Epoxy-Based Nonlinear Optical Polymers Functionalized with Tricyanovinyl Chromophores

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Two types of new nonlinear optical polymers have been synthesized by postreaction of an epoxy-based polymer prepared from the diglycidyl ether of bisphenol A and aniline. The new polymers DGEBA-AZO-TCV and DGEBA-AN-TCV were synthesized by azo coupling of the epoxy polymer with 4-(tricyanovinyl)aniline and by reacting the epoxy polymer with tetracyanoethylene, respectively. Using an azo coupling reaction to functionalize the polymer allows introduction of the tricyanovinyl (TCV) group and extension of the conjugation length to take place in a single-step reaction. In both synthetic routes, TCV groups are introduced at the last stage of the polymer preparation, thus preventing the exposure of the TCV chromophores to harsh reaction conditions. The d_{33} values for polymers DGEBA-AN-TCV and DGEBA-AZO-TCV were determined to be 27 and 66 pm/V at 1.542 μm, respectively, after corona poling. The two polymers retained 65% and 83% of the initial d_{33} values after they had been heated at 80 °C for 1000 h.

Introduction

Second-order nonlinear optical (NLO) polymeric materials have been investigated extensively for potential applications in the areas of optical communications and data processing.[1−9] The second-order NLO properties originate from noncentrosymmetric alignment of NLO chromophores incorporated in the poled polymers. Typically, these NLO chromophores consist of electron-donating and accepting groups connected by conjugating π-electron systems. Chromophores with higher NLO susceptibilities can be obtained either by increasing electron-donating and/or -accepting effect or by extending the conjugation length between the donors and acceptors.[10−12] Several theoretical studies on the structure and property relationships in NLO molecules have been reported.[11,12] For practical use, chromophores need to be integrated in polymer matrixes in a manner that desired bulk properties, such as thermal stability, optical properties, processability, etc., can be achieved. Even though tremendous effort has been made in this area, the stringent requirements for real applications have yet to be completely achieved. Novel synthetic approaches to prepare designed polymers as well as simultaneous optimization of their properties are indeed essential in the development of new NLO polymeric materials.

For the design and synthesis of more efficient NLO chromophores, the tricaynovinyl (TCV) group is a good candidate as a substituent due to its strong electron-withdrawing ability.[13,14] A number of chromophores containing TCV groups have been investigated for enhanced optical nonlinearity.[15−17] Chromophores with TCV substituents have also been incorporated into a number of NLO polymeric systems.[16,18−20] Tamura et al. have synthesized poly[5-(*N*-carbazolyl)pentyl methacrylate] which was subsequently reacted with tetracyanoethylene (TCNE) to tricyanovinylate the carbazole units.[18] With 20% of tricyanovinylated carbazole units,

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(1) Chemla, D.; Zyss, J. *Nonlinear Optical Properties of Organic Materials and Crystals*; Academic Press: Orlando, FL, 1987; Vol. 1, 2.

(2) Prasad, P.; Williams, D. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley and Sons: New York, 1991.

(3) Zyss, J. *Molecular Nonlinear Optics; Materials, Physics and Devices*; Academic Press: Orlando, FL, 1987, 1994.

(4) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.

(5) Eaton, D. F. *Science* **1991**, *253*, 281.

(6) Zyss, J. *J. Mol. Electron.* **1985**, *1*, 25.

(7) Ulrich, D. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 3.

(8) Boyd, G. *J. Opt. Soc. Am. B* **1989**, *6*, 685.

(9) Möhlmann, G. *Synth. Met.* **1990**, *37*, 207.

(10) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.

(11) (a) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Gorman, C. B.; Gilmour, S.; Biddle, S. L.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, *115*, 2524. (b) Mayers, F.; Marder, S. R.; Pierce, B. M.; Bredas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703. (c) Bourhill, G.; Bredas, J. L.; Cheng, L. T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc.* **1994**, *116*, 2619.

(12) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(13) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561.

(14) Katz, H. E.; Dirk, C. W.; Schilling, M. L.; Singer, K. D.; Sohn, J. E. In *Nonlinear Optical Properties of Polymer*; Heeger, A. J., Orenster, J., Ulrich, D. R., Eds.; Material Research Society: Pittsburgh, 1988; Vol. 109, pp 127−131.

