having relatively long and bulky pendant group. As for the film surface hardness and compression recovery property, photopolymers [A] to [D]

showed high film hardness caused by photo curing ability of photoreactive pendant group. Finally it was concluded that the designed and synthesized photopolymers, especially photopolymer [C] can be applied effectively for the photosensitive negative working photoresist.

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