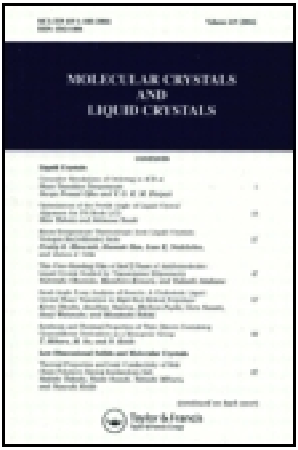

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Characterization of Networked Poly(urethane-(methacrylate-co-styrene)) Prepared with NCO-Terminated Prepolymer for Negative Photoresist

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Characterization of Networked Poly(urethane-(methacrylate-co-styrene)) Prepared with NCO-Terminated Prepolymer for Negative Photoresist

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The synthesis and characterization of the photoresist polymer for using as spacer in LCD panel were investigated. The poly(methacrylate-co-styrene) (PMHS) and NCO-terminated prepolymer were synthesized using radical initiator and catalyst, respectively, and in-situ, the poly(urethane-(methacrylate-co-styrene)) (PMHSU) was prepared with the PMHS and NCO-terminated prepolymer. The PMHS and the PMHSU were characterized by FT-IR, ^{1}H-NMR and thermal properties were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). After the films were prepared by the sequential processes of spin-coating propylene glycol monoethyl ether acetate solution containing PMHSU, multifunctional monomer, and photoinitiator, pre-baking, UV-exposing and post-baking, the compression recovery of the films was investigated by nano-indenter. The negative patterns of the PMHSU were obtained by developing.

Keywords: compression recovery; 2-hydroxyethyl methacrylate; NCO-terminated prepolymer; spacer; photoresist

INTRODUCTION

Photoresist polymers have found applications in microlithography including integrated circuit, printing, and LCD technology, etc. [1–3].

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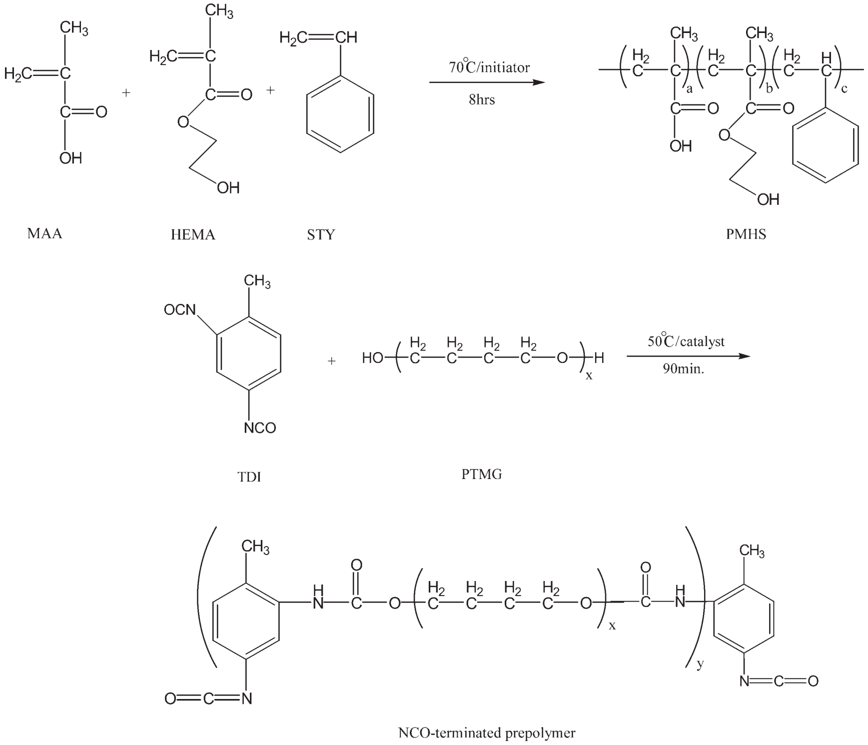
Generally the photoresist polymers with pendant photofunctional groups have been prepared as photoreactive polymer and tested for their photosensitivity [4,7]. The several organic photoresist materials in LCD panel are used such as color filter, black matrix [8], spacer, etc. The spacer among them controls the cell gap between opposite two panels in the process of manufacturing LCD panel, that is, the spacer plays a role to retain the uniform thickness of the liquid crystal layer. The spacer is made of the glass or the plastics. Recently, the researches concerning the plastic spacer have attracted a great deal of attention [9,10] because the movement of the spacer at high temperature and the generation of the bubbles at low temperature are prevented by using the plastic spacer with the thermal expansion coefficient close to that of liquid crystal. The thickness of the liquid crystal in LCD panel is closely related with display properties such as response time, contrast, viewing angle, and color tone etc. and thus the thickness of the liquid crystal should be exactly maintained by using the spacer material with an appropriate compression recovery.