(15) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.

(16) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Miller, R. D. *Proc. SPIE* **1994**, *2285*, 17.

(17) Rao, V. P.; Wong, K. Y.; Jen, A. K. Y.; Drost, K. J. *Chem. Mater.* **1994**, *6*, 2210.

(18) Tamura, K.; Padias, A. B.; Hall, H. K.; Peyghambarian, N. *Appl. Phys. Lett.* **1992**, *60*, 1803.

(19) (a) Jen, A. K.-Y.; Liu, Y.-J.; Cai, Y.; Rao, V. P.; Dalton, L. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2711. (b) Jen, A. K.-Y.; Cai, Y.; Drost, K. J.; Liu, Y.-J.; Rao, V. P.; Chen, T.-A.; Mininni, R. M.; Kenney, J. T. *Polym. Mater. Sci. Eng.* **1995**, *72*, 213.

(20) Drost, K. J.; Jen, K. Y.; Drzewinski, M. A. *Polym. Prepr.* (*Am. Chem. Soc. Div. Polym. Chem.*) **1994**, *35*, 252.

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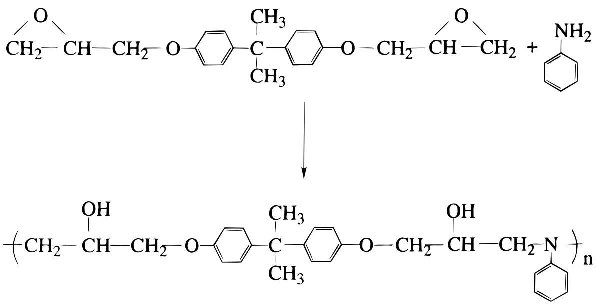
the resulting photorefractive polymer showed the electrooptical coefficient (r_{33}) of 6.1 pm/V. Jen et al. synthesized polyimides containing (*N*,*N*-diethylamino)benzene moieties. The polymers were post-tricyanovinylated by treating with TCNE. An r_{33} of 15 pm/V was reported for one of the polymers.[19] Drost et al. have also reported on the synthesis of poly(styrene-*co*-imide) systems functionalized with TCV-based chromophores. The tricyanovinylation was carried out on the thiophene moieties pendant from main chains.[20] The synthetic methods mentioned above were all carefully designed to incorporate the TCV group into polymers in the final step. Therefore, harsh environments such as high temperature during the imidization process and free radicals from polymerization process were avoided.[19,20]

As shown above, the most common technique to introduce a TCV functionality for NLO polymers is by post-tricyanovinylation. However, this technique has encountered some limitation. TCNE is an electrophile that will readily attack an aromatic ring only at positions with high electron densities forming TCV functionalities at these positions.[21,22] Our attempts to introduce a TCV group at the para position of an azo dye, 4-(*N*,*N*-dimethyl)aminophenylazobenzene, and of a similar chromophore incorporated in an epoxy-based polymer resulted in a very low degree of functionalization. Even with the help of catalysts such as pyridine and silver nitrate,[23] the results of the tricyanovinylation were unsatisfactory. Although direct tricyanovinylation with TCNE has been reported to be successful on chromophores with short conjugation length[19] and those with heterocyclic rings,[17,20] this technique is obviously not a cure-all to prepare various kinds of tricyanovinyl-functionalized chromophores.

Katz et al. have reported an azo coupling reaction performed on a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl)aniline.[24] An isolated diazonium salt was added to an acetic acid solution of the copolymer to allow the functionalization of an azo dye to the copolymer. In this study, we found that the azo coupling reaction between polymers and diazonium salts can also be carried out in polar organic solvents, such as dimethylformamide (DMF), with high reaction yields. In our experiments, the azo coupling reaction was performed by adding a diazonium salt solution directly into a polymer/DMF solution. Due to the good solubility of a number of polymers in polar organic solvents, the azo coupling reaction can be performed on the polymers, such as epoxy-based polymers and polyimides containing aniline moieties.

