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SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF A POLYMER EXHIBITING OPTICAL TRANSPARENCY DOWN TO 340 nm

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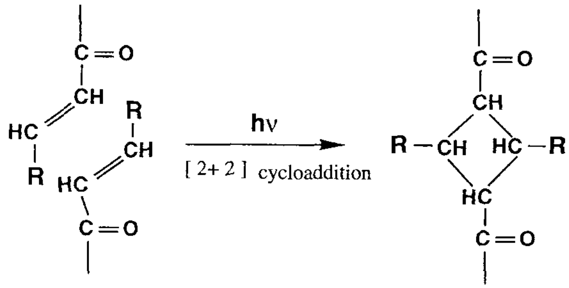
ABSTRACT

The synthesis and characterization of an epoxy-based nonlinear optical (NLO) polymer exhibiting optical transparency down to 340 nm is reported. The synthesized polymers show spectroscopic properties (NMR, IR, UV) in accordance with the proposed structures. A glass transition temperature (T_g) of 92°C and a thermal degradation temperature (T_d) of 322°C were recorded. The poled polymer film exhibits stable second-order nonlinear optical activity ($d_{33} = 4.2$ pm/V) over a period of 800 hours as characterized by the temporal response of the second harmonic signal at room temperature.

INTRODUCTION

In recent years, polymeric second-order nonlinear optical (NLO) materials have shown continuing promise in progress 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 noncentrosymmetric way within the polymer matrix. The noncentrosymmetric alignment is typically achieved by a corona poling process [3]. A typical organic second-order NLO species consists of electron donating and withdrawing groups separated by a π-delocalized moiety. Such NLO active chromophores typically exhibit large second-order nonlinearities. However, a direct consequence of the substantial delocalization in some NLO chromophores, which is needed to enhance the second-order nonlinearities, is longer cutoff wavelengths (NIR region) in thin films of the polymers. This leads to substantial absorptive loss when the doubled frequency is in this region. For frequency doubling, this should 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]. Yet, some of the largest second-order nonlinearities are associated with highly delocalized NLO chromophores. Thus, one must contend with a trade-off between optical nonlinearities and cutoff wavelengths.

In order to obtain the desired optical transparency, some effort has been devoted to the pursuit of NLO active materials with blue shifted cutoff wavelengths [9, 10]. We have chosen to investigate a polymeric system which possesses a relatively low cutoff wavelength with the hope of synthesizing a clear and transparent second-order NLO system. This polymer has been designed through a modification of an earlier system prepared in our laboratory [11]. This system consists of an NLO active species and a photocrosslinkable group which are covalently attached to an epoxy-based polymer. The polymer can be poled and photocrosslinked in the poled state through a 2 + 2 cycloaddition reaction (see below) to yield a material with stable second-order NLO properties [11, 12]. A photocrosslinkable polymer was chosen because of its compatibility with photolithographic techniques [13]. Our modification to this system involves the attachment of an NLO active chromophore (4-aminobenzonitrile) with a blue-shifted absorption maximum (λ_{max}(THF) = 290 nm).



A method for the synthesis of both the prepolymer of Bisphenol-A diglycidyl ether with 4-aminobenzonitrile and the cinnamoyl functionalized polymer is presented here. Details of the characterization procedures, preliminary results of second-order NLO measurements, and the temporal stability of the system are presented.

EXPERIMENTAL

Instrumentation

^{1}H-NMR spectral data were obtained on a Bruker WP-270 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 1760X FT-IR 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 μStyragel 500, 10^3, 10^4, and 10^5 Å. The glass transition temperatures (T_g) were obtained from differential scanning calorimetry using a TA Instrument DSC 2910 at a heating rate of 10°C/min. 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.

Materials

4-Aminobenzonitrile (Aldrich) and cinnamoyl chloride (Aldrich) were used without further purification. Bisphenol-A diglycidyl ether (**I**, Scheme 1) was obtained from a commercial source (Shell, Epon 828) and used without further purification. Tetrahydrofuran (Aldrich) and triethylamine (Aldrich) were used as received.

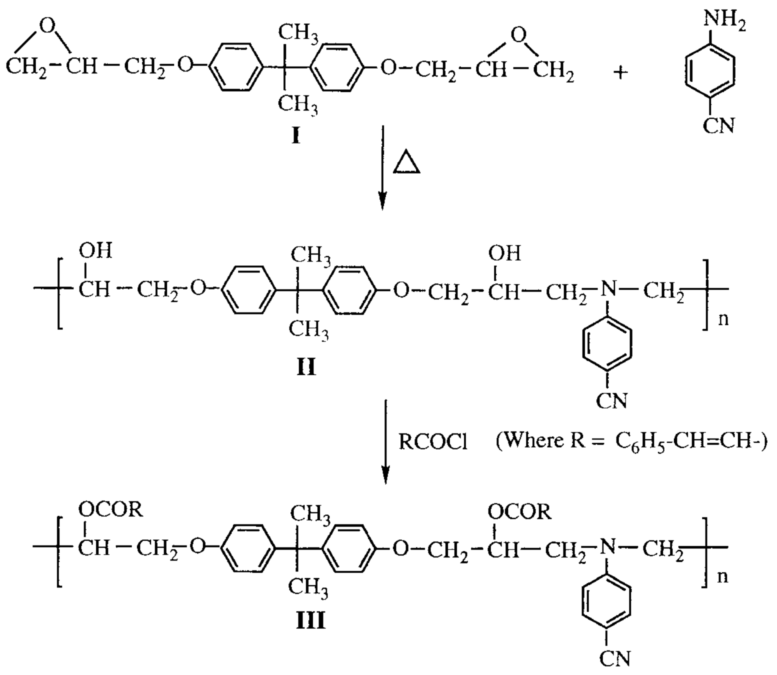
Synthesis of the Prepolymer (II)

