Epoxy-Based Nonlinear Optical Polymers from Post Azo Coupling Reaction

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ABSTRACT: A series of novel second-order nonlinear optical (NLO) polymers have been developed based on a precursor polymer prepared from the diglycidyl ether of Bisphenol A and aniline. The precursor polymer was postfunctionalized by azo coupling reaction and tricyanovinylation to form a number of NLO polymers with different conjugation lengths and electron acceptors. Post azo coupling reaction enabled the introduction of chromophores and extension of the conjugation lengths of the chromophores to take place in a single-step reaction. The chromophores introduced in the polymer system through covalent bonding not only define the NLO properties but also significantly modify other physical properties of the polymers. In this work, the correlation between chromophore structure and NLO polymer properties was extensively studied and the knowledge base was used to optimize polymer properties at the same time. The d_{33} value of 66 pm/V at 1.542 μm was determined for a representative polymer of the class containing tricyanovinyl azo chromophores. The NLO properties of these polymers exhibit long-term stability at 80 °C.

Nonlinear optical (NLO) polymers have been extensively studied as promising electrooptic materials over the past decade.[1−3] Due to intrinsic properties such as large optical nonlinearities, low dielectric constants, and excellent processibility, NLO polymers are considered candidate materials for application in high-frequency optical modulators and integrated semiconductor−NLO polymer circuits.[4−7] One of the current challenges is to fully exploit tailorability of polymers to design novel NLO materials with optimized properties and to find facile ways to prepare them.

A noticeable trend for preparing NLO polymers in the past few years is to employ postfunctionalization. NLO chromophores are introduced into precursor polymers at the last stage of the NLO polymer preparations; thus the exposure of the NLO chromophores to harsh polymerization conditions can be avoided. Marks et al. reported the postfunctionalization of two kinds of polystyrene derivatives.[8,9] Chloromethylated polystyrene was functionalized with Disperse Red 1 (DR1) and chiral prolinol chromophores by Williamson ether synthesis,[8] while poly(*p*-hydroxystyrene) was directly reacted with tosylated chromophores.[9] Recently, Jen et al. reported on postfunctionalization by tricyanovinylation and Mitsunobu reaction.[10−12] For tricyanovinylation, the polyimides and polyquinolines containing (diethylamino)-benzene moieties were prepared. The precursor polymers were reacted with tetracyanoethylene (TCNE) to introduce the tricyanovinyl (TC) group.[10,11] For Mitsunobu reaction, aromatic polyimides containing aryl hydroxyl groups were prepared, which were reacted with alkyl hydroxyl groups of the NLO chromophores when catalyzed by diethyl azodicarboxylate and triphenylphosphine.[12]

Azo coupling reaction was first used to functionalize a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl)aniline in acetic acid medium by Katz et al.[13] The same precursor polymer has also been used by Amano et al. to prepare a NLO polymer containing dicyanovinyl diazo chromophores through azo coupling reaction in acid medium (e.g., acetic acid and propionic acid).[14] Using an azo coupling reaction to functionalize polymers enables the introduction of NLO chromophores and extension of the conjugation length of the chromophore to take place in the same reaction step. However, the number of polymers which can be dissolved in such an acid medium are limited. To our knowledge, the copolymer mentioned above is the only reported polymer that has been used as a precursor to prepare NLO polymers through azo coupling reaction. In previous studies, we found that azo coupling reaction between polymer and diazonium salt can be carried out in polar organic solvents (e.g., dimethylformamide and dimethylacetamide) with high reaction yield.[15] Therefore, the approach can be extended to numerous precursor polymers with good solubility in polar organic solvents to prepare azo-containing NLO polymers. Direct writing of surface relief gratings has been carried out on azo polymers,[16] and polymers containing azo chromophores have been extensively used as second-order NLO polymers.[4−7] In this study, this method was further extended to synthesize a series of novel epoxy-based azo-containing NLO polymers.
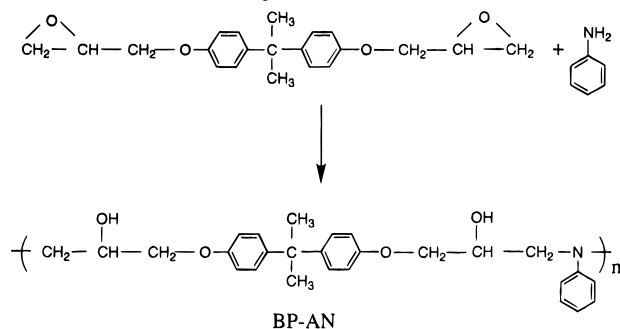
The epoxy-based polymers synthesized in this work provide not only a group of potential electrooptic materials but also a well-characterized system for studying the properties and structure correlation of different NLO chromophores. There are two reasons for the necessity to study such a relationship in polymer systems. First, the optical nonlinearities of chromophores have often been characterized by the hyperpolarizabilities measured through two popular methods: viz., electric field induced second harmonic gener-

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Scheme 1. Synthetic Scheme of the Precursor Polymer BP-AN