In this study, a post-azo-coupling reaction was used to prepare NLO polymers containing azobenzene chromophores with the TCV group. Our approach involved an azo coupling reaction between 4-(tricyanovinyl)aniline and an epoxy polymer containing aniline moieties. This synthetic route can significantly extend the conjugated bridge in an azo chromophore and attach the TCV group in a single-step reaction. In addition, TCV groups are introduced at the last stage of the polymer preparation thus preventing the exposure of the TCV chromophore to harsh reaction conditions. This method is a facile way to incorporate different azo dyes into polymers forming NLO polymers. Using both the post-azo-coupling reaction and the post-tricyanovinylation procedure, two kinds of epoxy-based NLO polymers have been prepared. The design, synthesis and characterization of these materials are reported.

Scheme 1. Synthetic Scheme of the Polymer DGEBA-AN



DGEBA-AN

Results and Discussion

The synthetic route for polymer (DGEBA-AN) is shown in Scheme 1. The polymer was synthesized from diglycidyl ether of bisphenol A (DGEBA) and aniline (AN). In general, the reactivity between an amino group and an epoxide group increases when the basicity of the amine increases.[25,26] The nucleophilicity of aniline used in this reaction is larger than that of chromophores such as 4-nitroaniline or 4-(4′-nitrophenylazo)phenylamine used in our previous studies.[27,28] Therefore the preparation of DGEBA-AN could be carried out at a relatively low temperature. The polymerization temperature was kept below 110 °C in order to avoid a reaction between the secondary −OH groups formed during the polymerization and the unreacted epoxide rings.[25,26,29] Such a side reaction can form ether linkages leading to cross-linking and decrease the solubility of the polymer. DGEBA-AN was further fractionated as previously described in order to remove low molecular weight oligomers that are mainly cyclic oligomers.[29] DGEBA-AN is a linear polymer with good solubility in solvents such as dimethylformamide and tetrahydrofuran.

DGEBA-AN was transformed into DGEBA-AN-TCV and DGEBA-AZO-TCV at the final stage of the synthesis route by tricyanovinylation with TCNE (Scheme 2) and by azo coupling reaction with 4-(tricyanovinyl)aniline (Scheme 3), respectively. The reactions were carried out in homogeneous solutions. Both TCNE and the diazonium salt of (tricyanovinyl)aniline readily attacked benzene rings at positions with high electron density. The bulkiness of both compounds makes steric hindrance a dominant factor that dictates the electrophilic substitution to take place exclusively at the para position.

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(21) McKusick, B. C.; Heckert, R. E.; Cairns, T. L.; Coffman, D. D.; Mower, H. F. *J. Am. Chem. Soc.* **1958**, *80*, 2806.

(22) Dhar, D. N. *Chem. Rev.* **1967**, *67*, 611.

(23) Roland, J. R.; Mckusick, B. C. *J. Am. Chem. Soc.* **1961**, *83*, 1652.

(24) Schilling, M. L.; Katz, H. E.; Cox, D. I. *J. Org. Chem.* **1988**, *53*, 5538.

(25) Rozenberg, B. A. *Adv. Polym. Sci.* **1986**, *75*, 113.

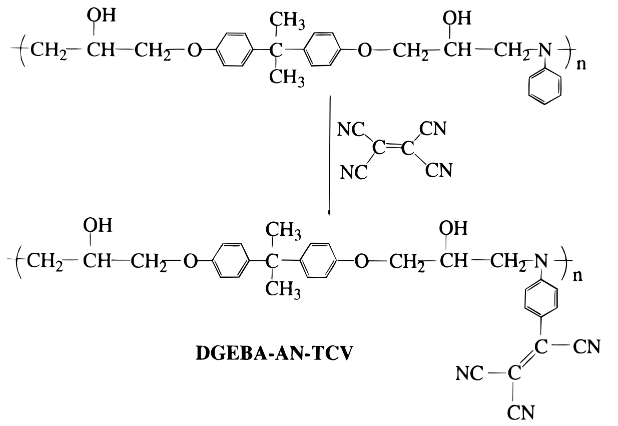
(26) Oleinik, E. F. *Adv. Polym. Sci.* **1986**, *80*, 49.

(27) Mandal, B. K.; Jeng, R. J.; Kumar, J.; Tripathy, S. K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 607.

