Synthesis and Electrooptic Characterization of a Novel Highly Active Indoline Nitroazobenzene Methacrylate Copolymer

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A novel methacrylate copolymer was synthesized, and the electrooptic activity of poled thin films was measured. The electrooptically active group was an indoline nitroazobenzene chromophore which was incorporated as a side-chain pendant on a methacrylate backbone. Thin film electrooptical devices were fabricated and the chromophores aligned through thermal electrical poling. Electrooptical coefficient measurements revealed that high-field poled samples exhibited high nonlinear optical activity and that at electrical poling fields of 190 V/μm, electrooptic coefficients of up to 42 pm/V were obtained at 1.3 μm.

Introduction

Recent research efforts have led to the development of organic materials for nonlinear optical applications.[1,2] In particular, polymers have been targeted as promising candidates for electrooptical device applications such as Mach Zhender modulators.[3] Organic chromophores exhibiting high molecular hyperpolarisabilities (β) are typically introduced as side-chain pendant groups on a polymer backbone, which is fabricated as a thin film between electrically conducting surfaces on substrates. To induce electrooptic activity, bulk asymmetrical orientation is facilitated through electrical poling[4] which orients the chromophores in the direction of the electric field. The electrooptic coefficient is a function of both the chromophore β value and the degree of alignment attained through the electrical field strength. Therefore, to maximize the effect, high-field poling is necessary as well as a highly active chromophore. Typically, the active chromophore is aligned at temperatures around the glass transition and then allowed to cool in the presence of the field, thus retaining the initial ordering before thermal relaxation processes occur. This paper reports the synthesis of a pendant polymer with exceptionally large nonresonant β values and both the high-field poling of fabricated thin films and their resultant electrooptic coefficients. A Reflection technique[5] was used to measure the electrooptic tensor element r_{33} of the poled films.

Indoline Nitroazabenzene Copolymers

A methacrylate polymer backbone was chosen to host the chromophores as pendant side groups. This was selected due to its ease of monomer synthesis and transparency and can be modified to have a suitably high T_g (over 140 °C). Due to the intractability of the homopolymer, methyl methacrylate was introduced as a comonomer to improve solubility and processing. The chromophore chosen for investigation was a nitroazobenzene moiety containing an indoline unit as the donor group. Previous research[6,7] has developed empirical structure–property relationships designed to enhance nonlinear susceptibility, and this molecular engineering approach was used in chromophore conception. As can be seen, there is π-orbital conjugation throughout the length of the molecule, with donor–acceptor functionalities at both ends. This allows an asymmetric electronic charge distribution of the delocalized π orbitals which has been shown to maximize the molecular hyperpolarizability β. In addition, the indoline ring conformation restricts rotation of the C–N bond, resulting in a more planar π conjugation from the donor group to the aromatic group. This improves the conjugation efficiency and hence β.

Synthesis

Figure 1 illustrates the synthesis of the target polymer. Hydroxyethylindoline (**2**) is first synthesized from the base-catalyzed nucleophilic attack of indoline on iodoethanol, prepared in situ from sodium iodide and bromoethanol. The diazonium salt prepared from *p*-nitroaniline was isolated as the fluoboric salt and then coupled by electrophilic addition to the indoline yielding the azo chromophore. The monomer (**4**) is then afforded on nucleophilic substitution of the anhydride by the alcohol (**3**) with pyridine as base in the standard way. It was necessary to exhaustively purify the monomer by both recrystallization and chromatography in order to ensure a high yield of the polymer (**5**). With the pure monomer, free-radical polymerization using AIBN initiator was inefficient unless

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[®] Abstract published in *Advance ACS Abstracts*, March 15, 1994.

(1) *Organic Materials for Nonlinear Optics 2*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1991.

(2) *Nonlinear Optical Properties of Organic Materials*, Khanarian, G., Ed.; Proc SPIE; 1989; p 1147.