BP-AN

Table 1. Polymers Synthesized by Post Azo Coupling Reaction or Tricyanovinylation, the Degree of Functionalization, and Glass Transition Temperature

polymer	deg of func (% ± 3%)	T_g (°C)
BP-1A-NT	93	121
BP-2A-NT	92	135
BP-3A-NT		128
BP-1A-DC	87	114
BP-2A-DC	86	128
BP-AN-TC	90	128
BP-1A-TC	94	140

Scheme 2. Post Azo Coupling Reaction of the Polymer BP-AN To Form NLO Polymers Containing Different Azo Chromophores

ation (EFISH) and hyper-Rayleigh scattering measurements.[17−20] These methods provide a well-defined platform to compare the second-order hyperpolarizabilities of the chromophores. However, it has been shown that the energy levels, the relative contributions of different resonance forms to the ground state, and the molecular geometry of the NLO chromophores will all depend on the medium in which they are embedded.[21−25] Moreover, the bulk NLO properties of the polymer systems also depend on the dynamic process which control the buildup and maintenance of noncentrosymmetric alignment of NLO dyes in polymer matrices.[26−28] Therefore, the hyperpolarizabilities of the chromophores measured in solution may not be appropriate for describing NLO properties of polymers containing these chromophores.[4] Second, the different chromophores introduced into the polymer systems will not only impart the desired NLO response, but as they are covalently bonded to the polymers, other physical properties such as thermal properties and processing features will be affected. Understanding the correlation between structure and properties of NLO polymers is necessary for developing the NLO polymers with optimized properties.

In this paper, post azo coupling reaction and tricyanovinylation were used to synthesize a series of novel epoxy-based polymers containing chromophores with different conjugation lengths and electron acceptors. The structure and properties of synthesized NLO polymers were extensively studied. The effect of chromophore structure on the bulk NLO and other physical properties is discussed in some detail.
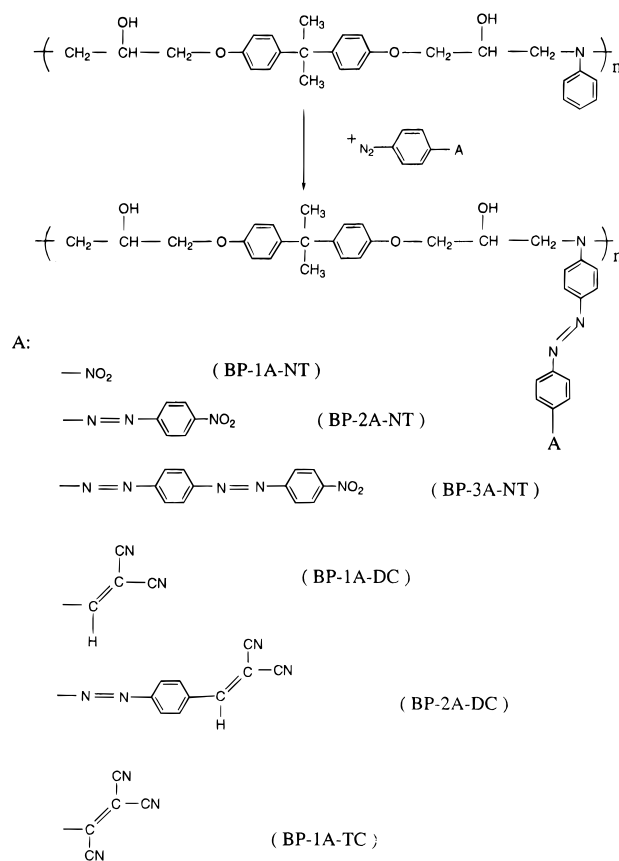
Results and Discussion