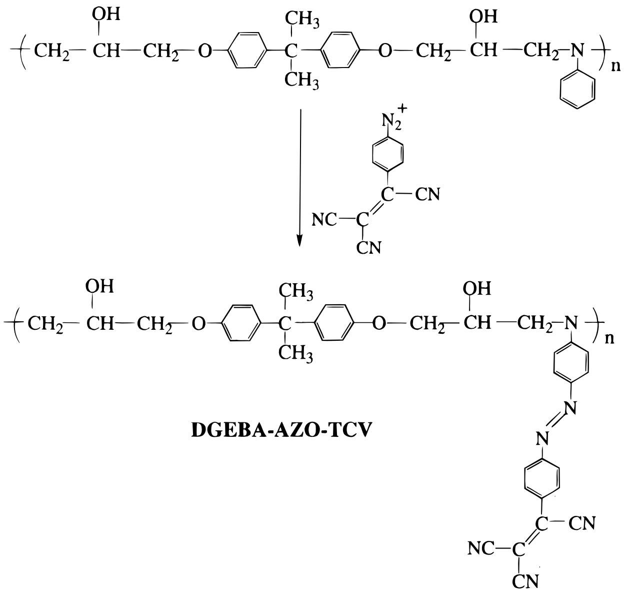
(28) Jeng, R. J.; Chen, Y. M.; Kumar, J.; Triphathy, S. K. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 1115.

(29) Klee, J. K.; Hagele, K.; Przybylski, M. *Macromol. Chem. Phys.* **1995**, *196*, 937.

Scheme 2. Post-tricyanovinylation of the Polymer DGEBA-AN To Form DGEBA-AN-TCV



Scheme 3. Azo Coupling of the Polymer DGEBA-AN with 4-(Tricyanovinyl)aniline



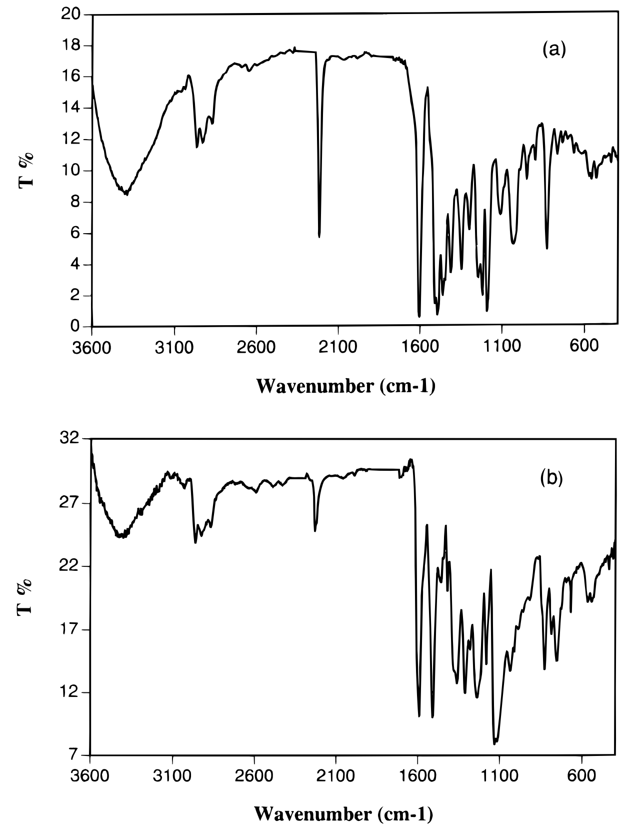


Figure 1. Infrared spectra of (a) DGEBA-AN-TCV and (b) DGEBA-AZO-TCV.

