

Second-Order Nonlinear Optical Properties of a Photocrosslinkable Epoxy-Based Polymer

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SYNOPSIS

The synthesis and characterization of a novel epoxy-based photocrosslinkable nonlinear optical (NLO) polymer exhibiting enhanced thermal stability is reported. The synthesized polymers show spectroscopic properties (NMR, IR, UV) in accordance with the proposed structures. A glass transition temperature (T_g) of 112°C and a thermal degradation temperature (T_d) of 310°C were recorded. The poled polymer film exhibits stable second-order nonlinear optical activity ($d_{33} = 19.5$ pm/V) over a period of 500 h as characterized by the temporal response of the second harmonic signal at room temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, polymeric second-order nonlinear optical (NLO) materials have shown continuing promise in the progression toward a practical organic NLO material for use in frequency doubling devices and electrooptical modulation.¹ These polymers are typically fashioned as either guest-host,^{2,3} main chain,⁴ side chain,⁵ or crosslinked systems.⁶⁻⁸ Second-order NLO effects are observed in a system when the NLO active species is oriented in a non-centrosymmetric way within the polymer matrix. The noncentrosymmetric alignment is typically achieved by a corona poling process.³ Epoxy-based polymeric systems, such as those based on bisphenol-A, have been utilized extensively in the development of second-order materials owing to the ease of processing, poling, and low optical losses in this class of polymers.⁹⁻¹¹ However, the main disadvantage encountered in these epoxy-based systems has been their low glass transition temperatures (T_g) that result in a polymer with poor thermal stability. In addition, the low T_g of these epoxy-based

systems results in a rapid decay of the second harmonic signal due to the ease of randomization of the poled order under experimental conditions. Various types of crosslinking reactions have been attempted to further enhance the T_g of the existing bisphenol-A systems.¹⁰ However, this leads to only modest increases in the T_g of the system and is dependent on the degree of crosslinking of a given sample.

We chose to investigate this problem further by employing diglycidyl ethers of bisphenol systems that contain rigid spacers between the phenolic rings of the bisphenol moiety. These higher T_g diglycidyl ethers were then polymerized via an epoxide ring opening reaction in which a nucleophilic NLO chromophoric amine initiates the polymerization reaction. These novel epoxy prepolymers were expected to exhibit higher T_g s than their bisphenol-A counterparts.⁹⁻¹¹ The prepolymers were subsequently functionalized with a photocrosslinkable group through esterification of the hydroxyl groups of the prepolymer. The polymer can be poled and photocrosslinked in the poled state through a 2 + 2 cycloaddition reaction to yield a material with stable second-order NLO properties.^{12,13} A photocrosslinkable polymer was chosen because of its compatibility with photolithographic techniques for potential device fabrication.¹⁴ A biphenyl-based NLO

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chromophore was chosen to reduce the absorptive loss of the polymer systems in the doubled frequency region of the spectrum, thus yielding polymer systems with lower optical losses than those containing azobenzene-based NLO chromophores.¹¹ Substantial absorptive losses must be avoided because the optical power density in most practical NLO waveguide devices is quite large. Therefore, even small absorptions can cause intolerable damage to the material.¹

Methods for the syntheses of the diglycidyl ether of the rigid bisphenol, the prepolymer of the bisphenol with 4-amino-4'-nitrobiphenyl, and the methacryloyl functionalized polymer are presented here. Details of the characterization procedures, preliminary results of second-order NLO measurements, and the temporal stability of the system are also presented.

EXPERIMENTAL

Instrumentation

¹H-NMR spectral data were obtained on a Varian-400 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 1760X FTIR spectrophotometer. Ultraviolet-visible (UV-vis) spectra were taken on a Perkin-Elmer Lambda 9 spectrophotometer. Number and weight average molecular weights (M_n and M_w) of the polymer were determined with a Waters 510 HPLC combined with a Waters 410 differential refractometer using chloroform as the eluent. The GPC calibration was based on polystyrene standards. The column set consisted of Waters Ultrastaygel 500, 10³, 10⁴, and 10⁵ Å. The T_g s were obtained from differential scanning calorimetry (DSC) using a TA Instrument DSC 2910 at a heating rate of 10°C/min under nitrogen. The thermal degradation temperature (T_d) of the polymer was determined on a TA Instrument TGA 2950 with a heating rate of 20°C/min under nitrogen. Elemental analysis was performed by Atlantic Microlab, Inc.

Materials

The 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol (TMC)¹⁵ was donated by Dr. W. Paul (Miles, Inc.) (I, Scheme 1) and used without further purification. Tetrahydrofuran (THF), epichlorohydrin, triethylamine, HPLC acetone, and potassium carbonate were obtained from Aldrich Chemical and used as received. The methacryloyl chloride was obtained

from Aldrich and was redistilled over molecular sieves immediately prior to use.