Polymer Synthesis and Characterization. The precursor polymer BP-AN was synthesized from diglycidyl ether of Bisphenol A (BP) and aniline (AN) as shown in Scheme 1. Polymerization was carried out at a relatively low temperature (110 °C) to avoid the reaction between the secondary OH groups formed during the polymerization and the unreacted epoxide rings.[29,30] Such a reaction will result in cross-linking and decrease the solubility of the polymer. Low molecular weight oligomers, which are mainly cyclic oligomers, were removed by the fractionation method described in ref 31. The gel permeation chromatography (GPC) characterized number-average molecular weight of the polymer was estimated to be 57 000 with a polydispersity index of 1.57. The precursor polymer BP-AN is a linear polymer with good solubility in polar organic solvents such as dimethylformamide and tetrahydrofuran among others.
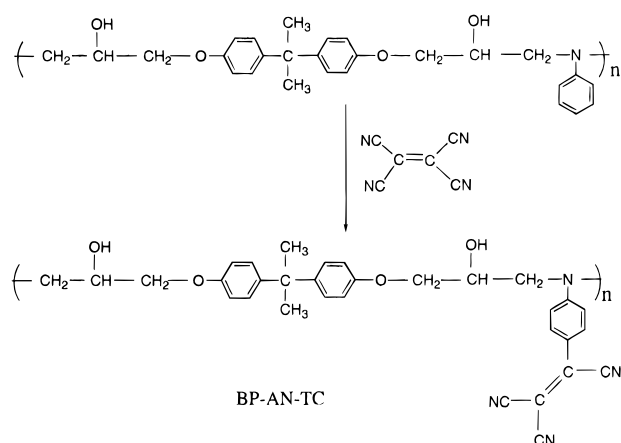
The polymer BP-AN was functionalized to introduce different chromophores at the final stage of the synthetic route. The NLO polymers synthesized in this work are listed in Table 1. The polymer nomenclature includes three parts as described in the following. The first part is an abbreviation of diglycidyl ether of Bisphenol A in order to distinguish them from other epoxy-based polymers. The second part refers to the conjugation system of the chromophores where the numbers represent the number of azo linkages in each chromophore. The third part refers to the different electron acceptors. The tricyanovinyl, dicyanovinyl, and nitro groups are abbreviated as TC, DC, and NT. All of the NLO polymers with azo chromophores were synthesized by post azo coupling reaction (Scheme 2). Polymer BP-AN-TC was synthesized by post tricyanovinylation (Scheme 3). Both diazonium salt and tetracyanoethylene readily attack the benzene ring of the aniline residue at positions with high electron densities. The bulkiness of the attacking groups and resulting steric hindrance control the eletrophilic substitution to take place exclusively at the para position. Strong and sharp CN stretching bands were observed in the range from 2210 to 2230 cm^{-1} from IR spectra of the polymers containing tricyanovinyl (TC) and dicyanovinyl (DC) acceptors. All
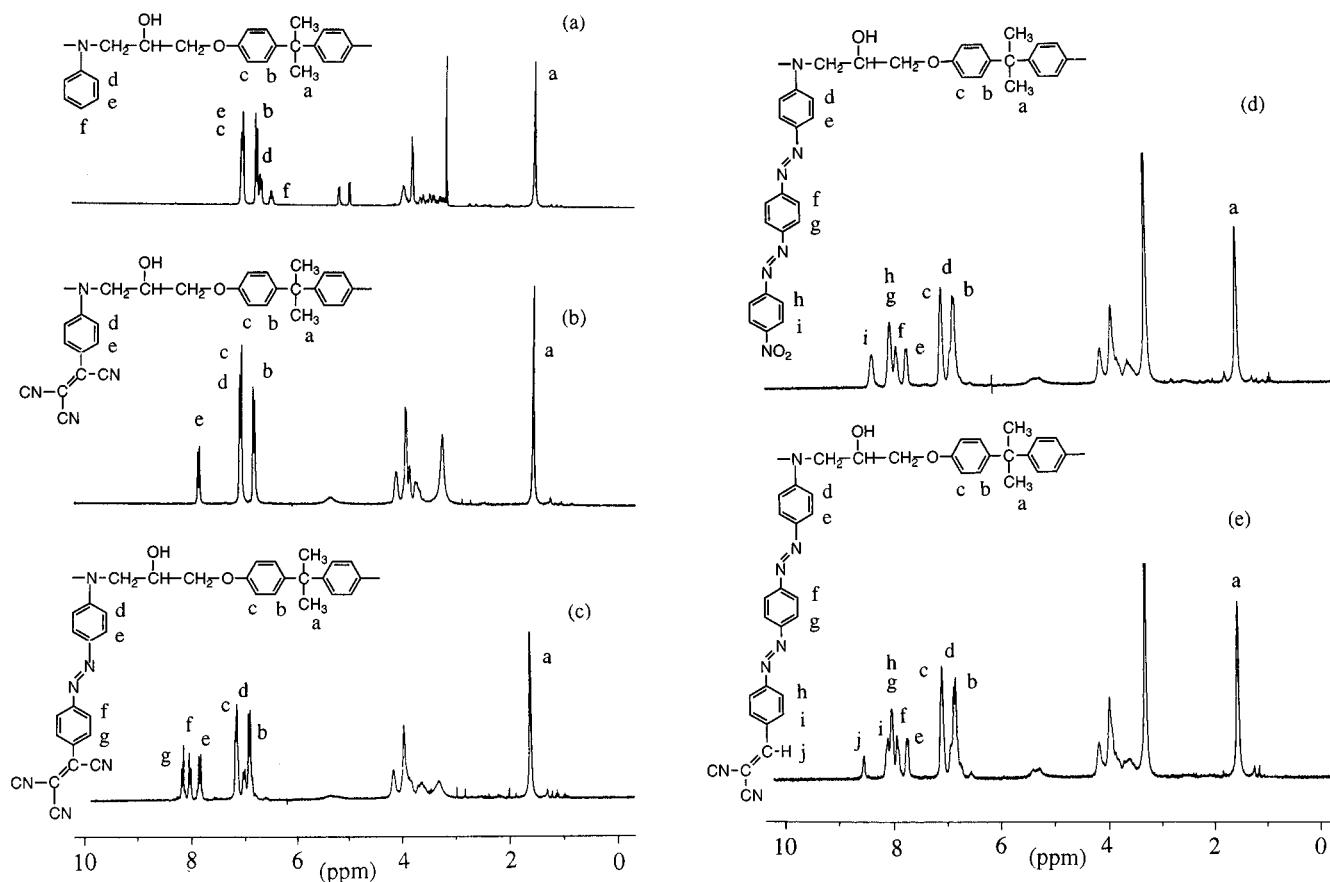
Scheme 3. Post Tricyanovinylation of the Polymer BP-AN To Form BP-AN-TC

