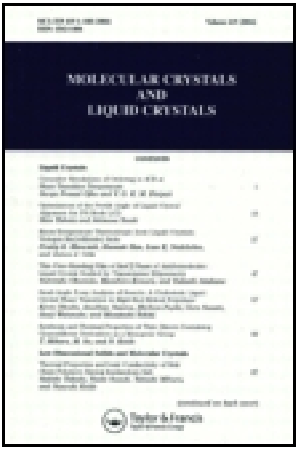

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Novel Photocrosslinking Nonlinear Optical Polymer Systems

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Novel Photocrosslinking Nonlinear Optical Polymer Systems

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We designed and synthesized novel photocrosslinking guest-host nonlinear optical (NLO) polymer systems. In the system, guest NLO molecules bearing two photocrosslinking groups such as cinnamate or acrylate double bonds were homogeneously dispersed in the host photocrosslinking polymer matrix. The NLO molecules are then aligned by using the corona poling technique at an elevated temperature and the system was subsequently crosslinked by irradiating UV light. We expect the photocrosslinking keeps the NLO molecules from relaxing to random orientation. Formation of network structure was confirmed by comparing the absorbances of the NLO moiety in the crosslinked film before and after washing the film with methanol or acetone, exhibiting little leaching out of the NLO moiety from the polymer matrix.

Keywords: corona poling; guest-host system; network structure; nonlinear optical polymer; photocrosslinking

1. INTRODUCTION

Polymers are most promising materials for practical applications in the fields of optics and electrooptics, which can possess various kinds

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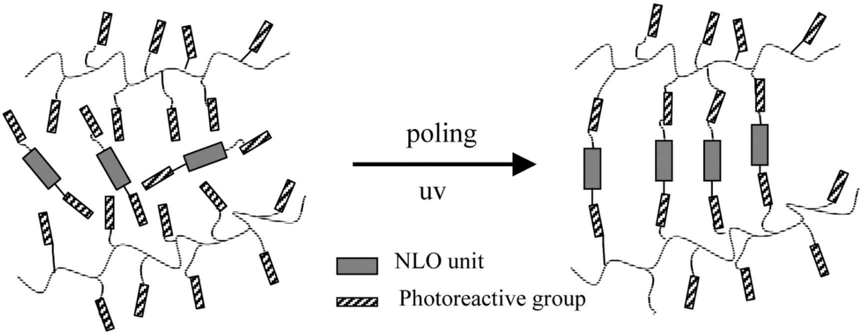

FIGURE 1 Schematic diagram of photocrosslinking NLO guest-host system.

of functionalities as well as can be easily processed to a desired shape. For second order nonlinear optical (NLO) polymer system, stable and high second order NLO response is required. Since the last decades, a number of researches have been focused on improvement of the NLO stability by obtaining high Tg polymers such as NLO polyimides [1,2] or by creating a thermo- or photocrosslinked polymer networks during poling [3,4].

Photocrosslinking for NLO applications has been achieved by either $[2+2]$ cycloaddition of cinnamates [5,6] or radical reaction of (meth)acrylates [7,8]. Photocrosslinkable NLO polymers can be directly patterned to a desired shape by irradiation of UV light through a mask, possibly fabricating channel waveguide and other integrated optical devices. Photocrosslinking NLO system can be processed within a very short time (about 20 minutes) even with weak light intensity.

In this study, design and syntheses of novel photocrosslinking second order NLO polymer systems are reported, where guest NLO molecules are aligned in one direction by applying an electric field and crosslinked to the polymer matrix by UV irradiation as shown in Figure 1. We expect the photocrosslinking keeps the NLO molecules from relaxing to random orientation. Formation of network structure was confirmed by comparing the absorbances of the NLO moiety in the crosslinked film before and after washing the film with methanol or acetone.

2. EXPERIMENTAL

The photocrosslinking host matrix polymers containing cinnamate or methacrylate groups were synthesized through two-step reactions. Figure 2(a) shows the typical synthesis scheme of the photocrosslinking polymer and the structures of the epoxy resins used in the study.