Synthesis of Diglycidyl Ether of Bisphenol TMC (II)

To a 50-mL, round-bottomed flask equipped with a stirring bar, reflux condenser, and nitrogen inlet, TMC (2.0 g/0.0064M), epichlorohydrin (2.4 g, 2.0 mL/0.026M), and potassium carbonate (1.8 g/0.0128M) were added. The reaction mixture was dissolved in 15 mL of HPLC grade acetone with stirring. The reaction mixture was purged with nitrogen and heated to reflux for 8 h. After cooling, the reaction mixture was poured onto 200 mL of water yielding a viscous oily layer on the water surface. The oily layer was extracted with three 50-mL portions of ether, and the ether layers were dried over anhydrous potassium carbonate. The ether was removed under reduced pressure to yield a viscous, clear, and colorless oil. The yield of TMC diglycidyl ether was 2.0 g (yield 95%). IR (KBr): 2924 cm⁻¹ (m, CH₃ stretch), 1608 cm⁻¹ (s, C=C of Ar. ring), 1245 cm⁻¹ (m, epoxide ring stretch).

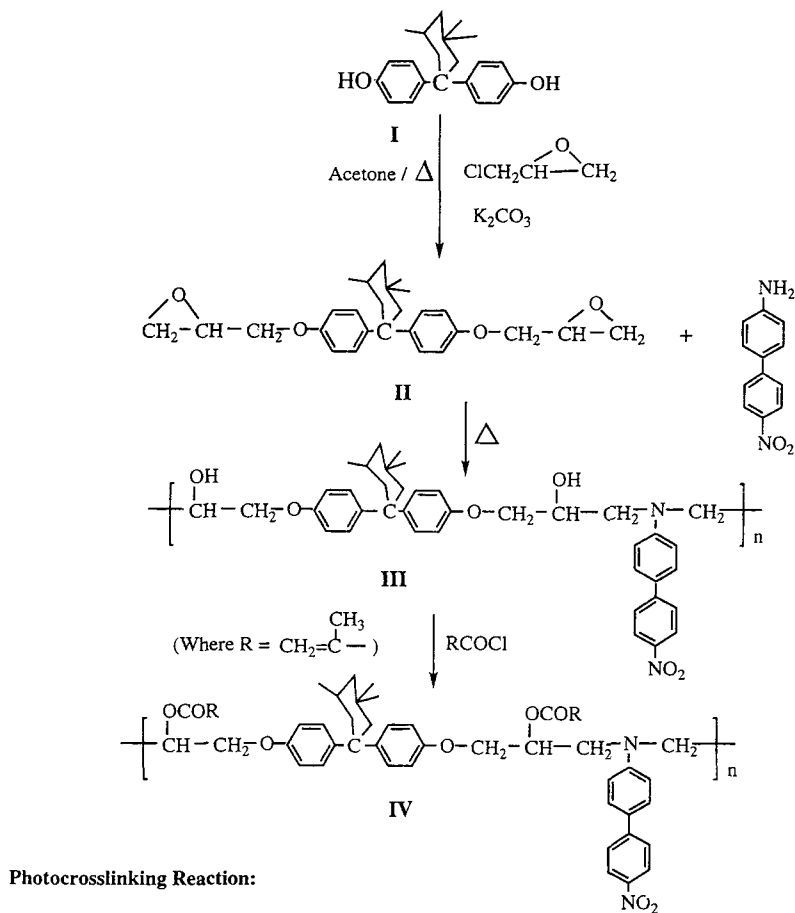
Synthesis of Prepolymer (III)

To a 10-mL, round-bottomed flask were added bisphenol-TMC diglycidyl ether (2.0 g/0.0061M) and 4-amino-4'-nitrobiphenyl¹⁶ (1.4 g/0.0064M), and the reaction vessel was subsequently sealed and purged with nitrogen. The reaction mixture was heated at 140°C for 4 h and at 160°C for 3 h. The deep orange glassy prepolymer was powdered and recrystallized from methanol to remove excess dye (yield 95%), T_g 97°C; IR (KBr): 3387 cm⁻¹ (m, O—H), 1590 cm⁻¹ (s, C=C of Ar. ring), 1510 cm⁻¹ (s, ν_{asym} (N=O)₂), 1339 cm⁻¹ (s, ν_{sym} (N=O)₂). UV-vis (Film): 405 nm (λ_{max}), 650 nm (λ_{cutoff}). ¹H-NMR (DMSO-*d*₆): δ = 0.33 (*d*, 2H, 4-cyclohex. CH₂); 0.82–1.17 (m, 6H, 3-cyclohex. (CH₃)₂); (3H, 5-cyclohex. CH₃); (1H, 5-cyclohex. H); 1.33 (s, 2H, 2-cyclohex. CH₂); 1.76–2.00 (*d*, 2H, 6-cyclohex. CH₂); 2.70 (s, 2H, OH); 3.41–4.20(m, 4H, NCH₂); (4H, OCH₂); (2H, CH); 6.58–8.34 (m, 16H, ArH).