To a 100-mL round-bottomed flask was added Bisphenol-A diglycidyl ether (7.5 g/0.022 M) and 4-aminobenzonitrile (3.0 g/0.025 M), and the reaction vessel was subsequently sealed. The reaction mixture was heated at 140°C for 4 hours and at 160°C for 3 hours. The prepolymer was then powdered (yield: 95%); T_g = 71°C.

IR(KBr): 3370 cm^{-1} (m, O—H) 2213 cm^{-1} (s, C≡N) 1617 cm^{-1}, 1510 cm^{-1} (s, C=C of Ar ring). UV-Vis(THF): 240 nm, 287 nm (λ_{max}). *UV-Vis (film): 287 nm* (λ_{max}), *340 nm* (λ_{cutoff}).

Synthesis of the Polymer (III)

A solution of cinnamoyl chloride (3.5 g/0.021 M) in 15 mL THF was added dropwise to a solution of the powdered prepolymer (3.5 g in 10 mL triethylamine and 15 mL THF). The solution was stirred for 24 hours at room temperature. The light brown colored solution was precipitated in 800 mL methanol. The polymer was filtered, washed with methanol, and dried in a vacuum oven at room tempera-



SCHEME 1

ture for 24 hours. The dried polymer was obtained as a white powder. The yield of the polymer was 4 g (yield: 95%); T_g = 92°C; M_n = 2670; M_w = 7560.

IR(KBr): 2216 cm^{-1} (s, C≡N) 1713 cm^{-1} (s, CO of cinnamoyl) 1244 cm^{-1} (m, C—O—C). UV-Vis(THF): 220 nm (Ph of cinnamoyl), 238 nm, 281 nm (λ_{max}, NLO dye). *UV-Vis(film): 287 nm* (λ_{max}), *340 nm* (λ_{cutoff}). ^{1}H NMR ($CDCl_3$): δ = 1.60 (s, 6H, CH_3); 3.08-4.11 (m, 4H, OCH_2; 4H, NCH_2; 2H, CH); 7.06-7.63 (m, 22H, ArH; 8H, CH=CH). $C_{46}H_{42}O_6N_2$ (718). Calculated: C, 76.86; H, 5.89; N, 3.90%. Found: C, 76.70; H, 6.07; N, 4.01%.

Film Preparation

The films used for the d_{33} measurements were prepared by dissolving the purified polymer in propylene glycol methyl ether acetate with a weight ratio of 1 to 8. Films were prepared by spin coating the polymer solution onto transparent glass microscope slides. The typical film thickness was approximately 1.3 μm. The films were dried at 40°C under vacuum for 24 hours.

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 93°C, and the poling was carried out for 20 minutes. The corona current was held at 2.1 μA with an electrode potential of 4.3 kV. The sample was then cooled slowly under the corona field. *All measurements were carried out using uncrosslinked samples of the polymer.*

The second-order NLO properties of the poled thin film samples were measured via a method discussed previously [14]. 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 sample at a fixed angle of 50°. The calculations of the second-order NLO coefficient (d_{33}) were previously discussed [15].

RESULTS AND DISCUSSION

Synthesis of the cinnamoylated polymer involves two steps (Scheme 1); the synthesis of the epoxy prepolymer containing the NLO chromophore and then the attachment of the photocrosslinkable cinnamoyl group to the backbone. The first step involves an epoxide ring opening in which the nucleophilic NLO chromophore initiates the polymerization reaction. During the synthesis, the color of the reaction mixture gradually changed from colorless to light yellow, and the formation of a clear, glassy solid was observed. The prepolymer was powdered and characterized. The second step of the synthesis involves the attachment of the cinnamoyl group through esterification of the hydroxyl group of the prepolymer using triethylamine.