(3) Teng, C. C. *Appl. Phys. Lett.* **1992**, *60*, 1538.

(4) Man, H. T.; Yoon, H. N. *Adv. Mater.* **1992**, *21*(3), 159.

(5) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990**, *56*(18), 1734.

(6) Nicoud, J. F.; Twieg, R. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J. Eds.; Academic Press: New York, 1987; Vol. 1, 2.

(7) Buckley, A.; Choe, E.; DeMartino, R.; Leslie, T.; Nelson, G.; Stamatoff, J.; Stuetz, D.; Yoon, H. Polymeric Materials Science and Engineering; Proceedings of the ACS Division of Polymeric Material Science: Science and Engineering **1986**, *54, 502.*

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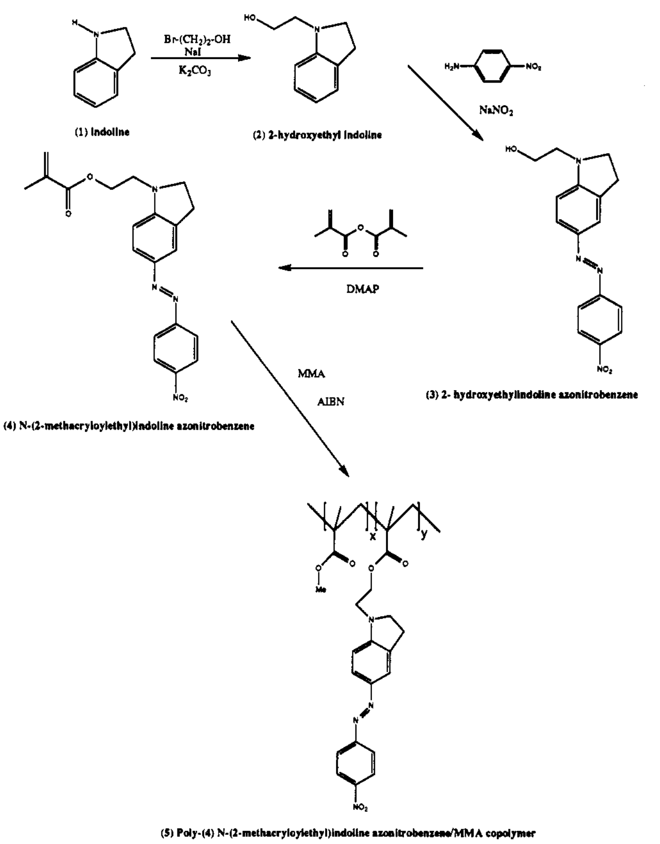

Figure 1. Synthesis of indoline nitroazobenzene methacrylate/MMA copolymer.

high levels (1–2 mol %) of initiator were used. This was felt at least in part due to the intrinsic chain-transfer ability of the chromophore moiety.

Experimental Part

Synthesis of (Hydroxyethyl)indoline. A solution of bromoethanol (375 g, 3 mol), NaI (450 g, 3 mol), and K_2CO_3 (415 g, 3 mol) in methanol (500 mL) was heated to reflux for 1 h under continuous stirring. Freshly distilled indoline (298 g, 2.5 mol) was then added dropwise under argon, and the reaction mixture allowed to reflux of 12 h. Methanol was then distilled off, methylene chloride (900 mL) was added, and the resultant slurry filtered to remove the residual insoluble salts. The solution was then washed with water and the organic layer distilled under vacuum (118 °C at 0.6 mmHg) to afford the product, a viscous clear liquid which must be stored under argon. ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 1 H) OH; 2.98 (t, 2H) ring CH_2 β to N; 3.33 (m, 4H) CH_2N CH_2; 3.79 (t, 2H) –CH_2OH; 6.56 (d, 1H) Ar H ortho to N; 6.71 (t, 1H) Ar H para to N; 7.08 (m, 2H) Ar H's meta to N.