Anal. Calcd for (C₃₉H₄₄N₂O₆)_{*n*} (637)_{*n*}: C, 73.56%; H, 6.96%; N, 4.40%. Found: C, 70.20%; H, 7.19%; N, 4.43%.

Synthesis of Polymer (IV)

A solution of methacryloyl chloride (1.6 g/0.015M) in 15 mL of THF was added dropwise to a solution



Scheme 1 Composition of compounds I–IV.

of the powdered prepolymer (2.4 g in 10 mL of triethylamine and 15 mL of THF). The solution was stirred for 27 h at room temperature. The reaction mixture was then refluxed for a period of 2 h. The orange colored solution was precipitated in 800 mL of methanol. The polymer was filtered, washed with methanol, and dried in a vacuum oven at room temperature for a period of 24 h. The dried polymer was obtained as a deep orange powder. The yield of the polymer was 2.0 g (yield 83%); T_g 112°C; M_n 1995; M_w 3178. IR (KBr): 1719 cm^{-1} (s, CO of methacryloyl

ester), 1510 cm^{-1} (s, $\nu_{\text{asym}}(\text{N}=\text{O})_2$), 1343 cm^{-1} (s, $\nu_{\text{sym}}(\text{N}=\text{O})_2$). UV-vis (film): 405 nm (λ_{max}), 650 nm (λ_{cutoff}).

Film Preparation

The polymer solutions used for the d_{33} measurements were prepared by dissolving the purified polymer in a 1 : 1 (v/v) propylene glycol methyl ether acetate/1,4-dioxane mixture in a weight ratio of 1 to 8. Films were prepared by spin coating the poly-

mer solution onto transparent glass microscope slides. The typical film thickness was approximately 0.5 μm . The films were dried at 60°C under vacuum for 24 h.

NLO Measurements

The corona poling technique was employed to align the NLO chromophores. The corona field was applied as the temperature of the stage was raised to 110°C and the poling was carried out for 20 min. The corona current was held at 2 μA with an electrode potential of 6.0 kV. The samples were cooled to 80°C and UV crosslinked at 254 nm for 5 min. The samples were then cooled slowly under the corona field.

The second-order NLO properties of the poled thin film samples were measured via a method discussed previously.¹⁷ 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) with the samples at a fixed angle of 10°. The calculations of the second-order NLO coefficient (d_{33}) were previously discussed.¹⁸

RESULTS AND DISCUSSION

The synthesis of the methacryloyl functionalized polymer involved three steps (Scheme 1): the synthesis of the diglycidyl ether of the bisphenol, the synthesis of the prepolymer containing the NLO chromophore, and then the attachment of the crosslinkable methacryloyl group to the backbone. The first step was a simple nucleophilic displacement reaction in which the bisphenol attacked epichlorohydrin with a subsequent ring closure to form the diglycidyl ether. This reaction is a convenient method for generating diglycidyl ethers of bisphenols and is quite general in its application to other bisphenols. The second step involved an epoxide ring opening in which the nucleophilic NLO chromophore initiated the polymerization reaction. During this synthesis, the reaction mixture gradually formed a deep orange, clear, and glassy solid. The prepolymer was powdered and recrystallized from methanol to remove excess dye. The final synthesis step involved the attachment of the photocrosslinkable methacryloyl group through esterification of the pendant hydroxyl groups of the prepolymer using triethylamine. The methacryloyl group underwent a [2 + 2] cycloaddition reaction upon exposure to UV radiation, as illustrated in Scheme 1.

The IR absorption spectrum of the diglycidyl ether was carried out in a neat liquid cell. The spectrum was consistent with the epoxy structure, exhibiting the characteristic epoxide ring stretch at 1245 cm^{-1} . The IR spectra of the prepolymer and polymer were carried out as pressed KBr disks. The functionalized polymer showed an additional sharp peak at 1719 cm^{-1} due to the carbonyl stretching of the methacryloyl functionality. Additionally, the intensity of the O—H stretch at 3387 cm^{-1} in the prepolymer diminished considerably in the polymer spectrum indicating the functionalization of the hydroxyl groups. UV-vis absorption measurements were performed on thin films of the prepolymer and polymer. The absorption spectrum of the prepolymer exhibited an absorption maximum at 405 nm and a cutoff wavelength of 605 nm, which is substantially lower than the cutoff wavelength exhibited by traditional azobenzene-based epoxy systems.¹⁰