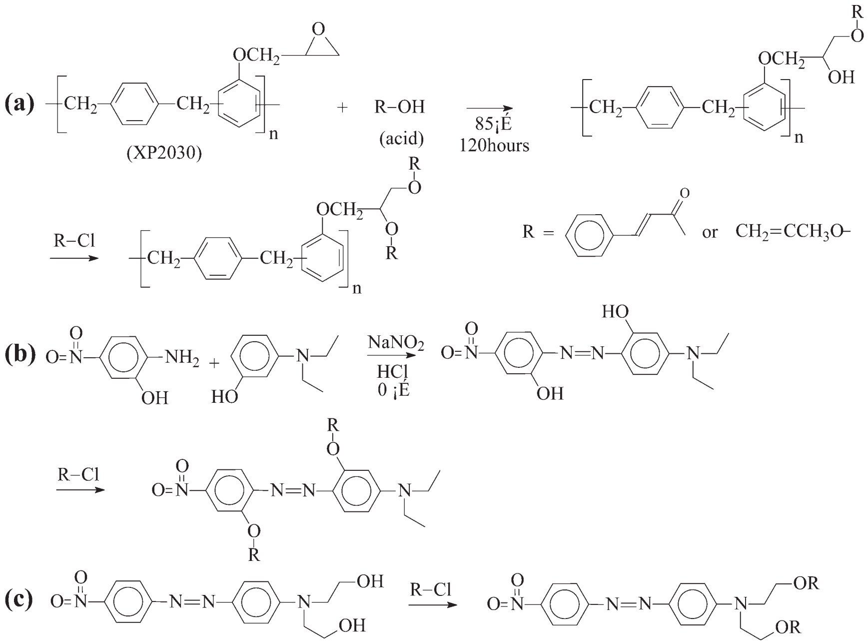

FIGURE 2 Synthetic schemes of (a) photocrosslinking matrix polymer and (b), (c) photocrosslinking NLO chromophores.

In the first step, XP2030/CA (or XP2030/MA) was prepared by reaction between XP2030 and cinnamic acid (or methacrylic acid). The reaction was carried out using tetramethyl ammonium chloride as a catalyst in MEK at 80°C for 120 h. In the second step, cinnamate (or acrylate) double bond was incorporated into XP2030/CA (or XP2030/MA) matrix polymer by the reaction between hydroxyl group of XP2030/CA and cinnamoyl (or methacroyl) chloride, resulting in XP2030/CA/CA (or XP2030/MA/MA). The reaction was carried out using triethylamine as a catalyst in THF at room temperature for 12 h.

Photocrosslinking NLO molecules were synthesized as shown in Figures 2(b) and 2(c). 0.12 mol of 2-amino-5-nitrophenol was dissolved in 75 ml of 0.78 M sulfuric acid aqueous solution and cooled down to 0°C, to which 100 mL of 0.8 M sodium nitrite ice-cold aqueous solution was slowly added. To the above solution, 115 mL of 2 M sodium hydroxide ice-cold solution containing 0.12 mol of 3-diethylaminophenol was added while stirring. The reaction was carried out for 12 h, where the temperature was slowly increased to room temperature. The precipitate, DADNAB was filtered, purified by column chromatography and dried under vacuum, giving rise to a deep purple powder.

Cinnamate (or methacrylate) double bond was incorporated into DADNAB by the reaction between hydroxyl group of DADNAB and cinnamoyl chloride. The reaction was carried out following the same procedure as that for matrix polymer. Disperse Red 19 (DR19) was purchased and also employed as NLO moiety.

The matrix polymer and guest NLO molecules were completely dissolved in THF and the solution was filtered through 0.2 μm PTFE membrane filter and spin-coated on a glass substrate at 1500 rpm for 60 s. The concentration of the NLO molecules was 20 wt% with respect to the polymer. The polymer film was then dried at 70°C for 30 min, leading to an excellent quality of film with a thickness of about 1 μm. NLO molecules were aligned by the corona poling technique at about 10°C below Tg of the corresponding polymers. Photocrosslinking of the polymer film was carried out by exposing the film to 254 nm UV light with the intensity of 9 mW/cm^2 on the surface of the film for about 20 min.

Photocuring behaviors of the acrylate and cinnamate double bonds with UV exposure time were quantitatively studied by using FT-IR and UV-vis spectroscopies, respectively. Photocrosslinking between polymer matrix and NLO molecules was confirmed by comparing the absorbances of the NLO moiety in the crosslinked film before and after washing the film with methanol or acetone.