Synthesis of (Hydroxyethyl)indoline Azonitrobenzene. *p*-Nitroaniline (152.5 g, 1.11 mol) was dissolved in a mixtue of fluoboric acid (280 g, 1.53 mol of a 48 wt % solution in water) and acetic acid (800 g). The solution was chilled below 15 °C and stirred. To this was added dropwise a solution of sodium nitrite (82.5 g, 1.2 mol) in water (200 mL), and the salt allowed to stir for 1 h. The solid product was filtered, then added to a stirred mixture of water (1.5 L) and acetic acid (200 mL), and both stirred and cooled below 10 °C. To this slurry was added dropwise (hydroxyethyl)indoline (150 g, 0.92 mol) while maintaining the temperature below 10 °C. After a further 3 h, and solution of sodium acetate (410 g, 5 mol) in water (1.5 L) was added, and the precipitate filtered, washed with water, and then recrystallized from a 2:1 volume mixture of isopropyl alcohol and ethyl acetate. The product was observed to be photosensitive and protected from light; yield 77%, mp 168 °C, λ_{max} (CH_2Cl_2) 498 nm. ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 1H) OH; 3.09 (t, 2H) ring CH_2 β to N; 3.40 (t, 2H) HOCH$_2$CH_2N–; 3.68 (t, 2H) –CH_2NCH$_2$; 3.85 (t, 2H) HOCH_2–; 6.50 (d, 1H) Ar H ortho to N; 7.7 (m, 2H) Ar H's ortho to —N=N—; 7.85 (d, 2H) Ar H's meta to NO_2; 8.29 (d, 2H) Ar H's ortho to NO_2. $C_{16}H_{16}N_4O_3$ (312.32) calcd: C 61.53; H 5.16; N 17.94; O 15.37. Found: C 61.35; H 5.21; N 17.86; O 15.43.

Synthesis of (Hydroxyethyl)indoline Azonitrobenzene Methacrylate. To a solution of the azoindoline alcohol (59 g, 0.189 mol) in ethyl acetate (1000 mL) was added (dimethylamino)pyridine catalyst (3.3 g, 27 mmol) and methacrylic anhydride (34.9 g, 0.226 mol). The reaction mixture was allowed to warm to 50 °C, protected from light, and stirred overnight. The solvent was then reduced to 200 mL by vacuum rotoevaporation, and hexane (1500 mL) added. On cooling, the product crystallized out and was collected by filtration then washed with water. This was then purified by recrystallization from a 3:1 acetonitrile: water volume mixture; yield 84%, mp 135 °C. ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 3H) CH_3; 3.11 (t, 2H) ring CH_2 β to N; 3.57 (t, 2H) –OCH$_2$CH_2N–; 3.73 (t, 2H) –CH_2NCH$_2$; 4.38 (t, 2H) OCH_2–; 5.56 (d, 1H) CH_2=; 6.07 (d, 1H) CH_2=; 6.49 (d, 1H) Ar H ortho to N; 7.7 (m, 2H) Ar H's ortho to —N=N—; 7.88 (d, 2H) Ar H's meta to NO_2; 8.28 (d, 2H) Ar H's ortho to NO_2.