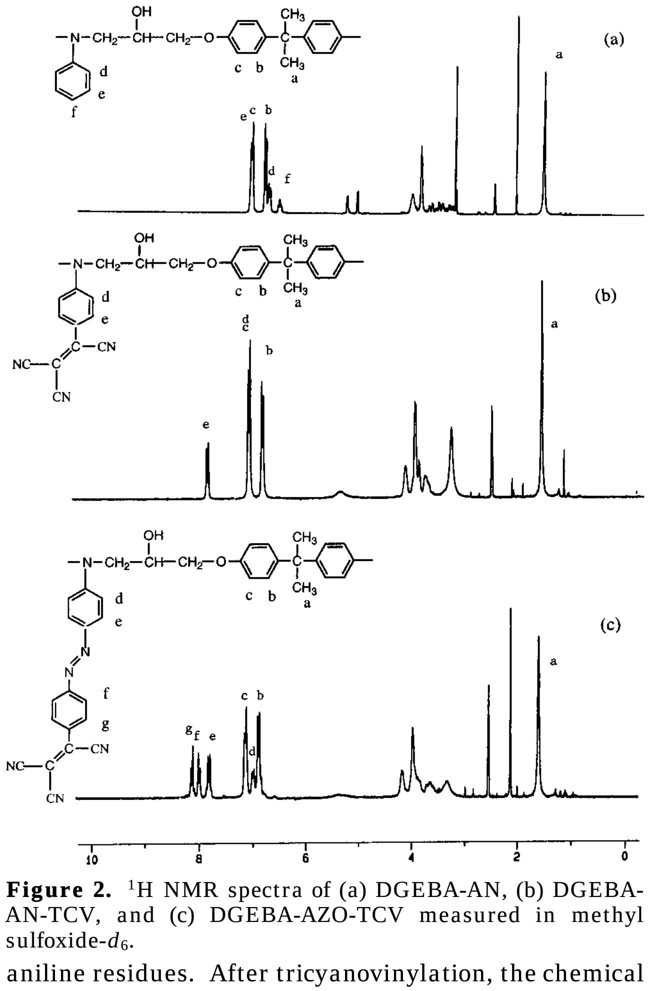


Figure 2. ^1H NMR spectra of (a) DGEBA-AN, (b) DGEBA-AN-TCV, and (c) DGEBA-AZO-TCV measured in methyl sulfoxide-d_6.

The IR spectra of DGEBA-AN-TCV and DGEBA-AZO-TCV are shown in Figure 1. Strong −CN stretching bands were observed at 2217 and 2230 cm^{-1} for DGEBA-AN-TCV and DGEBA-AZO-TCV, respectively. The strong absorption bands of the −CN group attest to the incorporation of the tricyanovinyl group on both polymers. Due to the conjugation of the −CN to C=C bonds in the TCV groups, the −CN absorption peaks for both polymers appeared at lower wavenumbers than those for alkyl nitriles (2250−2245 cm^{-1}).[30]

The polymer structures before and after the tricyanovinylation and the azo-coupling reaction as well as the degree of functionalization were characterized by ^1H NMR spectroscopy (Figure 2). DGEBA-AN has strong resonance at 7.10 ppm (doublet), which corresponds to overlapped chemical shifts of benzene ring protons in both bisphenol A and aniline moieties. The bisphenol A moieties have another resonance at 6.84 ppm (doublet). The resonances appearing at 6.76 ppm (doublet) and 6.55 ppm (triplet) correspond to benzene ring protons ortho and para to the amino group in aniline residues. After tricyanovinylation, the chemical shift of benzene protons meta to the amino group in

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[30] Lin-Vien, D.; Colthup, N. B.; Falteley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, 1991.

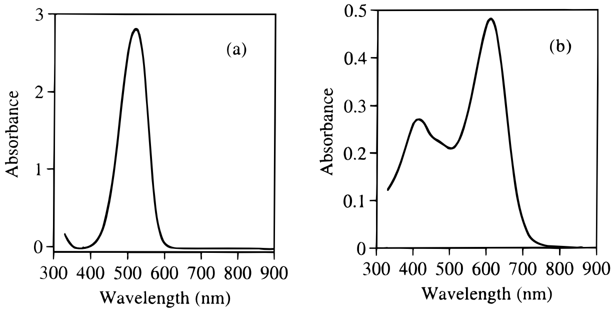

Figure 3. UV/vis absorption spectra of (a) DGEBA-AN-TCV and (b) DGEBA-AZO-TCV.

