# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
September 18, 1996

3. REPORT TYPE AND DATES COVERED
technical; 01JUNE 95 to 30SEPT96

4. TITLE AND SUBTITLE
Epoxy Based Nonlinear Optical Polymers from Post Azo-Coupling Reaction

5. FUNDING NUMBERS
C: N00014-90-J-1148
R&T Code: 4132016
Dr. Kenneth J. Wynne

6. AUTHOR(S)
X. Wang, J. Kumar, S.K. Tripathy, L. Li, J.-I. Chen, S. Marturunkakul

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, MA 01854

8. PERFORMING ORGANIZATION REPORT NUMBER
1148-96-04

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research-Physical S&T Division, ONR 331
Department of the Navy
Arlington, Virginia 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United States Government.
This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

A series of novel second order nonlinear optical (NLO) polymers have been developed based on a precursor polymer prepared from the diglycikyl ether of Bisphenol A and aniline. The precursor polymer was post-functionalized by azo coupling reaction and tricyanovinylation to form a number of NLO polymers with diferent conjugateion lengths and electrom 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 cobalent 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 $\mu$m was determined for a representative polymer of the calss containing tricyanovinyl azo chromophores. The NLO properties of these polymers exhibit long term stability at 80 °C.

14. SUBJECT TERMS
Epoxy based; nonlinear optical polymers; post azo coupling reaction.

15. NUMBER OF PAGES
33

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

19961016 046

**OFFICE OF NAVAL RESEARCH**

GRANT N0014-95-1-1292

R&T Code 3102134---01

Scientific Officer: Dr. Kenneth Wynne

Technical Report No. 96-04

# Epoxy Based Nonlinear Optical Polymers from Post Azo-Coupling Reaction

by

X. Wang, J. Kumar, S.K. Tripathy, L. Li, J.-I. Chen, S. Marturunkakul

Submitted to

Macromolecules

University of Massachusetts Lowell
Department of Chemistry
Lowell, Massachusetts

September 18, 1996

# Epoxy Based Nonlinear Optical Polymers from Post Azo-Coupling Reaction

Xiaogong Wang, Jayant Kumar#, and Sukant K. Tripathy*
Center for Advanced Materials, Departments of Chemistry and Physics#,
University of Massachusetts Lowell, Lowell, MA 01854

Lian Li, Jeng-I Chen, Sutiyao Marturunkakul
Molecular Technologies Inc., Lowell, MA 01886

## 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 post-functionalized 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.

---

* To whom correspondence should be addressed

Non-linear 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 post-functionalization. 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 condition can be avoided. Marks et al. reported the post functionalization of two kinds of polystyrene derivatives.[8,9] The chloromethylated polystyrene was functionalized with Disperse Red 1 (DR1) and the chiral prolinol chromophores by Williamson ether synthesis,[8] while the poly(para-hydroxystyrene) was directly reacted with tosylated chromophores.[9] Recently, Jen et al. reported on post functionalization by tricyanovinylation and Mitsunobu reaction.[10-12] For tricyanovinylation, the polyimides and polyquinolines containing N,N-diethylamino-benzene moieties were prepared. The precursor polymers were reacted with tetracyanoethylene (TCNE) to introduce the tricyanovinyl (TCV) 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-(hydroxylethyl)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, 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 have 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 not only provide 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 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 generation (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 ground state and the molecular geometry of 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 build up and maintenance of non-centrosymmetric 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 crosslinking and decrease the solubility of the polymer. Low molecular weight oligomers, that 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 57000 with a polydispersity index of 1.57. Precursor polymer named as 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 (TCV) and dicyanovinyl (DCV) acceptors.