Preparation of 50/50 Indoline/MMA Copolymer. A solution of indoline monomer (18 g, 36.8 mmol) in γ-butyrolactone (65 g, 25 wt % total monomer concentration) was warmed to 65 °C and degassed by vigorously bubbling argon through the mixture for 2 h. Previously degassed methyl methacrylate (3.68 g, 36.8 mmol) was then injected through a rubber septum into the reaction mixture. After an additional 20 min, an aliquot from a solution of AIBN (0.061 g, 0.6 mol% total monomers) in γ-butyrolactone (2 mL) was also injected. (In total, four aliquots (0.5 mL each) were injected at intervals of approximately 2.5 h.) Both inlet and outlet needles were then removed, and the sealed vessel was allowed to stir at 65 °C for 18 h. This resultant solution was diluted to twice its original volume with dichloromethane and then precipitated into a 5-fold excess of isopropyl alcohol. The product was collected by filtration, then redissolved in THF, and precipitated into 2-propanol. Purification was further carried out by successive reprecipitation of the polymer solution in THF into isopropyl alcohol until no monomer was observed to be present in the polymer by either HPLC or TLC. For reprecipitations, the polymer solution was prepared at about 5 wt % or less of polymer. This increased the quantity of monomer which remains in solution after precipitation and improves the purification process efficiency; yield 84%, T_g (DSC) 145 °C. λ_{max}(CH_2Cl_2) 491 nm. ^{1}H NMR ($CDCl_3$) δ 0.9 (m, 4H) backbone CH_2; 1.8 (m, 6H) CH_3; 3.1 (m, 2H) ring CH_2 β to N; 3.5 (m, 5H) –OCH$_2$CH_2N–, OCH_3; 3.7 (m, 2H) –CH_2NCH$_2$; 4.2 (m, 2H) OCH_2–; 6.4 (m, 1H) Ar H ortho to N; 7.7 (m, 4H) Ar H's ortho to —N=N—, Ar H's m to NO_2; 8.2 (m, 2H) Ar H's ortho to NO_2. M_w 210 000, M_n 88 000. $|\eta|$ = 0.23 dL/g (NMP 0.2% LiBr). Molecular weight was calculated from a universal calibration curve and analyzed using a Waters 150C GPC equipped with a Viscotec differential viscosity detector. The onset of thermal decomposition was measured by TGA to be 250 °C: $(C_{25}H_{28}N_4O_6)_n$ (480.5) Calcd: C 62.49; H 5.87; N 11.66; O 19.98. Found: C 62.21; H 5.96; N 11.38; O 19.74.

Poling. The macroscopic electrooptic properties of glassy polymers require electrical poling to induce asymmetry, a property that is required by the third-order tensorial properties of the second-order nonlinear optical response. This thermal poling procedure has been previously described[4] for side-chain NLO polymers. Thin films are fabricated by solvent casting techniques onto a conductive indium tin oxide (ITO) coated glass slide. Film thicknesses were of the order of a few microns. The top electrode was in the form of a thermally sputtered gold layer of approximately 0.15 μm. Poling involved heating the sample close to the T_g while a poling field was applied across the electrodes for a period of time sufficient to reach alignment equilibrium. The waveform characteristics of both poling and depoling as well as subsequent relaxation is related to the segmental motion and rotation of the chromophore in the polymer matrix. These orientation mechanisms are influenced by factors such as NLO chromophore concentration, molecular weight, method of chromophore incorporation, and poling field strength.[8] The time taken for attainment of alignment equilibrium is particularly sensitive to the poling temperature in relation to the materials

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(8) Hoffman, C. L.; Man, H. T.; Fuller, G. G. *Acta Polym.* **1993**, *44*, 39.

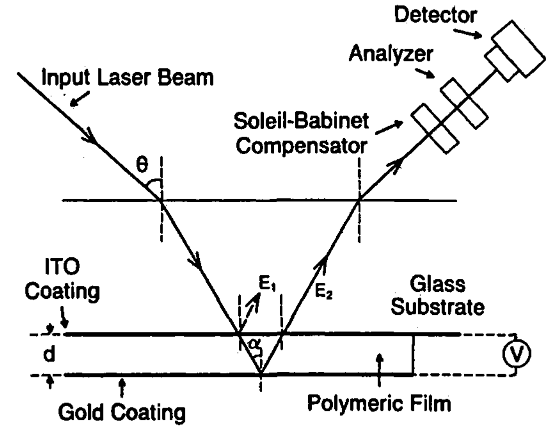

Figure 2. Experimental configuration of the electrooptic measurement by reflection technique.

glass transition. In situ poling experiments on a number of similar side-chain copolymers[4] revealed that poling equilibrium occurred after about 1 min at T_g. The time used in the present poling procedure was typically 5 min. The chromophores are aligned by cooling the sample well below the glass transition with the field still present (Figure 2).