azo coupling reaction and tricyanovinylation, the 6.55 ppm resonance corresponding to protons at the para position of the amino group in the aniline moieties almost disappeared. This is a direct evidence of the substitutions that have taken place at the para positions with high yield. Further, the chemical shift of protons ortho and meta to the amino groups shifted to lower magnetic field as a result of the introduction of electron withdrawing groups and increase of conjugation length. Additional resonances corresponding to chemical shifts of introduced benzene ring protons can be seen after the post azo coupling reaction. The degree of functionalization was determined from the peak areas for the proton meta to the amino group in substituted aniline moieties and the peak area at 1.58 ppm (singlet) that corresponds to the methyl protons of Bisphenol A moieties. The degree of functionalization for the polymers was estimated to be about 90% (Table 1).

Thermal Properties. The glass transition temperatures (T_gs) of these polymers were determined by differential scanning calorimetry (DSC). The DSC curves are shown in Figure 2. All these polymers with different acceptors and conjugation lengths show thermal behavior of typical amorphous state. The T_gs of these polymers are listed in Table 1 and compared in Figure 3. The T_gs of the functionalized polymers are much higher than the precursor polymer (87 °C), which is a result of the significant increase in both the size of and the dipole moment of the side groups. For the same conjugation bridge, the polymers containing TC groups have the highest T_g which is mainly due to their strong electron-withdrawing effect and resultant large dipole moment. As a general trend, T_g increases when conju-

of the polymers were carefully purified following the procedure given in the Experimental Section. The structures and purity of the polymers were investigated and confirmed by various spectroscopic methods.

The substituted position and the degree of functionalization were characterized by ^{1}H NMR spectroscopy. Selected NMR spectra of the NLO polymers are shown in Figure 1. Strong resonances at 7.10 (doublet) and 6.84 ppm (doublet) correspond to the chemical shift of the benzene ring protons in the Bisphenol A moieties. For precursor polymer before functionalization (BP-AN), the chemical shifts of the aniline moieties appear at 7.10 (overlapped), 6.76 (doublet), and 6.55 ppm (multiplet), attributed to the protons at meta, ortho, and para positions of the amino groups, respectively. After post

Figure 1. ^{1}H NMR spectra of (a) BP-AN, (b) BP-AN-TC, (c) BP-1A-TC, (d) BP-2A-NT, and (e) BP-2A-DC measured in dimethyl-d_6 sulfoxide.
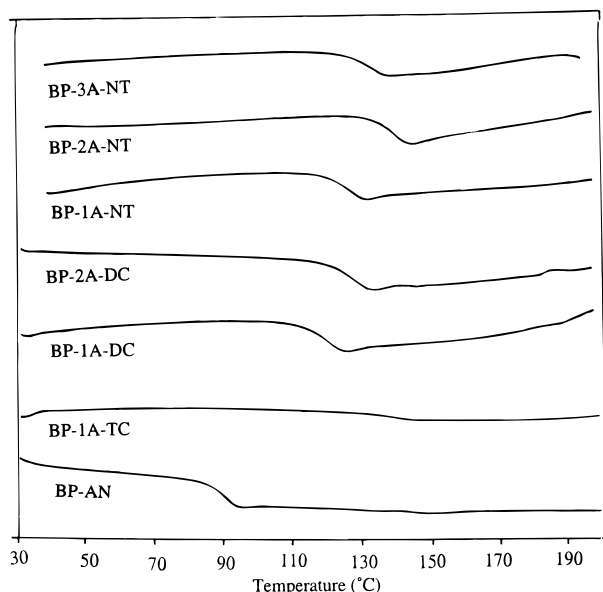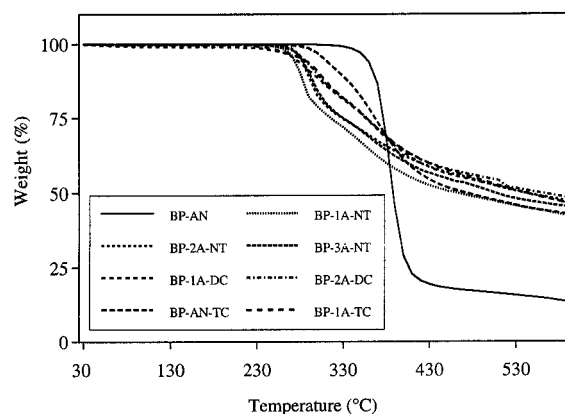
**Figure 2.** DSC thermograms of the epoxy-based polymers with different chromophores.
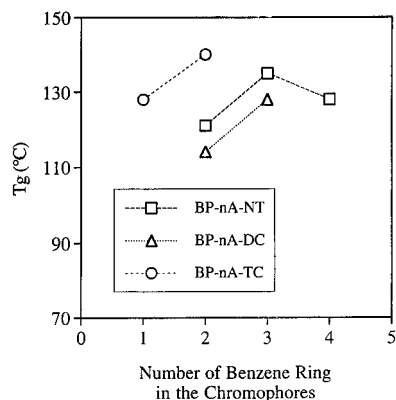
Figure 3. Relationship between the chromophore structure and T_gs of the polymers.

gation length becomes longer for polymers with the same acceptor. However, when side groups become extremely bulky, they prevent tight packing between polymer main chains and result in a T_g decrease. The effect can be clearly seen by comparing the T_gs of BP-2A-NT and BP-3A-NT.