The substituted position and the degree of functionalization were characterized by $^1H$ NMR spectroscopy. Selected NMR spectra of the NLO polymers are shown in Figure 1. Strong resonances at 7.10 ppm (doublet) and 6.84 ppm (doublet) correspond to chemical shift of benzene ring protons in Bisphenol A moieties. For precursor polymer before functionalization (BP-AN), the chemical shifts of aniline moieties appear at 7.10 ppm (overlapped), 6.76 ppm (doublet) and 6.55 ppm (multiplet), attributed to the protons at meta, ortho, and para positions of amino groups respectively. After post azo coupling reaction and tricyanovinylation, the 6.55 ppm resonance corresponding to protons at para position of amino group in 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 amino group in substituted aniline moieties and the peak area at 1.58 ppm (singlet) that correspond 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 ($T_g$s) 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 $T_g$ of these polymers are listed in Table 1 and compared in Figure 3. The $T_g$s of the functionalized polymers are much higher than the precursor polymer (87°C), which is a result of the significant increase both in the size of and the dipole moment of the side groups. For the same conjugation bridge, the polymers containing TCV 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 conjugation length become 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 $T_g$s 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 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 decomposed 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.

## Optical and Non-linear Optical Properties

The UV-Vis spectra of the thin films of the series of epoxy based polymers are given in Figure 5. All the polymer 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 $\pi$-$\pi^*$ charger-transfer can be observed in the visible range. However, for chromophores with larger conjugation length, another absorption band emerges at shorter wavelength in the visible range. As conjugation length increase, the second absorption band exhibits intensity increase and red shift. The $\lambda_{max}$ of all the polymers are compared in Figure 6. Increasing both the conjugation length and electron withdrawing effect result in red shift of the $\lambda_{max}$, which correspond to a lower transition energy and higher hyperpolarizability. The increase of $\lambda_{max}$ 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 are still in tolerable range.

The noncentrosymmetric alignment of chromophores were achieved by the corona poling. The poling was performed at 10-15 °C higher than the $T_g$s 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 $\Phi$ 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 $\Phi$ 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 TCV group. For chromophores with the same acceptor, the NLO response increase as the conjugation length is extended.

For electric field poled polymer system, the long-term stability of NLO properties is a critical requirement for real application. 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 hours), 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 BP-AN-TC and BP-1A-TC, after an initial decay, the NLO response of the polymers tend to be stable. The percentage of the SHG signal initial decay and final retention depends on the chromophore structures. For BP-1A-TC, 91% retention of the effective NLO coefficient $d_{eff}$ was achieved after 235 hours. Meanwhile, For BP-AN-TC where the chromophore contains the same acceptor and a shorter conjugation bridge, 86% retention was observed. It appears that the extended chromophores in BP-1A-TC play a role in increasing polymer temporal stability. The same tendency can be observed for the polymer containing the nitro group as acceptor. For BP-2A-NT, a diazo chromophore, no decay was observed at 80 °C and SHG signal intensities are stable at the initial level for 235 hours. It is interesting to notice that the initial decay of polymers containing TCV group is larger than polymers containing DCV and nitro acceptors, even though the Tg of BP-1A-TC is the highest. A possible explanation is that a part of initial decay for polymers containing TCV groups is due to the dissipation of the static dipole moment in the NLO molecules which is induced by the deposited charges on the film surface.[33]

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. The polymers containing chromophores with longer conjugation length exhibit larger SHG response and higher temporal stability. The polymer containing TCV substituted azo chromophores has the largest second order optical nonlinearity (66 pm/V) 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 methyl sulfoxide-$d_6$ 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, Model 410 differential refractometer with 500-, $10^3$-, $10^4$-, and $10^5$-Å ultrastyragel columns placed in series. Dimethylformamide (containing 0.1 wt/v% LiBr) was used as the eluent at a flow rate of 1.0 mL/min.

### Materials

Commercially available tetracyanoethylene and 4-(4-nitrophenylazo) -aniline (DO3) was purified by recrystallization in dry chlorobenzene and toluene prior to reaction. Tricyanovinylaniline (synthetic method based on ref. 34), 4-(4-dicyanovinylphenylazo)aniline and 4-[4-(nitrophenyl)-1-phenylazo]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 synthesis of polymers were carried out according to the reaction schemes shown in Schemes 1, 2, and 3 as described in detail below.

### 4-Aminobenzalmalononitrile

4-Aminobenzaldehyde (12 g, 0.1 mole) and malononitrile (6.6 g, 0.1 mole) 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 mole) and potassium cyanide (2.6048 g, 0.04 mole) 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 C=C and -CN groups.