DGEBA-AN-TCV shifted to lower magnetic field at 7.89 ppm (doublet) as a result of the strong electron-withdrawing effect from the TCV group. The degree of functionalization was determined to be 90% based on the peak area at 7.89 ppm and the area at 1.58 ppm (singlet) that correspond to the methyl protons of bisphenol A moieties. For DGEBA-AZO-TCV, the resonance of benzene protons meta to the amino group shifted to 7.79 ppm (doublet) after the azo-coupling reaction. Two additional resonances were observed at 7.97 ppm (doublet) and 8.10 ppm (doublet) for aromatic protons at the meta and ortho positions to the TCV group. Similarly, the degree of azo-coupling reaction was calculated to be 94% for DGEBA-AZO-TCV by using the peak areas at 7.79 and 1.58 ppm.

The UV−vis spectra of DGEBA-AN-TCV and DGEBA-AZO-TCV are shown in Figure 3. DGEBA-AZO-TCV which was functionalized with azobenzene chromophores has much longer λ_{max} (610 nm) than DGEBA-AN-TCV (λ_{max} at 518 nm) which has a chromophore consisting a single tricyanovinylated benzene ring, corresponding to a lower transition energy between the ground and excited states. It has been experimentally and theoretically illustrated that a longer λ_{max} (i.e., lower transition energies) is often directly associated with an enhanced second-order NLO response.[31,32] Therefore, it is expected that DGEBA-AZO-TCV prepared from the azo-coupling reaction will exhibit a significantly higher second order NLO susceptibility than DGEBA-AN-TCV prepared from post-tricyanovinylation. In addition to the strong absorption at 610 nm, another weak absorption at around 400 nm was also observed in DGEBA-AZO-TCV. The ratios of the absorbance of this minor peak and that of the λ_{max} were different when DGEBA-AZO-TCV was in solution or in spin-coated films. Similar phenomena have been observed by Singer et al. for a low molecular weight azo dye containing a TCV group.[33]

The DSC curves of DGEBA-AN, DGEBA-AN-TCV, and DGEBA-AZO-TCV are compared in Figure 4. The T_g's of these polymers are determined to be 89, 127, and 140 °C, respectively. For a side-chain polymer, variation in the T_g of the polymer incorporating an NLO dye depends on the distance between the chromophore and the backbone as well as the dipole moment of the chromophore.[20] Generally, the T_g of a polymer with a given chromophore decreases with the increase of incorporation ratio for long spacers and slightly increases for a short spacer.[20,34,35] In our case, the chromophores are considered to be directly incorporated on the main chain. Significant increase of the T_g's for both DGEBA-AN-TCV and DGEBA-AZO-TCV compared to that for DGEBA-AN is mainly a result of a significant increase in the size of and the dipole moment of the side group.

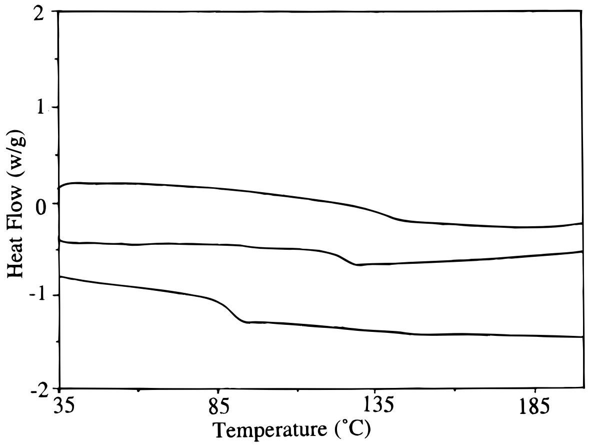

Figure 4. DSC thermograms of DGEBA-AZO-TCV (top), DGEBA-AN-TCV (middle), and DGEBA-AN (bottom).

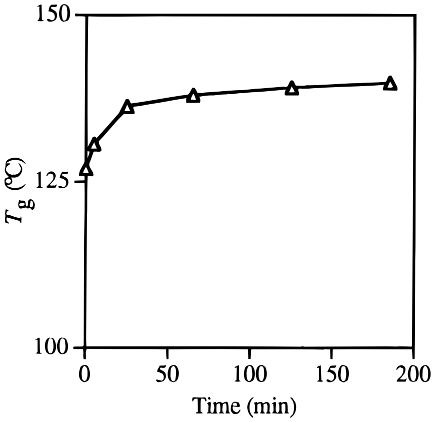

Figure 5. T_g of DGEBA-AN-TCV as a function of time at 180 °C.