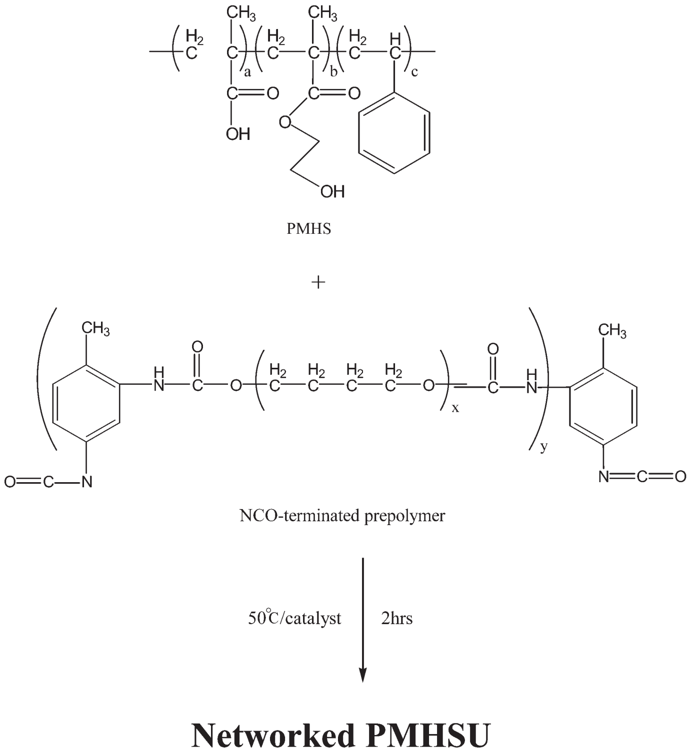
In this paper, the poly(methacrylate-co-styrene) (PMHS) and NCO-terminated prepolymer were synthesized and then networked poly(urethane-(methacrylate-co-styrene)) (PMHSU) was synthesized. Photopolymer solutions were prepared by the dissolution of the PMHSU (or PMHS), multifunctional monomer (MFM) for crosslinking by UV-exposure, solvent, and photoinitiator. The films were prepared by the sequential processes of spin-coating the photopolymer solutions, pre-baking, UV-exposing, and post-baking. The compression recovery, thermal stability, and development were investigated for the prepared films.

EXPERIMENTAL

The synthesis of the PMHS was accomplished via free-radical polymerization of a mixture of methacrylic acid (MAA) (15% w/w), 2-hydroxyethyl methacrylate (HEMA) (30% w/w), and styrene (STY) (55% w/w) (all monomers were supplied by Aldrich). 2,2′-Azobis(2,4-dimethyl-valeronitrile) (Aldrich) was used as initiator (5% w/w on total weight of the monomers) and propylene glycol monomethyl ether acetate (PGMEA, Aldrich) as solvent. The mixture was refluxed for about 8 hrs at 70°C under N_2 atmosphere. The molecular weight (Mn) and the polydispersity measured by gel permeation chromatography with THF were 2230 and 2.09, respectively. In the preparation of the NCO-terminated prepolymer, 2,4-toluene diisocyanate (TDI, Aldrich) and polytetramethyene glycol (PTMG, Aldrich) (Mw = 1015) were used (NCO/OH = 1.5). Dibutyltin dilaurate (Aldrich) was used as catalyst (1% w/w on total weight of the mixture) and PGMEA as solvent. The reaction was carried out for about 90 min at 50°C under N_2 atmosphere. For the in-situ synthesis of networked PMHSU composed of 10 and 20mole% HEMA content in PMHS (PMHSU10 and PMHSU20, respectively), NCO-terminated prepolymers were added into PMHS and the solutions were refluxed for about 2hrs at 50°C under N_2 atmosphere. The synthetic routes for the PMHS, NCO-terminated prepolymer, and PMHSU are shown in Schemes 1 and 2, respectively. The photopolymer solutions were prepared by the dissolution of the PMHS or PMHSU, PGMEA, dipentaerythritol hexa-acrylate (DPHA, Aldrich) as MFM, and 2-benzyl-2-dimethyl-amino-1-(4-morpholinophenyl)- butanone-1 (Ciba, IRCURE 369) as photoinitiator. The solutions were filtered with a 0.45 μm membrane filter before coating. The film thickness of about 3.5 μm was prepared by spin coating. The film thicknesses were measured with a Tencor Alpha-Step 200 surface profiler and an interference type profiler on



SCHEME 1 The synthetic routes for PMHS and NCO-terminated prepolymer.