### 4-Tricyanovinyl-aniline

4-Tricyanoethyl-aniline (3.6346 g, 0.0185 mole) and lead tetraacetate (8.867 g, 0.02 mole) 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).

### 4-(4-Dicyanovinylphenylazo)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 water) dropwise into a solution of 4-dicyanovinyl aniline (0.845 g, c.a. 5 mmole) in a homogeneous mixture of 0.5 ml sulfuric acid and 10 ml glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by an addition of 0.5 g of sulfamic acid in suitable amount of water. The diazonium salt solution was added dropwise into a solution of aniline (0.93 g, 10 mmole) in 100 ml formic acid aqueous solution at 0 °C. 4-(4-Dicyanovinylphenylazo)aniline was precipitated by slowly adding sodium acetate in period of 8 h at 0 °C. Solid was collected by filtration and was washed with plenty of water until 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)-1-phenylazo]aniline

A diazonium salt of 4-(4-nitrophenylazo)aniline (DO3) was prepared by adding an aqueous solution of sodium nitrite (0.8 g, 11.56 mmole in 2 ml water) dropwise into a solution of 4-(4-nitrophenylazo)aniline (2.241 g, 10 mmole) 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 an addition of 1 g of sulfamic acid in suitable amount of water. The diazonium salt solution was added dropwise into a solution of aniline (1.86 g, 20 mmole) in 100 ml formic acid aqueous solution at 0 °C. 4-[4-(Nitrophenyl)-1-phenylazo]aniline was precipitated by slowly adding sodium acetate in period of 8 h at 0 °C. Solid was collected by filtration and was washed with plenty of water until 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 mole) and aniline (1.86 g, 0.02 mole) 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 $cm^{-1}$ and 3058 $cm^{-1}$ have nearly disappeared. The Tg of the polymer was determined to be 87 °C.

## Preparation of BP-AN-NT and BP-AN-DC

Via a similar procedure to that described above for the synthsis of BP-AN. Diglycidyl ether of Bisphenol A and equal molar 4-nitroaniline or 4-dicyanovinylaniline polymerized at 140 °C for 24 h.

## Preparation of BP-AN-TC

BP-AN (0.473g, 1 mmole) was dissolved in dimethylformamide (10 ml) at room temperature. Recrystallized tetracyanoethylene (0.5123 g, 4 mmole) 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 12h. 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 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 mmole in 0.1 ml water) dropwise into a solution of 4-tricyanovinyl aniline (0.1 g, c.a. 0.5 mmole) in a homogeneous mixture of 0.05 ml sulfuric acid and 1 ml glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by an addition of 0.05 g of sulfamic acid in suitable amount of water. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmole) in 25 ml N,N'-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 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 similar procedure to that described above for the synthesis of BP-1A-TC. The diazonium salt of 4-nitroaniline or 4-dicyanovinylaniline was prepared in sulfuric acid-water ($H_2SO_4/H_2O$) or hydrochromic acid-acetic acid(HCl/HOAc) mediums respectively.

### Preparation of BP-2A-NT

A diazonium salt of 4-(4-nitrophenylazo)aniline was prepared by adding an aqueous solution of sodium nitrite (0.04 g, 0.578 mmole in 0.1 ml water) dropwise into a solution of 4-(4-nitrophenylazo)aniline (0.121 g, c.a. 0.5 mmole) in a homogeneous mixture of 0.05 ml sulfuric acid and 1 ml glacial acetic acid. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by an addition of 0.05 g of sulfamic acid in suitable amount of water. The diazonium salt solution was added dropwise into a solution of BP-AN

(0.1892 g, 0.4 mmole) in 50 ml N,N'-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 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 similar procedure to that described above for the synthesis of BP-2A-NT. The diazonium salt of 4-(4-Dicyanovinylphenylazo)aniline or 4-[4-(Nitrophenyl)-1-phenylazo]aniline was prepared in hydrochromic 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 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 (~10wt%) 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 desiccater 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 *Tg* 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.

## Acknowledgments

Partial funding from ONR and NSF is gratefully acknowledge.

