Photocrosslinked Polymer and Interpenetrating Polymer Network for Nonlinear Optics

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ABSTRACT: Two photocrosslinkable NLO polymers of poly(glycidyl methacrylate) substituted with 4-nitro-4′-hydroxyl stilbene (PGMAS) and acryloyl-functionalized epoxy-based polymer (PENAA) carrying 4-nitroaniline moieties were synthesized and characterized. By using the sulfonium salt cationic photoinitiator BDS · $2PF_6$ which can induce cationic or/and radical polymerization, the photocrosslinking of PGMAS and the interpenetrating polymer network (IPN) formed by the photocrosslinking of PGMAS and PENAA simultaneously were reported. The poled and photocrosslinked polymer films and IPN films exhibit relatively stable second-order nonlinear optical activity. The influence of stilbene isomerization in PGMAS films with different crosslink densities on the SHG stability was also investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1081–1087, 1999

Key words: photocrosslinking; interpenetrating polymer network; nonlinear optics; stilbene isomerization; SHG stability

INTRODUCTION

Polymers are most promising materials for practical applications in the fields of optics and electrooptics. They combine the possibility of easy processing with an infinite potential for functionalization. A stable and high second-order nonlinear optical (NLO) response is required for these NLO polymers. Since the last decade, much research has focused on improving the NLO stability by synthesizing high T_g polymers, such as NLO polyimides,[1–3] or by creating a thermo-[4,5] or photocrosslinked polymer networks while poling.

For photocrosslinkable polymers, there is a great advantage because these polymers can be directly patterned by shining UV light through a mask for making channel waveguides and other integrated optical devices. Photocrosslinking for second harmonic generation (SHG) has been achieved via either a [2 + 2] cycloaddition of cinnamates,[6–8] a radical polymerization or [2 + 2] cycloaddition of (meth)acrylate,[9–11] a photoactivated reaction of benzophenone with butenyl side groups,[12,13] or a photocleavage of azides to nitrenes.[14]

In this article, we present a novel photocrosslinkable NLO polymer of poly(glycidyl methacrylate (PGMA) substituted with 4-nitro-4′-hydroxyl stilbene (PGMAS) functionalized from PGMA. The polymer with pendant epoxy groups was designed to enable it to be crosslinkable through a cationic photopolymerization at a lower temperature without excluding oxygen from air. To enhance the NLO stability, a photocrosslinkable interpene-

trating polymer network (IPN) consisting of NLO-active acryloyl-functionalized epoxy-based polymer (PENAA) and PGMAS networks was designed via a simultaneous cationic and radical photocrosslinking process initiated by the photoinitiator BDS · 2PF$_6$ for PGMAS and PENAA, respectively. The UV crosslinking process, the second-order NLO property, and the NLO temporal stability of these two photocrosslinkable systems were investigated.

EXPERIMENTAL

Materials

4-Nitro-4′-hydroxyl stilbene (NHS) was prepared as a reference.[15] Glycidyl methacrylate (Aldrich, Milwaukee, WI) were purified and polymerized by a common free-radical polymerization procedure in our lab. 4-Nitroaniline (Aldrich) and acryloyl chloride (Aldrich) were used without further purification. Bis-[4-(diphenylsulfonium)phenyl]sulfide bishexafluorophosphate (BDS · 2PF$_6$) was purchased from Degussa Co. (Switzerland). Benzyltriphenyl phosphonium chloride (BPC) was prepared as a reference[16]; mp 305–307°C. E$_{44}$ epoxy resin was obtained from a commercial source and used as received. Its epoxy value (0.447) was measured by the HCl/acetone method. All the solvents, CHCl$_3$, THF, and 1,4-dioxane (DOX), were purified before use.

Synthesis of Photocrosslinkable Polymer PGMAS

PGMAS was synthesized according to Scheme 1. A certain amount of PGMA and NHS were dissolved in CH$_3$Cl/THF (v/v = 1/1), and 1 wt % benzyltriphenyl phosphonium chloride (BPC) was added as a catalyst. The mixture was stirred and refluxed for 24 h, and the polymer was isolated by precipitation into methanol and washed with dry ethyl ether and vacuum-dried. The chromophore

content of PGMAS determined by ^{1}H-NMR is 19 mol %, which coincides well with the value calculated from elementary analysis.