SCHEME 2 The synthetic routes for PMHSU.

a Canon TM-005S. The films were prebaked at 100°C for 2 min, exposed to UV light (NANOTEK Co. 200 mJ/cm^2), and postbaked at 220°C for 30 min. The compression recovery of the sample films (PMHS, PMHSU10, and PMHSU20) were determined with the force of 5 gf, the loading speed of 0.45 gf/sec, and the hold time of 5 sec by nano-indenter (Shimadzu Co. DUH). Triangular type was used as indenter. The compression recovery (%) was calculated as:

$$\text{Compression recovery}\,(\%) = \frac{(D_r - D_c)}{(D_o - D_c)} \times 100$$

where, D_c is the compressed film thickness, D_o the original thickness of the film, and D_r the film thickness after recovery. The decomposition temperature (T_d) was determined with a Hi-Res TGA 2950 Thermogravimetric Analyzer (TGA) in N_2 atmosphere at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined with a Du Pont Instruments 910 Differential Scanning

Calorimeter (DSC) in N_2 atmosphere at a heating rate of 5°C/min. Potassium hydroxide solutions of 0.76 M was used as the developer, developing time was for 60 s, and deionized water was used for rinsing.

RESULTS AND DISCUSSION

The synthesized terpolymer, PMHS is composed of MAA, HEMA, and STY. The MAA segment offers appropriate solubility in an alkaline developer, the HEMA segment reactive hydroxyl groups with NCO-terminated prepolymer, and the styrene segment morphologic and thermal stability.The NCO-terminated prepolymer was employed to obtain the high compression recovery. The structures of the PMHS, NCO-terminated prepolymer and PMHSU were analyzed using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopy. The FT-IR spectra of the PMHS, NCO-terminated prepolymer and PMHSU are presented in Figure 1. All of these FT-IR spectra were obtained from KBr pellets. The signals of OH and carbonyl bands in Figure 1(a) are presented at 3200–3400 and 1720cm^{-1}, respectively. The spectrum of Figure 1(b) shows the existence of absorption at 2270 and 3200cm^{-1} associated with NCO and OH band, respectively. No NCO absorption in Figure 1(c) was observed at 2270cm^{-1}, which indicated that the reaction was complete.

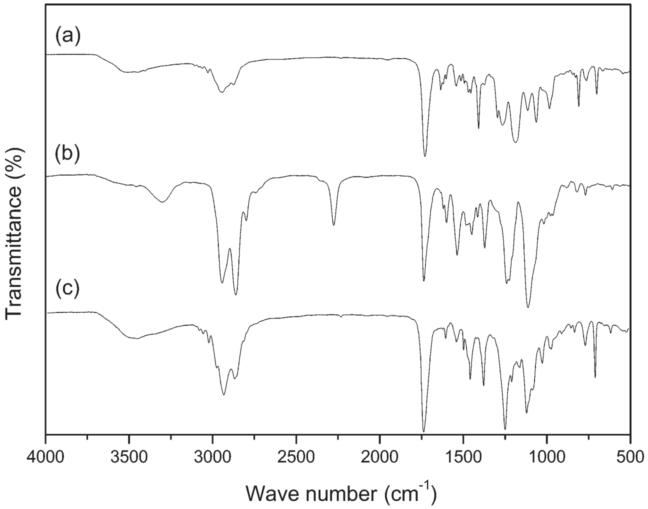


FIGURE 1 FT-IR spectra of (a) PMHS, (b) NCO-terminated prepolymer, and (c) PMHSU.

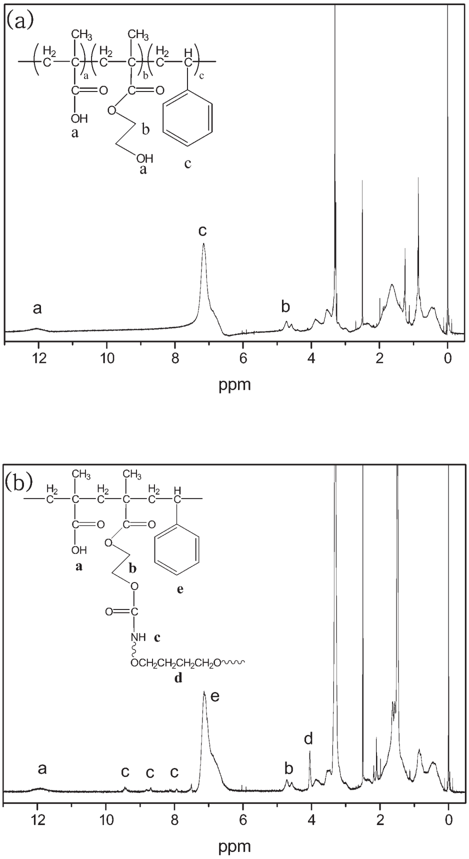


FIGURE 2 ^{1}H-NMR spectra of (a) PMHS and (b) PMHSU.