The T_g's of both polymers slowly increased when they were subjected to thermal treatment. In the case of DGEBA-AN-TCV, T_g increased from 127 to 140 °C when the polymer was subjected to an isothermal heating at 180 °C for 1 h. However, no significant increase of the T_g was observed when the polymer was subjected to an additional 2 h of isothermal heating (see Figure 5). One possible explanation of the T_g increase was a result of the reaction between residual epoxy rings at the polymer chain ends and the pendant secondary −OH groups. Therefore, poling at a temperature above T_g can help in increasing the molecular weight and hence stabilize the chromophore orientation induced during the poling process.

The noncentrosymmetric orientation of chromophores was achieved by the corona poling process to impart the

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(31) Cheng, L. T.; Tam, W.; Stevenson, S. H.; Meredith, G. R. *J. Phys. Chem.* **1991**, *95*, 10631.

(32) Burland, D. M.; Rice, J. E.; Stähelin, M. *Mol. Cryst. Liq. Cryst.* **1992**, *216*, 27.

(33) Legrange, J. D.; King, L. A.; Kuzyk, M. G.; Singer, K. D.; Katz, H. E. Schilling, M. L. In *Nonlinear Optical Properties of Polymer*; Heeger, A. J., Orenster, J., Ulrich, D. R., Eds.; Material Research Society: Pittsburgh, 1988; Vol. 109, pp 133−138.

(34) Robello, D. R. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1.

(35) Zhao, M.; Bautista, M.; Ford, W. T. *Macromolecules* **1991**, *24*, 844.

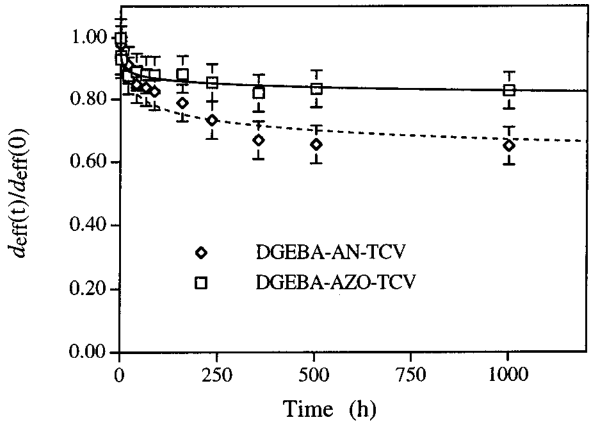

Figure 6. Temporal behavior of the poled DGEBA-AN-TCV and DGEBA-AZO-TCV subjected to heat treatment at 80 °C.

Table 1. Second-Order NLO Coefficient, d_{33}, of DGEBA-AN-TCV and DGEBA-AZO-TCV at 1.542 μm

polymer	d_{33} (pm/V)
DGEBA-AN-TCV	27
DGEBA-AZO-TCV	66

second-order NLO properties.[36] The samples were characterized by UV/vis spectroscopy[37,38] before and after poling. It was found in our experiments that the largest orientational order parameter was achieved when the sample was heated stepwise to a temperature approximately 15 °C higher than its T_g.

The second-order NLO coefficients, d_{33}, of both DGEBA-AN-TCV and DGEBA-AZO-TCV as shown in Table 1 were measured at 1.542 μm to avoid resonant enhancement of the NLO properties. The d_{33} values of the two polymers containing TCV chromophores DGEBA-AN-TCV and DGEBA-AZO-TCV were determined to be 27 and 66 pm/V, respectively. These results clearly showed that chromophores functionalized with the TCV groups significantly increase the optical nonlinearities of epoxy-based NLO polymers.[27,28] The larger NLO responses of DGEBA-AZO-TCV compared to that of DGEBA-AN-TCV is a direct result of the extended conjugation length of the chromophore in the former.