Characterization for PGMAS: T_g = 103°C; $\overline{M}_n$ = 20810, $\overline{M}_w$ = 30881; λ_{max} (DOX) = 373 nm. ^{1}H-NMR (CDCl$_3$, ppm): 8.0–8.3 (0.38H, nitrophenyl), 7.3–7.7 (0.76H, aromatic), 6.8–7.2 (0.76H, aromatic and CH=CH), 4.0–4.5 (3.24H, O—CH$_2$—C of PGMA and OH—CH of substituted PGMA), 3.6–4.0 (0.8H, O—CH$_2$—C of PGMA and OH—CH of substituted PGMA), 3.4–4.0 (0.76H, —O—CH$_2$—C of substituted PGMA), 3.0–3.4 (0.81H, CH of the epoxy group), 2.4–2.9 (1.62H, CH$_2$ of the epoxy group), 1.6–2.2 [2H, —CH$_2$—C(CH$_3$)—COO], 0.6–1.4 (3H, CH$_3$). IR(KBr): 3410 cm^{-1} (OH), 1728 cm^{-1} (C=O), 1630 cm^{-1} (CH=CH), 1510, 1342 cm^{-1} (—NO$_2$), 1257 cm^{-1} (Ar—O), 906 cm^{-1} (epoxy group).

ANAL. Calcd for (C$_7$H$_{10}$O$_3$)$_{0.81}$(C$_{21}$H$_{21}$NO$_6$)$_{0.19}$: C, 61.36%; H, 6.14%; N, 1.46%. Found : C, 61.09%; H, 6.31%; N, 1.34%.

Synthesis of Polymer PENA

4-Nitroaniline (2.8 g) and epoxy resin (7.8 g) were heated at 140°C under nitrogen for 4 h and 160°C for 3 h. The deep brown polymer was precipitated and recrystallized from THF to remove excess dye. Yield 94%, T_g = 72°C; λ_{max} (DOX) = 375 nm. IR (KBr): 3381 cm^{-1} (OH); 1509, 1352 cm^{-1} (—NO$_2$).

Synthesis of Photocrosslinkable Polymer PENAA

A solution of acryloyl chloride (3.0 g) in 15 mL of THF was added dropwise to a solution of the polymer PENA (3.0 g) in 15 mL of THF. The solution was stirred for 24 h at room temperature. The reaction mixture was precipitated in 800 mL of methanol, filtered, and washed with methanol. Then, the polymer was vacuum-dried at room temperature for 12 h. Yield 90%; T_g = 83°C; $\overline{M}_n$ = 6700, $\overline{M}_w$ = 20,800; λ_{max} (DOX) = 375 nm. IR(KBr): 1735 cm^{-1} (C=O of methacryloyl ester); 1657 cm^{-1} (C=C); 1514, 1326 cm^{-1} (—NO$_2$).

Instrumentation

^{1}H-NMR spectra were obtained on a JEOL FX 90Q NMR spectrometer, IR spectra were recorded on a Nicolet 205 FTIR spectrophotometer, and ultraviolet-visible spectra were taken on a Shimadzu 240 spectrophotometer. Elementary analysis was performed by Perkin–Elmer 240 elementary analyzer. Number- and weight-average molecular weights of the polymer were determined with a Waters 208LC using THF as the eluent.

Scheme 1

The GPC calibration was based on polystyrene standards. T_g was obtained from a differential scanning calorimeter (DSC) using a Perkin–Elmer DSC-7c at a heating rate of 10°C/min under nitrogen. The thermal degradation was determined by a TA instrument TGA with a heating rate of 10°C/min.

For monitoring the crosslinking process, PGMAS films were cast on sodium chloride plates. The films were irradiated under a high-pressure mercury lamp (400 W) with a filter. The actual concentration of epoxy groups was determined from the intensity of their vibration (906 cm^{-1}) in the IR spectrum. The C=O vibration at 1728 cm^{-1} was used as an internal standard.

Film Preparation

The polymer solutions were obtained by dissolving PGMAS/BDS · 2PF$_6$ (w/w = 1 : 0.05) in DOX for the photocrosslinkable system and PGMAS/ PENAA/BDS · 2PF$_6$ (w/w/w = 1 : 1 : 0.05) in a DOX/DMF mixture (v/v = 4 : 1) for the IPN system. Films were prepared by spin-coating the above polymer solution onto a transparent glass substrate, sodium chloride plates, and quartz plates. The typical thickness was approximately 5 μm. The films were dried at 50°C under a vacuum for 12 h.