The infrared absorption spectra of the prepolymer and polymer were carried out as pressed KBr disks. The functionalized polymer showed the presence of an additional sharp peak at 1713 cm^{-1} due to carbonyl stretching of the cinnamoyl ester. Meanwhile, the intensity of the O—H stretch at 3370 cm^{-1} in the prepolymer spectrum diminished considerably in the polymer spectrum, indicating the functionalization of the hydroxyl groups. Ultraviolet-Visible absorption measurements were performed on thin films of the prepolymer and polymer, and investigated as a function of time. The absorption spectra of the prepolymer, pristine polymer, and poled polymer after a period of 800 hours at room temperature are shown in Fig. 1. Both the prepolymer and polymer showed absorptions at approximately 240 and 280 nm due to the NLO chromophore. Finally, as was anticipated, both the prepolymer and polymer showed a relatively low absorption cutoff at around 340 nm. The peak widths were measured to be 35 and 25 nm for the prepolymer and the pristine polymer, respectively.

A thermal analysis was conducted on both the prepolymer and polymer samples. A TGA scan at 20°C/min of the polymer led to a T_d of 322°C as taken from the onset point of the step transition. DSC scans at 10°C/min establish an advancement of the T_g from 71°C for the prepolymer to 92°C for the cinnamoyl functionalized polymer. *The thermal stability of our polymer system was found to be comparable to other systems exhibiting a similar optical transparency. Recently, Nalwa et al.* [*9*] *designed such a system based on an aromatic polyurea which has a* T_g *of 122°C.*

The optical losses of the polymer films were measured using the prism coupling technique [16]. The optical losses of the poled polymer film were found to be 8.54 dB/cm at 0.633 μm and 3.54 dB/cm at 0.830 μm. Its refractive indices were determined to be 1.632 and 1.603 at 0.532 and 1.000 μm, respectively. The NLO measurements were carried out as described earlier and resulted in a d_{33} value of 4.2

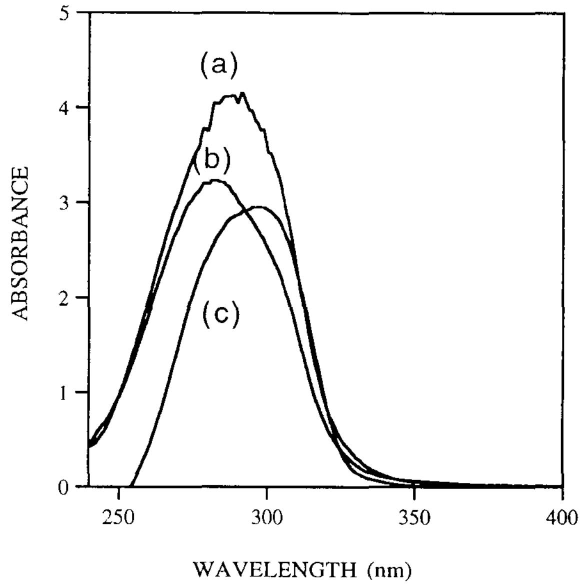


FIG. 1. UV-visible spectra of: (a) pristine polymer (**III**), (b) poled polymer (**III**), and (c) prepolymer (**II**) coated on glass slides.

pm/V at 1.064 μm. The temporal stability of the samples was studied by the decay of d_{33} as a function of time at room temperature (25°C), and the values were normalized to the initial d_{33} measurement. The temporal stability of the polymer is shown in Fig. 2. Over an 800-hour period at 25°C, a reduction of 20% in d_{33} was observed for the poled polymer film. Most of the reduction occurred in the first 24 hours of heating.

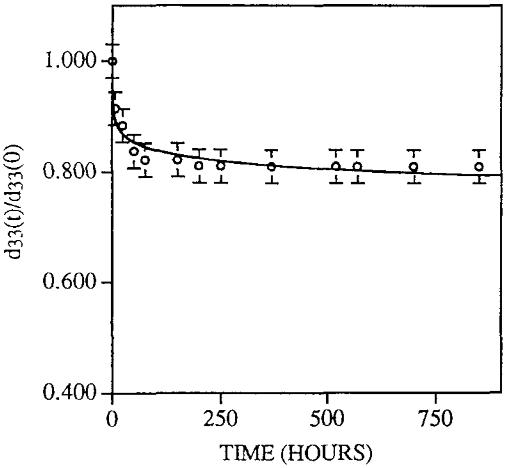


FIG. 2. Time behavior of second-order nonlinear optical coefficient of poled polymer at room temperature.

CONCLUSIONS

A new epoxy-based NLO polymer exhibiting optical transparency down to 340 nm has been synthesized and characterized. The poled polymer film exhibited a second-order nonlinear coefficient of 4.2 pm/V and retained 80% of its original d_{33} value over 800 hours as characterized by the temporal response of the second harmonic signal at room temperature. The optical losses of the poled polymer film was found to be 8.54 dB/cm at 0.633 μm and 3.54 dB/cm at 0.830 μm. Only limited photocrosslinking of the polymer films was possible due to extensive photodegradation of the NLO chromophore close to the photocrosslinking wavelength. It is anticipated that the magnitude of the second-order nonlinearity can be enhanced in this system by increasing the NLO chromophore density in the polymer matrix. This may be accomplished via the use of a dye-functionalized epoxy in the polymerization reaction.

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