3. RESULTS AND DISCUSSION

We confirmed the chemical structures of the synthesized photocrosslinking matrix polymers and photocrosslinking NLO molecules by ^{1}H-NMR and FT-IR spectroscopies. In the ^{1}H-NMR spectra of XP2030/CA/CA and XP2030/MA/MA, the peak at 2.7–2.9 ppm corresponding to the epoxide ring proton disappeared and new peaks at 6.48–7.95, 5.6, and 6.1 ppm corresponding to the proton of the double bond appeared. In the FT-IR spectra of XP2030/CA/CA and XP2030/MA/MA, new characteristic absorption peaks were observed at 1720 cm^{-1}(carbonyl group), 1620 cm^{-1}(C=C).

In the ^{1}H-NMR spectra of DADNAB/CA, new peaks at 6.48–7.95 ppm corresponding to the proton of the double bond appeared. In the FT-IR spectra of the DADNAB/CA, new characteristic absorption peaks were observed at 1720 cm^{-1} (carbonyl group), 1518 cm^{-1} and 1330 cm^{-1} (nitro group).

Photocrosslinking behaviors of the cinnamate and methacrylate double bonds were studied by monitoring change of the absorbances at 275 nm of UV-Vis spectrum and at 810 cm^{-1} of FT-IR spectrum, respectively. We confirmed very effective photocuring of the cinnamate

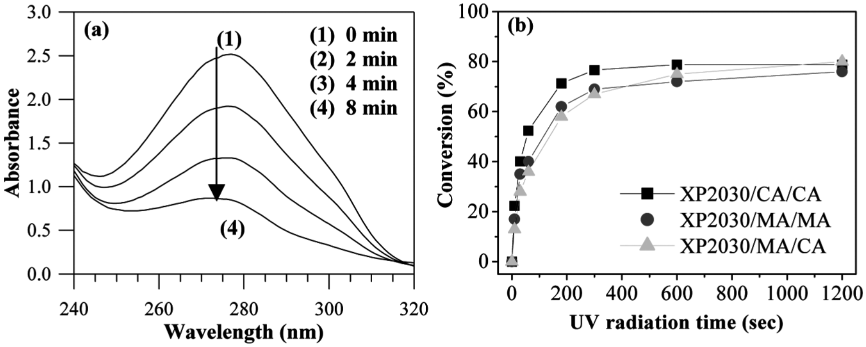

FIGURE 3 (a) UV-visible absorption spectra and (b) photocure conversions of the photocrosslinking polymers with UV exposure time.

and acrylate double bonds in the matrix polymers as shown in Figure 3. The absorption peak at 275 nm corresponding to cinnamate C=C bond decreased with UV irradiation time as shown in Figure 3(a). We also figured out photocrosslinking of the cinnamate and methacrylate double bonds took place extremely rapidly. Figure 3(b) shows the photocure conversion obtained from the change of absorbances of cinnamate and acrylate double bonds normalized with respect to the absorbance of the double bonds before UV irradiation. In all polymers prepared in this study, photocrosslinking occurred rapidly within the initial 300 s, even though a little difference in the reaction rate and the final conversion were observed.

We also confirmed the effective photocrosslinking of the polymer systems from glass transition behavior. Tg of XP2030/CA/CA and XP2030/MA/MA were found to be 90 and 87.5°C, respectively. Even though Tg decreased with the amount NLO molecules, the plasticizing effect of NLO molecule is not so pronounced as that in other common plasticizers. The polymer system irradiated by UV for 20 min did not show any observable glass transition behavior, confirming the formation of network structure with high degree of crosslinking.

During the radiation of UV light, two different types of photoreaction can occur in the NLO molecules. One is the photocrosslinking reaction of photoreactive units and the other is the photoinduced degradation of the NLO chromophore. The absorbance of NLO moiety slightly decreased with irradiation time as shown in Figure 4, possibly because of the photoinduced degradation of the NLO chromophore.