Electrooptic Characterization. A simple reflection technique[5] was used to measure the electrooptic coefficient induced in the polymer film by the poling process. The experimental setup is depicted in Figure 2 where a laser beam, at 1.3-μm wavelength and polarized at 45°, propagates into the polymer film from the back of the glass substrate at an angle θ. It is back reflected at the top gold electrode and propagates through a Soleil–Babinet compensator and an analyzer before reaching the photodetector. When a modulating voltage, V_m, is applied across the electrodes, the polarization of the beam is rotated by the electrooptically induced refractive index change. The output analyzer converts this polarization rotation into intensity modulation. With the use of the approximations $n_e \cong n_o \cong n$ and $r_{33} = 3r_{31}$, where n_e and n_o are the refractive indices along and perpendicular to the poling direction, r is the electrooptic tensor, and subscripts 3 and 1 represent the perpendicular and parallel directions to the film, the electrooptic coefficient can be obtained by eq 1, where I_m is the amplitude of the detected modulation

$$r_{33} = \frac{3\lambda I_m \sqrt{n^2 - \sin 2\theta}}{4\pi V_m I_c n^2 \sin 2\theta} \qquad (1)$$

and I_c is the dc intensity of the output beam (Figure 3).

Discussion

To attain high poling voltage breakdown thresholds, the polymer must be of a high enough molecular weight[9] to enhance mechanical toughness through interchain entanglements. The breakdown voltage is also particularly susceptible to low molar mass impurities such as solvents, as well as any inorganic contaminants. It was shown that the chromophore can be incorporated at molar equivalents of 1:1 with the comonomer MMA while still maintaining amorphous morphology. The drying procedure was optimized to ensure negligible solvent concentrations while preventing chromophore thermal decomposition. Careful fabrication and good film quality ensured high dielectric strength material, enabling high poling voltages to be attained.

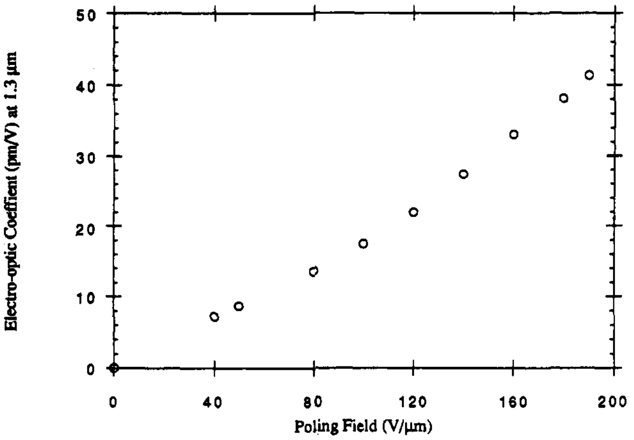

Figure 3. Electrooptic coefficient of poled thin-film indoline nitroazobenzene methacrylate/MMA copolymer as a function of poling field. Measured at 1.3 μm.

Figure 3 illustrates the electrooptic coefficients of a poled film as a function of poling voltage. The results show that extremely high electrooptic coefficients of up to 42 pm/V measured at 1.3 μm can be obtained. By either increasing the poling voltage or the number density of the chromophore, optimization of the material and processing should increase this value further.

Conclusions

The indoline nitroazobenzene chromophore has been shown to exhibit a large electrooptic coefficient, when incorporated as a side-chain unit in a methacrylate copolymer. Key factors in enabling high electrical poling fields to be applied across the thin film were identified as being film toughness and purity. These were optimized to allow routine poling at up to 190 V/μm which corresponded to an electrooptic coefficient of 42 pm/V when measured at 1.3 μm.

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[9] McCulloch, I. A.; Man, H. T.; Song, K. *J. Appl. Polym. Sci.*, in press.