NLO Measurements

The corona poling technique was employed to align the NLO chromophores. The temperature was increased to 100°C while the corona field was applied, and the poling was carried out for 20 min. The corona current was held at 2 μA with an electrode potential of 8 kV. The samples were cooled slowly to 30°C and UV-crosslinked for 20 min.

The temporal stability of the samples was studied by the decay of the second-order NLO coefficient (d_{33}) as a function of time at room temperature (25°C). The calculation of the d_{33} value was described in ref. 17.

RESULTS AND DISCUSSION

Synthesis of Photocrosslinkable Polymers

The synthesis of the PGMAS polymer involved the hydroxyl groups of NHS to undergo an epoxide ring-opening reaction with glycidyl groups of PGMA (Scheme 1). PGMAS with different con-

tents of stilbene can be synthesized under various molar ratios of PGMAS/NHS and temperatures. In this study, PGMAS containing 19 mol % stilbene was selected. Its pendant epoxy groups can undergo the ring-opening reaction under UV irradiation.

The synthesis of the acryloyl-functionalized polymer PENAA involved two steps as described by Tripathy and co-workers (Scheme 2).[18] In the first step, the nucleophilic 4-nitroaniline initiated the ring-opening polymerization of the epoxy resin. The second step involved the attachment of the photocrosslinkable acryloyl groups through esterification of the hydroxyl groups of the epoxy polymer PENA. PENAA and PGMAS were chosen as the components of IPN because they have good compatibility and their absorption spectra match each other.

Photocrosslinking Process

The photocleavage of the photoinitiator BDS · 2PF$_6$, which is the same as typical sulfonium salt photoinitiators,[19] thus produces free-radical and H$^+$ as initiating species. The theoretic and practical research on the photopolymerization of the epoxy resin using sulfonium salt are rather developed. Actually, the sulfonium salt can photoinitiate the polymerization of acrylates and epoxy resin simultaneously.[20]

The photocrosslinking of PGMAS was observed by monitoring the IR absorption disappearance of its pendant epoxy groups at 906 cm^{-1}. At the same time, the hydroxyl absorption resulting from the ring opening of the epoxy groups at 3437 cm^{-1} actually increased (Fig. 1). After the UV irradiation, the CH=CH absorption of the stilbene chromophores at 1630 cm^{-1} without an observable change implied that the stilbene chromophores have no cyclodimerization or cyclization during the crosslinking process.[21] The

Scheme 2

Figure 1 FTIR spectra of PGMAS films before (a) and after (b) 5 min and (c) 20 min of UV crosslinking with filtered UV light.

conversions grew almost linearly with time (Fig. 2). That is exactly the advantage of cationic photopolymerization which is free from the inhibition of oxygen. The UV-cured PGMAS films are insoluble in common organic solvents such as THF and

Figure 2 Conversion of epoxy groups of PGMAS under various UV irradiation times.

DMSO, while the uncured samples can be dissolved within seconds.

For the photo-IPN system (PGMAS/PENAA), the IR spectra showed that the stretching vibration of epoxy groups at 906 cm^{-1} disappeared completely after 20-min UV irradiation (Fig. 3), indicating that the PGMAS polymer network was achieved by the photocrosslinking of its epoxy pendant groups. Meanwhile, the C=C stretching of the acrylate double bond at 1657 cm^{-1} also disappeared, and the C=O stretching shifted from 1721 to 1728 cm^{-1}, which is consistent with a loss in conjugation due to the crosslinking reaction of the acrylate double bond. The results from the IR spectra indicate that the photocrosslinking of PGMAS based on the cationic reaction of its epoxy pendant groups and PENAA based on the radical reaction of its acrylate double bonds occurred simultaneously and separately and that a photo-IPN system was formed.

DSC experiments indicated that both the photocrosslinking system of PGMAS and the photo-

Figure 3   FTIR spectra of PGMAS/PENAA films (a) before and (b) after 20 min of UV crosslinking with filtered UV light.

IPN system of PGMAS/PENAA exhibited no T_g. Also, the TGA scans for them led to a T_d of 307 and 300°C, respectively.