The ^{1}H-NMR spectra of the PMHS and PMHSU are shown in Figure 2. The signals at $\delta = 6.5$–7.4 and 12.01 ppm in Figure 2(a) present the aromatic and the hydroxyl protons, respectively. The signals at $\delta = 7.94$, 8.69, 9.44 ppm in Figure 2(b) were observed due to the protons of NH groups, which indicates that NCO groups reacted with the OH groups of the HEMA. The hydroxyl protons signal of the HEMA and MAA was observed at 11.9 ppm. The signals of the HEMA methylene(-CH_2) protons appeared at $\delta = 4.71$, 4.58 ppm and the PTMG methylene protons at $\delta = 4.05$ ppm. TGA curves for the PMHS, PMHSU10, and PMHSU20 are shown in Figure 3. The initial decomposition of the PMHSU in Figure 3(b) and (c) starts at about 230°C and a 10% weight loss occurs at about 280°C showing a good

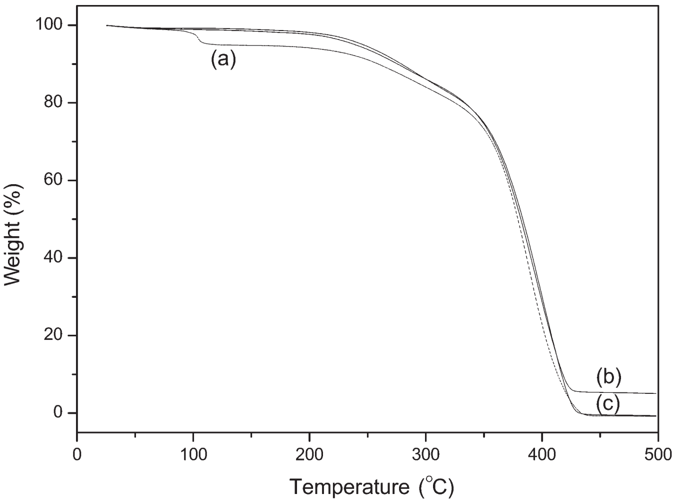


FIGURE 3 TGA curves of PMHS, PMHSU10, and PMHSU20.

thermal stability for a photoresist polymer. The T_d of the PMHSU was higher than that of the PMHS in Figure 3(a). The T_g of the PMHSU determined by DSC was found to be about 22°C. This low T_g value of the PMHSU is due to the flexible NCO-terminated prepolymer. Table 1 shows the percent compression recovery of the PMHS, PMHSU10, and PMHSU20. The PMHSU had higher percentage values of compression recovery than the PMHS. The percent compression recovery which represents the resilience increased as the percentage of the NCO-terminated prepolymer increased. The PMHSU20 had the highest percent compression recovery as high as 50.6%. Figure 4 shows optical microscope image of negative patterns of PMHSU. The 50 μm lines were obtained.

TABLE 1 The Percent Compression Recovery of the PMHS, PMHSU10, and PMHSU20

Polymer	D_1 [μm]	D_2 [μm]	D_1–D_2 [μm]	Compression Recovery (%)
PMHS	1.937	1.241	0.696	35.93
PMHSU10	2.119	1.258	0.861	40.63
PMHSU20	2.781	1.374	1.407	50.59

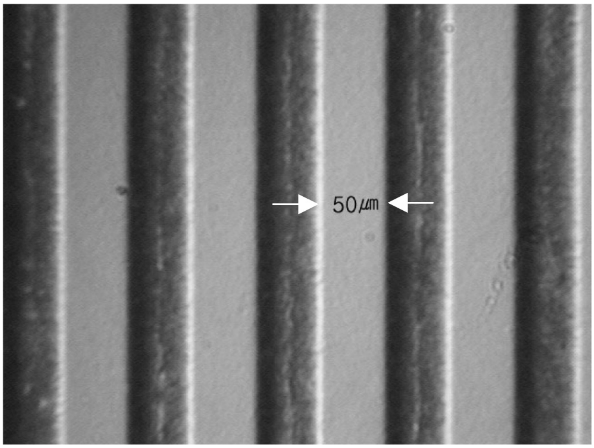


FIGURE 4 Optical microscope image of a negative pattern of PMHSU.

CONCLUSIONS

The PMHS was polymerized by free-radical polymerization using 2,2′-Azobis(2,4-dimethyl-valeronitrile) as initiator and the NCO-terminated prepolymer was synthesized using dibutyltin dilaurate as catalyst. Then, the PMHSU was successfully prepared with the PMHS and the NCO-terminated prepolymer. The synthesized polymers were characterized by the FT-IR and ^{1}H-NMR spectral techniques. The TGA results show that the polymers possess a good thermal stability required for a photoresist polymer. The PMHSU had the higher compression recovery than the PMHS. The negative pattern of the PMHSU was obtained by developing and it might be useful as a spacer in LCD requiring the high compression recovery.

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