Thermal analysis was conducted on both the prepolymer and polymer samples. A TGA scan of the polymer led to a T_d of 310°C as taken by the onset point of the step transition. DSC scans established an advance of the T_g from 97°C for the prepolymer to 112°C for the methacryloyl functionalized polymer. The DSC curve of the crosslinked polymer exhibited no T_g . The thermal stability of our polymer system was found to be at least comparable to the best known bisphenol-A epoxy systems.^{9,10}

The corona poling technique was employed to align the NLO chromophores. Careful adjustment of the poling field strength and temperature was found to be critical, as high field strengths and temperatures were found to degrade the polymer films. It is also essential that the UV crosslinking be carried out at lower temperatures to avoid photodegradation of the polymer films.

The NLO measurement techniques were carried out as described earlier and resulted in an initial d_{33} value of 20.6 pm/V. The temporal stability of the polymer film was studied by the decay of the d_{33} as a function of time at 25°C and the values normalized to the initial d_{33} value. Over a 500 h period at 25°C, the crosslinked polymer film exhibited a d_{33} of 19.5 pm/V, retaining 95% of the initial d_{33} value compared to the uncrosslinked sample that exhibited a reduction of over 50% of its original d_{33} value under the same conditions (Fig. 1). The majority of the decay was seen in the first 60 h of the study.

The optical loss of the polymer films was measured using the prism coupling technique.¹¹ The optical loss of the poled and crosslinked polymer film was found to be 5.6 dB/cm at 0.633 μm . Substantial

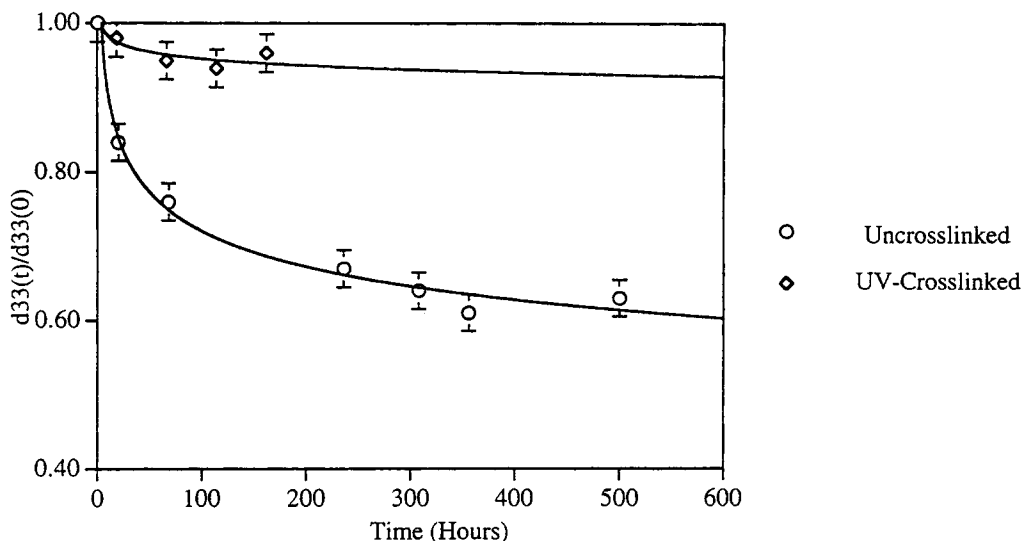


Figure 1 Temporal stability of the second harmonic intensity of the uncrosslinked and crosslinked TMC polymers at 25°C.

scattering loss due to surface irregularities constituted a large component of this total loss. The optical loss was found to be a substantial improvement of lower cutoff epoxy systems recently developed in our laboratory.¹⁹

CONCLUSIONS

A new epoxy-based photocrosslinkable NLO polymer exhibiting substantial stability upon crosslinking was synthesized and characterized. The poled and crosslinked polymer film exhibits a stable d_{33} value of 19.5 pm/V, while the uncrosslinked polymer experiences a greater than 50% reduction in the initial d_{33} value over the same time period at 25°C. The optical loss of the poled and crosslinked polymer film was found to be 5.6 dB/cm at 0.633 μm . As anticipated, the combination of a higher T_g epoxy with a photocrosslinkable group improves the temporal stability of the polymer films as compared to similar bisphenol-A epoxy systems.¹⁰ In addition, the use of a biphenyl NLO chromophore resulted in lower cutoff wavelengths and optical losses than are typically obtained with azobenzene chromophores. It is anticipated that higher T_g epoxy systems can be poled and photochemically crosslinked to achieve enhanced temporal stability at higher temperatures. Higher degrees of functionalization of the prepolymer and crosslinking efficiencies will enhance the temporal stability of the polymer system and are currently being optimized in our laboratory.

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