Thermal stability of the polymers was characterized by thermogravimetric analysis (TGA). Representative TGA curves of the epoxy based polymers are shown in Figure 4. The epoxy-based precursor polymer is thermally stable up to 350 °C under a nitrogen atmosphere. After functionalization, the thermal stability of the formed NLO polymers declines. The magnitude of the decrease depends on the type of electron acceptor. For polymers containing azo chromophores with the same acceptor and different conjugation lengths, the decomposition temperature and the shape of TGA curves which exhibit the details of the decomposition process are similar. However, for polymers with different acceptors, the decomposition temperatures and the shape of TGA curves are different. The polymers containing tricyanovinyl or dicyanovinyl azo chromophores such as BP-1A-TC and BP-1A-DC start to lose weight in the temperature range 230–240 °C. This is lower than for polymers containing nitro acceptors, e.g., BP-1A-NT (260 °C). Polymer BP-AN-TC starts to lose mass at 280 °C which is more stable than the corresponding polymers containing azo chromophores.

Figure 4. TGA curves of the epoxy-based polymers with different chromophores.
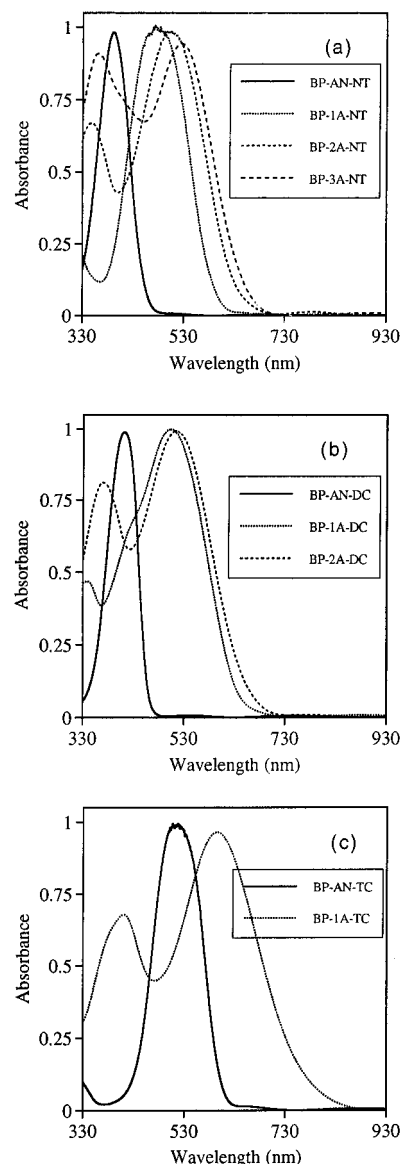
Figure 5. UV–vis absorption spectra of (a) BP-nA-NT, (b) BP-nA-DC, and (c) BP-nA-TC spin-coated films.

Optical and Nonlinear Optical Properties. The UV–vis spectra of the thin films of the series of epoxy based polymers are given in Figure 5. All the polymers exhibit strong absorption in the visible range. For NLO chromophores containing a single benzene ring (e.g., BP-AN-TC), only one strong absorption band due to the π–π^* charger transfer can be observed in the visible
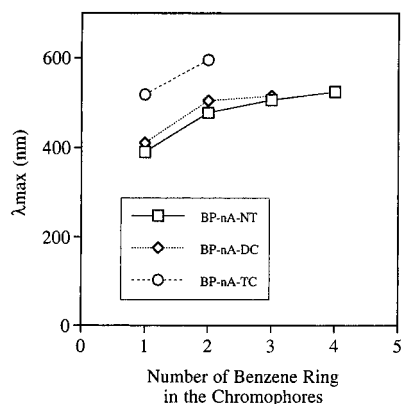
Figure 6. Relationship between the chromophore structure and λ_{max} of the polymers.

Table 2. Second-Order NLO Coefficient, d_{33}, of Some Epoxy-Based NLO Polymers Measured at 1.542 μm

| polymer	order parameter	d_{33} (pm/V)
BP-1A-NT	0.18	28
BP-2A-NT	0.26	42
BP-1A-DC	0.16	38
BP-AN-TC	0.18	27
BP-1A-TC	0.11	66

range. However, for chromophores with larger conjugation length, another absorption band emerges at shorter wavelength in the visible range. As conjugation length increases, the second absorption band exhibits an intensity increase and red shift. The λ_{max} values of all the polymers are compared in Figure 6. Increasing both the conjugation length and electron withdrawing effect results in a red shift of the λ_{max}, which corresponds to a lower transition energy and higher hyperpolarizability. The increase of λ_{max} with conjugation length levels off for longer conjugation lengths. As pointed out by a number of authors, the effort to enhance optical nonlinearity often presents the risk of pushing the optical band edge too near to the operating wavelength of the E-O devices.[4,6] However, if the optical operating wavelength of 1.3 μm is our main consideration for E-O modulation, the absorption of all these polymers is still in the tolerable range.