We confirmed the formation of network structure, which was formed by crosslinking between NLO molecules and polymer matrix. Before UV irradiation the NLO molecules could be completely leached

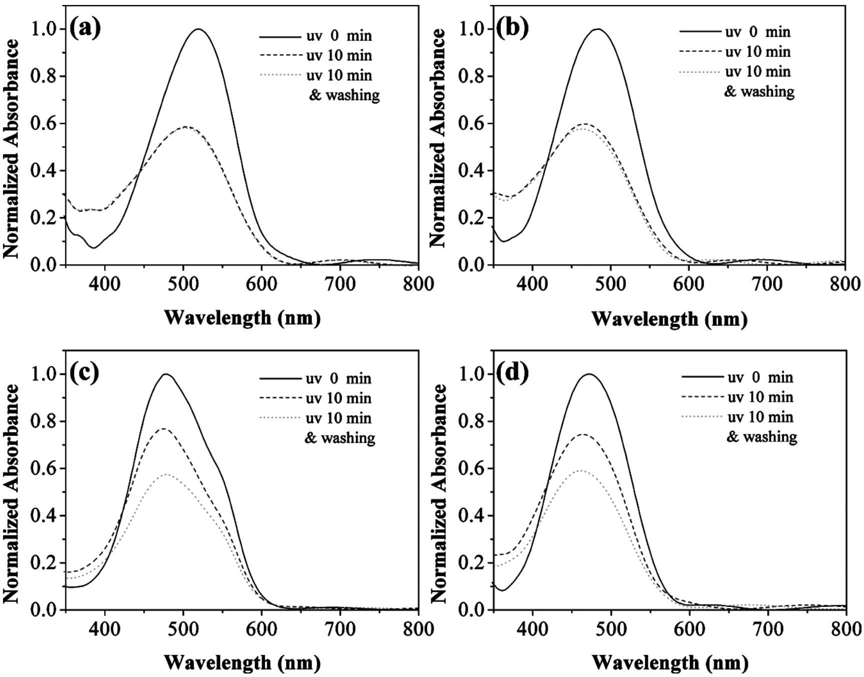

FIGURE 4 UV-vis spectra of the pristine film, the photocrosslinked film and the film photocrosslinked and washed with acetone. (a) XP2030/CA/CA + DADNAB/CA, (b) XP2030/CA/CA + DR19/CA, (c) XP2030/MA/MA + DADNAB/MA and (d) XP2030/MA/MA + DR19/MA.

out from the polymer matrix by dipping the film in acetone or methanol, while after UV irradiation the NLO molecules could not be washed out from the polymer matrix. This implies the NLO molecules are employed as the part of the network structure.

The formation of crosslinked network was also confirmed by UV-vis spectra as shown in Figure 4. The absorbances of NLO molecules changed a little even after washing the photocrosslinked film with acetone or methanol, indicating no leaching out of the NLO molecules from the polymer matrix. As shown in Figure 4, it seemed that cinnamate double bonds produced better network structure than acrylate double bonds. The crosslinked system bearing cinnamate double bonds exhibited no change in the absorbance after washing, while the system bearing acrylate double bonds showed a little decrease in the absorbance after washing. We, therefore, strongly believe the photoinduced crosslinking can keep the NLO molecules from relaxing to random orientation. The

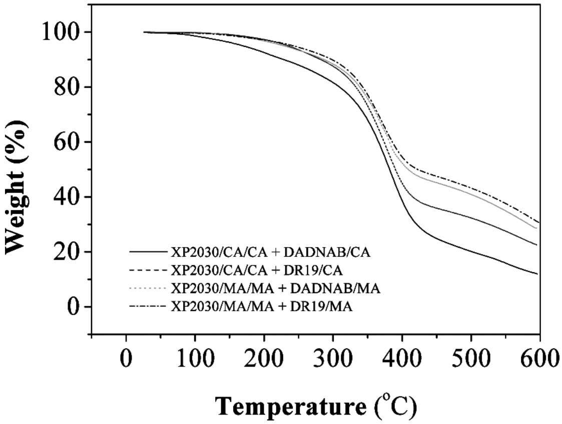

FIGURE 5 TGA curves of the photocrosslinked polymers.

photocrosslinked polymer showed good thermal stability as shown in Figure 5, exhibiting little weight loss up to about 250°C.

4. CONCLUSION

Novel photocrosslinking guest-host nonlinear optical (NLO) polymer systems were designed and synthesized. In the system, guest NLO molecules bearing two photocrosslinking groups were homogeneously dispersed in the host photocrosslinking polymer matrix. The NLO molecules are then aligned by using the corona poling technique at an elevated temperature and the system was subsequently crosslinked by irradiating UV light. We confirmed formation of network structure by comparing the absorbances of the NLO moiety in the crosslinked film before and after washing the film with methanol, exhibiting little leaching out of the NLO moiety from the polymer matrix. Therefore, we believe the photocrosslinking can keep the NLO molecules from relaxing to random orientation.

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