The temporal stability of the NLO properties of the poled polymers was studied by monitoring the SHG signal. The SHG intensities of both DGEBA-AN-TCV and DGEBA-AZO-TCV were stable at room temperature for as long as the measurement was carried out (1000 h). The temporal behavior of the second order optical nonlinearity at 80 °C is shown in Figure 6. After an initial decay of 10% observed within 24 h, the NLO response of DGEBA-AZO-TCV tends to be stable. An 83% retention of the effective NLO coefficients, d_{eff}, was achieved when the poled DGEBA-AZO-TCV sample was subjected to heat treatment for over 1000 h. For DGEBA-AN-TCV, an initial decay of the NLO response was also observed in a similar fashion as that in DGEBA-AZO-TCV. However, only 65% of the initial d_{eff} value was retained when the polymer was heat treated under the same conditions as that of DGEBA-AZO-TCV. We believe that the extended chromophore in DGEBA-AZO-TCV not only plays a major role in the larger second-order optical nonlinearities but also contributes to the improved stability of the poled alignment.

In summary, we have synthesized two kinds of NLO epoxy-based polymers by post-tricyanovinylation and azo-coupling reaction of an epoxy polymer. The polymers exhibit very large second-order nonlinearities which are relatively stable at 80 °C. The technique using azo-coupling reaction to functionalize the polymer at the final stage is a versatile way to the synthesis of aromatic azo polymers for NLO applications.

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 either in acetone or as spin-coated films were determined on a Perkin-Elmer Lambda 9 spectrophotometer. ^{1}H nuclear magnetic resonance (NMR) spectra of polymers in methyl sulfoxide-d_6 were obtained on an Bruker 250 MHz FT-NMR spectrometer. The thermal properties of the compounds were investigated with a TA Instrument DSC 2910 at a heating rate of 10 °C/min.

Materials. Commercially available tetracyanoethylene was purified by recrystallization in dry chlorobenzene prior to reaction. (Tricyanovinyl)aniline was prepared in our laboratory as described below (based on ref 21). All other starting materials, reagents, and solvents, purchased from Aldrich, TCI, and Shell, were used without further purification unless otherwise mentioned. The syntheses of polymers were carried out according to the reaction schemes shown in Schemes 1−3 as described in detailed 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, 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 (2.6048 g, 0.04 mol) was 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 C=C and −CN groups.

4-(Tricyanovinyl)aniline. 4-(Tricyanoethyl)aniline (3.6346 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 (C=C) cm^{-1}; ^{1}H NMR δ 8.01 (d, 2H), 6.94 (d, 2H), 6.83 (s, 2H, N−H).

Preparation of DGEBA-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 36 h. The polymer was fractionated as described in detail in ref 29 to remove low molecular weight oligomers. The typical IR absorption bands of the expoxide groups at 915 and 3058 cm^{-1} have nearly disappeared. The T_g of the polymer was determined to be 89 °C.

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(36) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248.

(37) Cahill, P.; Singer, K.; King, L. *Opt. Lett.* **1989**, *14*, 1137.

(38) Cahill, P.; Tallant, D.; Kowalczyk, T.; Singer, K. *Proc. SPIE* **1991**, *1560*, 130.

Preparation of DGEBA-AN-TCV. DGEBA-AN (0.473 g, 0.001 mol) was dissolved in dimethylformamide (10 mL) at room temperature. Recrystallized tetracyanoethylene (0.5123 g, 0.004 mol) 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 was further purified by Soxhlet extraction with benzene for 4 h.

Preparation of DGEBA-AZO-TCV. 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 0.08 mL of sulfuric acid and 1 mL of glacial acetic acid. The mixture was stirred at 20 °C for 5 min before the excess nitrous acid was decomposed by an addition of 0.05 g of sulfamic acid in 1 mL of water. The diazonium salt solution was added dropwise into a solution of DGEBA-AN (0.1892 g, 0.4 mmol) in 25 mL *N*,*N'*-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. DGEBA-AZO-TCV 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.

Polymer Film Preparation and Poling. The polymers were dissolved in spectroscopic grade *N*,*N'*-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 room temperature and were stored in a desiccator for further measurements.

Poling was performed by the corona poling technique in a wire-to-plane arrangement.[39,40] 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 comparison of 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 indexes and thicknesses of the polymer films were measured with an ellipsometer (Rudolph Research) and a profilometer (Dektak IIA), respectively.

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(39) Eich, M.; Rech, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.

(40) Mortazavi, M. A.; Knoesen, A.; Kowell, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733.