The noncentrosymmetric alignment of chromophores was achieved by corona poling. The poling was performed at 10−15 °C higher than the T_gs of the polymers. As the angle between the transition dipole moment and ground-state dipole moment for the azo dyes is small, the orientation order parameter Φ can be estimated by measuring the absorbance of an unpoled film (A_0) and of a poled film with light polarized perpendicular to the poling direction ($A_\perp$)[32,33]

$$\Phi = 1 - A_\perp/A_0$$

The orientation order parameters Φ measured by UV−Vis spectroscopy are given in Table 2.

The second-order NLO coefficients (d_{33}), of the epoxy polymers were measured by second harmonic generation. The measurement was performed at a wavelength of 1.542 μm to avoid resonant contribution to the d_{33} values. The results are shown in Table 2. Comparing among the chromophores with the same conjugation bridge, the chromophores functionalized with the tricyanovinyl groups have significantly larger optical nonlinearities as a direct consequence of strong electron-withdrawing effect of the TC group. For chromophores
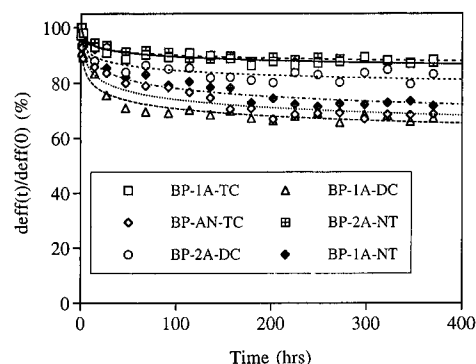
Figure 7. Temporal behavior of poled polymers subjected to heat treatment at 80 °C.

with the same acceptor, the NLO response increases as the conjugation length is extended.

For an electric field poled polymer system, the long-term stability of NLO properties is a critical requirement for real applications. In this study, the temporal stability of the NLO properties was studied by monitoring the SHG signal variation as a function of time and temperature. In our measurement period (1000 h), no SHG intensity decay was observed at room temperature for the polymers prepared in this work. The temporal behavior for the second order nonlinearity at 80 °C is shown in Figure 7. For all of the polymers, after an initial decay, the NLO response of the polymers tends to be stable. The percentage of the SHG signal initial decay and final retention depends on the chromophore structures. Except for extremely long chromophores such as those in BP-3A-NT, which hinder the tight packing of polymer chains and plasticize the material, it appears to be a general tendency that the extended chromophores increase the polymer temporal stability. For BP-1A-TC, 88% retention of the effective NLO coefficient d_{eff} was achieved after 400 h. Meanwhile, for BP-AN-TC, where the chromophore contains the same acceptor and a shorter conjugation bridge, 69% retention was observed. The same tendency was observed for the polymers containing the nitro and dicyanovinyl groups as acceptors. For BP-2A-NT, a diazo chromophore, a decay of about 13% was observed for its initial SHG signal intensities after 400 h at 80 °C compared to 28% decay for BP-1A-NT in the same period. Increasing polarity of the chromophores also plays a role in enhancing the temporal stability of the polymers. The decay of the polymers containing the TC group is obviously smaller than that of the polymers containing the DC and nitro acceptors. Polarity and conjugation length of the chromophores affect both the polymer T_gs and the temporal stability of the chromophore alignment induced by the poling field in the same manner. The explanation for this correlation is not exactly known, but it is believed that for the current system in which the chromophores are directly attached to the polymer main chain, the mechanism is different from that reported for the systems in which chromophores and the polymer main chain are separated by long flexible spacers.[36]

In summary, we have synthesized a series of epoxy-based NLO polymers by post azo coupling reaction and tricyanovinylation of a precursor polymer. The physical properties of the polymers were significantly influenced by the chromophore structure. Except for extremely long chromophores, the polymers containing chromophores with longer conjugation length exhibit larger SHG response and higher temporal stability. The

polymer containing TC-substituted azo chromophores has the largest second-order optical nonlinearity (66 pm/V) and highest temporal stability among them. The polymers possess long-term stability of the optical nonlinearities at 80 °C.

Experimental Section

Characterization. Infrared spectra were measured using a Perkin-Elmer 1720 FT-IR spectrometer by incorporating samples in KBr disks. The UV−vis absorption spectra of the polymers as spin-coated films were determined on a Perkin-Elmer Lambda 9 spectrophotometer. ^{1}H nuclear magnetic resonance (NMR) spectra of polymers in dimethyl-d_6 sulfoxide were obtained on a Bruker ARX 250 MHz FT-NMR spectrometer. The thermal properties of the polymers were investigated with a TA Instrument DSC 2910 and Hi-Res TGA 2950 at a heating rate of 10 °C/min. The molecular weight were determined by gel permeation chromatography (GPC) utilizing a Waters Model 510 pump and a Model 410 differential refractometer with 500-, 10^3-, 10^4-, and 10^5-Å ultrastyragel columns placed in series. Dimethylformamide (containing 0.1 w/v% LiBr) was used as the eluent at a flow rate of 1.0 mL/min.