Second Harmonic Generation Measurements

To align the chromophores effectively and avoid photodegradation of the polymer films at elevated temperature, the polymer films were poled at 100°C and then cooled to lower temperature (30°C) before UV crosslinking. The NLO measurements were carried out as described earlier and resulted in initial d_{33} values of 1.25×10^{-8} esu and 7.35×10^{-9} esu for the PGMAS and PGMAS/PENAA systems, respectively. The temporal stability of the PGMAS and PGMAS/PENAA films was studied by the decay curves of the d_{33} values before and after UV crosslinking as shown in Figures 4 and 5. The UV-cured respective polymer films retained $\sim$ 55 and $\sim$ 70% of their initial d_{33} values after 750 min at 25°C (Fig. 5). The UV crosslinking obviously improved the SHG stability. In Figure 5, the majority of the decay was seen in the first 150 min for both PGMAS and PGMAS/PENAA. The UV-crosslinked PGMAS decayed more slowly within 150 min, then decayed more quickly than did the photo-IPN system of PGMAS/PENAA, due to the

physical entanglements between two polymer networks which can suppress the relaxation of the poling-induced chromophore alignment.

Photoinduced Isomerization

Stilbenes and azobenzenes are known to undergo a reversible *cis–trans* isomerization by UV irradiation. As the *cis*-isomer has a much lower NLO activity, *trans–cis* isomerization has to be avoided

Figure 4   SHG decay of the uncrosslinked and poled polymer samples at 25°C.

Figure 5 SHG decay of the crosslinked and poled polymer samples at 25°C.

as much as possible. By using a filter, limiting the transmission to > 320 nm, we could sharply reduce the absorption decrease of the *trans* isomer, as seen in Figure 6. Actually, the absorption of *trans*-stilbene at 378 nm showed a decrease of ∼ 35% after 20 min of UV irradiation without a filter. In contrast, only a decrease of ∼ 12% was observed with a filter.

In our experiments, it was discovered that the *trans–cis* isomerization of stilbenes depended greatly on the crosslink density monitored by FTIR. When the films of PGMAS were cured under UV light after a shorter curing time (5 min),

Figure 6 Change in UV-vis absorption of PGMAS films after 20 min of UV crosslinking with and without a filter.

Figure 7 SHG decay of the crosslinked and poled PGMAS samples under 5-min UV irradiation at 25°C.

the recovery of the absorption of *trans*-stilbene at 378 nm reached ∼ 66% of the original absorption decrease after 12 h at room temperature. But for the films after a longer curing time (20 min), the absorption recovery at 378 nm was not observed. The above observations indicate that the stilbenes in the slightly crosslinked films of PGMAS can partially undergo *cis–trans* isomerization; this reversible isomerization did not occur for those highly crosslinked films due to the hindrance of the high-density networks. The photo-induced isomerization strongly affects the NLO property and the NLO stability of the PGMAS films.

An interesting phenomenon was found for the d_{33} decay of PGMAS films after 5-min UV irradiation. The d_{33} value increased promptly instead of decreasing at the first stage and then it decreased rapidly. As mentioned above, in the slightly crosslinked films of PGMAS, the *cis*-stilbene could isomerize thermally back to *trans*-stilbene, which shows greater NLO activity than that of the *cis*-stilbene. Meanwhile, since the poling alignments of stilbenes remained unchanged at this stage, this explains the increasing of the d_{33} value. However, the *cis–trans* thermal recovery causes the change of the free volume in crosslinked PGMAS films. The perturbation of the free volume makes the stilbenes more mobile and results in a rapid decrease of the d_{33} value. The d_{33} decay curve can be fitted by a Lorentzian equation (Fig. 7). This situation was not found for the highly crosslinked films.

CONCLUSIONS

A new photocrosslinkable NLO polymer (PGMAS) was synthesized and characterized. As antici-

pated, its photocrosslinking through cationic polymerization of pendant epoxy groups was faster and easier compared with other photocrosslinkable polymer systems. The poled and UV-cured polymer film exhibits a much more stable d_{33} value than that of the uncured polymer at 25°C. By using the BDS $\cdot$ 2PF$_6$ photoinitiator, the photo-IPN system based on the networks of PGMAS and PENAA was obtained. Owing to the physical entanglements between the networks, the IPN samples have an enhanced temporal NLO stability compared with photocrosslinked PGMAS samples. The crosslink density of cured PGMAS films had a great effect on the isomerization of stilbenes and, hence, the SHG stability.

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