Materials. Commercially available tetracyanoethylene and 4-((4-nitrophenyl)azo)aniline (DO3) was purified by recrystallization in dry chlorobenzene and toluene prior to reaction. (Tricyanovinyl)aniline (synthetic method based on ref 34), 4-((4-(dicyanovinyl)phenyl)azo)aniline, and 4-[(((4-nitrophenyl)-azo)phenyl)azo]aniline were prepared in our laboratory as described below. All other starting materials, reagents, and solvents, purchased from Aldrich, TCI, and Shell, were used without further purification unless otherwise mentioned. The syntheses of the polymers were carried out according to the reaction schemes shown in Schemes 1−3 as described in detail below.

4-Aminobenzalmalononitrile. 4-Aminobenzaldehyde (12 g, 0.1 mol) and malononitrile (6.6 g, 0.1 mol) were dissolved in ethanol (100 mL). A catalytic mixture of diethylamine (0.125 mL) in acetic acid (0.375 mL) was added to the above solution. The reaction mixture was refluxed for 2 h and then filtered. The precipitate, which was 4-aminobenzalmalononitrile, was washed several times with ethanol. Yield 13.6 g (80%); IR (KBr) 2210 (s, CN), and 1651 (C=C) cm^{-1}.

4-(Tricyanoethyl)aniline. 4-Aminobenzalmalononitrile (3.38 g, 0.02 mol) and potassium cyanide (2.60 g, 0.04 mol) were dissolved in 50% ethanol (50 mL). The mixture was stirred at 90 °C until a homogeneous solution was obtained. The solution was filtered and the filtrate was diluted with 50 mL of water containing 4 mL of acetic acid. The 4-(tricyanoethyl)aniline as crystals slowly precipitated from the solution. IR spectra of the 4-(tricyanoethyl)aniline crystals show a medium absorption at 2915 cm^{-1}, which corresponds to CH stretching in the tricyanoethyl group. The band at 1651 cm^{-1} for 4-aminobenzalmalononitrile has totally disappeared and the 2210 cm^{-1} band of 4-aminobenzalmalononitrile has shifted to 2259 cm^{-1} with a tremendous decrease in the intensity due to the disappearance of conjugation between the C=C and CN groups.

4-(Tricyanovinyl)aniline. 4-(Tricyanoethyl)aniline (3.634 g, 0.0185 mol) and lead tetraacetate (8.867 g, 0.02 mol) were dissolved in acetic acid (40 mL). The solution was stirred at 100 °C for 2 h. 4-(Tricyanovinyl)aniline precipitated out upon cooling to room temperature. The product was further purified by column chromatography using a mixture of dichloromethane and ethyl acetate (1:1 v/v) as eluent. Yield 30%; mp 197−198 °C (DSC); IR (KBr) 2222 (s, CN), 1630 (s, C=C) cm^{-1}; ^{1}H NMR δ 8.01 (d, 2H), 6.94 (d, 2H), 6.83 (s, 2H, NH).

4-(4-(Dicyanovinyl)phenyl)azo)aniline. A diazonium salt of 4-(dicyanovinyl)aniline was prepared by adding an aqueous solution of sodium nitrite (0.4 g, 5.78 mmole in 1 mL of water) dropwise into a solution of 4-(dicyanovinyl)aniline (0.845 g, ca. 5 mmole) in a homogeneous mixture of 0.5 mL of sulfuric acid and 10 mL of glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by addition of 0.5 g of sulfamic acid in a

suitable amount of water. The diazonium salt solution was added dropwise into a solution of aniline (0.93 g, 10 mmol) in 100 mL of formic acid aqueous solution at 0 °C. 4-((4-(Dicyanovinyl)phenyl)azo)aniline was precipitated by slowly adding sodium acetate over a period of 8 h at 0 °C. The solid was collected by filtration and washed with plenty of water until a neutral stage was achieved. The product was further purified by column chromatography using a mixture of hexane and ethyl acetate (1:1 v/v) as eluent. Yield 45%; ^{1}H NMR δ 8.35 (s, 1H), 8.20 (d, 2H), 8.00 (d, 2H), 7.83 (d, 2H), 6.85 (d, 2H).

4-[(((4-Nitrophenyl)(azo)phenyl)azo]aniline. A diazonium salt of 4-((4-nitrophenyl)azo)aniline (DO3) was prepared by adding an aqueous solution of sodium nitrite (0.8 g, 11.56 mmol in 2 mL of water) dropwise into a solution of 4-((4-nitrophenyl)azo)aniline (2.241 g, 10 mmol) in a homogeneous mixture of sulfuric acid (1.6 mL, 98%) and water (20 mL). The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by addition of 1 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of aniline (1.86 g, 20 mmol) in 100 mL of formic acid aqueous solution at 0 °C. 4-[(((4-Nitrophenyl)azo)phenyl)azo]aniline was precipitated by slowly adding sodium acetate of 8 h at 0 °C. The solid was collected by filtration and washed with plenty of water until a neutral stage was achieved. The product was washed with acetone and further purified by column chromatography using a mixture of hexane and tetrahydrofuran (1:1 v/v) as eluent. Yield 20%, ^{1}H NMR: δ 8.49 (d, 2H), 8.20 (d, 2H), 8.16 (d, 2H), 8.04 (d, 2H), 7.84 (d, 2H), 6.85 (d, 2H).

Preparation of BP-AN. Diglycidyl ether of Bisphenol A (7.6 g, 0.02 mol) and aniline (1.86 g, 0.02 mol) were homogeneously mixed under slow heating and polymerized at 110 °C for 48 h. The polymer was fractionated as described in detail in ref 31 to remove low molecular weight oligomers. The typical IR absorption bands of the epoxide groups at 915 and 3058 cm^{-1} have nearly disappeared. The T_g of the polymer was determined to be 87 °C.

Preparation of BP-AN-NT and BP-AN-DC. Via a procedure similar to that described above for the synthesis of BP-AN, diglycidyl ether of Bisphenol A and 4-nitroaniline or 4-(dicyanovinyl)aniline were polymerized in equimolar quantities at 140 °C for 24 h.

Preparation of BP-AN-TC. BP-AN (0.473 g, 1 mmol) was dissolved in dimethylformamide (10 mL) at room temperature. Recrystallized tetracyanoethylene (0.512 g, 4 mmol) was added slowly into the polymer solution in small portions under vigorous stirring. After the addition of tetracyanoethylene, the reaction temperature was raised to 45 °C at which the reaction solution was stirred for 12 h. The solution was subsequently precipitated in water. The precipitate was collected by filtration. The polymer was repeatedly washed with water and further purified by Soxhlet extraction with benzene for 4 h.

Preparation of BP-1A-TC. A diazonium salt of 4-(tricyanovinyl)aniline was prepared by adding an aqueous solution of sodium nitrite (0.04 g, 0.578 mmol in 0.1 mL of water) dropwise into a solution of 4-(tricyanovinyl)aniline (0.1 g, ca. 0.5 mmol) in a homogeneous mixture of 0.05 mL of sulfuric acid and 1 mL of glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by addition of 0.05 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 25 mL of dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-1A-TC was obtained by precipitation of the above solution in water and was washed with plenty of water until a neutral stage was achieved. The polymer was further purified by Soxhlet extraction with chloroform for 4 h.

Preparation of BP-1A-NT and BP-1A-DC. Via a procedure similar to that described above for the synthesis of BP-1A-TC, the diazonium salt of 4-nitroaniline or 4-(dicyanovinyl)-aniline was prepared in sulfuric acid−water (H_2SO_4/H_2O) or hydrochloric acid−acetic acid (HCl/HOAc) mediums, respectively.

Preparation of BP-2A-NT. A diazonium salt of 4-((4-nitrophenyl)azo)aniline was prepared by adding an aqueous solution of sodium nitrite (0.04 g, 0.578 mmol in 0.1 mL of water) dropwise into a solution of 4-((4-nitrophenyl)azo)aniline (0.121 g, ca. 0.5 mmol) in a homogeneous mixture of 0.05 mL of sulfuric acid and 1 mL of glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by addition of 0.05 g of sulfamic acid in a suitable amount of water. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 50 mL of dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-2A-NT was obtained by precipitation of the above solution in water and was washed with plenty of water until a neutral stage was achieved. The polymer was further purified by Soxhlet extraction with acetone for 4 h.

Preparation of BP-2A-DC and BP-3A-NT. Via a procedure similar to that described above for the synthesis of BP-2A-NT, the diazonium salt of 4-((4-dicyanovinyl)phenyl)azo)-aniline or 4-[(((4-Nitrophenyl)azo)phenyl]azo]aniline was prepared in hydrochloric acid−acetic acid (HCl/HOAc) or sulfuric acid−acetic acid (H_2SO_4/HOAc) medium, respectively.

Polymer Film Preparation and Poling. The polymers were dissolved in spectroscopic grade dimethylformamide. The homogeneous solutions were filtered through 0.2 μm membranes. The solutions were spin-coated onto glass slides. The film thickness was controlled to be about 0.5 μm by adjusting the solution concentration (~10 wt %) and the spin speed (800-900 rpm). The spin-coated films were dried under vacuum for 48 h at 50 °C and were stored in a desiccator for further measurements.

Poling was performed by the corona poling technique in a wire to plane arrangement.[33,35] The corona discharge was generated from a tungsten wire which was placed parallel across a 1.0 cm gap above the polymer film. The corona field was applied after the film was slowly heated to 100 °C. The sample was then slowly heated to a temperature 15 °C above the T_g of the polymer. The sample was held at this temperature for an additional 20 min. before cooling.

Nonlinear Optical Property Measurement. The second-order NLO coefficients (d_{33}) of the poled films were measured by second harmonic generation (SHG). The measurements were carried out at 1.542 μm by using a Raman shifter in conjunction with a Q switched Nd:YAG laser at 1.064 μm (Quantel 660A). The SHG signal at 0.771 μm, selected with an interference filter, was detected by a photomultiplier tube and measured with a boxcar integrator. A Y-cut quartz crystal was used as the reference. By comparing the SHG intensity from the poled polymer sample with that from the quartz crystal, the d coefficients of the poled polymers were determined. The refractive indices and thicknesses of the polymer films were measured with an ellipsometer (Rudolph Research) and a profilometer (Dektak IIA), respectively.

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