## References

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. 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. *Chemical Reviews* **1994**, *94*, 31.
5. 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.

6. Dalton, L. R.; Harper, A. W.; Wu, B.; Ghosn, R.; Laquindanum, J; Liang, Z.; Hubbel, A.; Xu, C. *Adv. Mater.* **1995**, *7*, 519.

7. Marks, T. J. and Ratner, M. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155.

8. Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1987**, *20* , 2322.

9. Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1988**, *21*, 2901.

10. (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.

11. Chen, T.; Jen, A. K.-Y; Cai, Y. *Chem. Mater.* **1996**, *8*, 607.

12. Chen, T.; Jen, A. K.-Y; Cai, Y. *J. Am. Chem. Soc.* **1995**, *117*, 7295.

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

14. Amano, M.; Hikita, M.; Shuto, Y.; Watanabe, T.; Tomaru, S.; Yaita, M.; Nagatsuma, T. *SPIE* **1994**, *2143*, 68.

15. Wang, X.; Li, L.; Chen, J.; Marturunkakul, S.; Kumar, J.; Tripathy, S. K. "Epoxy Based Nonlinear Optical Polymers Functionalized with Tricyanovinyl Chromophores" to be published, *Chem. Mater.*

16. Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166.

17. Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572.

18. Teng, C. C.; Garito, A. F. *Phys. Rev.* **1983**, *28*, 6766.

19. Clays, K.; Persoons, A.; De Maeyer, L. *Adv. Chem. Phys.* **1994**, *85*, 455.

20. Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.

21. Mayers, F.; Marder, S. R.; Pierce, B. M.; Bredas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703.

22. Willetts, A. and Rice, J. E. *J. Chem. Phys.* **1993**, *99*, 426.

23. Mikkelsen, K. V.; Luo, Y.; Ågren, H.; Jørgensen, P. *J. Chem. Phys.* **1994**, *100*, 8240.

24. Yu, J.; Zerner, M. C. *J. Chem. Phys.* **1994**, *100*, 7487.

25. Bella, S. D.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 4440.

26. Wang, H.; Jarnagin, R. C. and Samulski, E. T. *Macromolecules* **1994**, *27*, 4705.

27. Dirk, C. W.; Devanathan, S.; Velez, M.; Ghebremichael, F.; Kuzyk, M. G. *Macromolecules* **1994**, *27*, 6167.

28. Goodson III, T.; Gong, S. S. and Wang, C. H. *Macromolecules*, **1994**, *27*. 4278.

29. Rozenberg, B. A. *Adv. Poly. Sci.* **1986**, *75*, 113.

30. Oleinik, E. F. *Adv. Poly. Sci.* **1986**, *80*, 49.

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

32. Page, R.; Jurich, M.; Reck, B.; Sen, A.; Twieg, R.; Swalen, J.; Bjorklund, G.; Willson, C. *J. Opt. Soc. Am. B* **1990**, *7*, 1239.

33. Mortazavi, M.; Knoesen, A.; Kowel, S.; Higgins, B.; Dienes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733.

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

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

# Figure and Table Captions

Scheme 1. Synthetic scheme of the precursor polymer BP-AN.

Scheme 2. Post Azo coupling reaction of the polymer BP-AN to form NLO polymers containing different azo chromophores

Scheme 2. Post tricyanovinylation of the polymer BP-AN to form BP-AN-TC.

Table 1. Polymers synthesized by post azo coupling reaction or tricyanovinylation, the degree of functionalization and glass transition temperature.

Table 2 Second order NLO coefficient, $d_{33}$, of some epoxy based NLO polymers measured at 1.542 mm

Figure 1. $^{1}$H NMR spectra of (a) BP-AN, (b) BP-AN-TC, and (c) BP-1A-TC, (d) BP-2A-NT, (e) BP-2A-DC measured in methyl sulfoxide-$d_6$.

Figure 2. DSC thermograms of the epoxy based polymers with different chromophores.

Figure 3. Relationship between the chromophore structure and $T_g$s of the polymers.

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, (c) BP-nA-TC spin coating film.

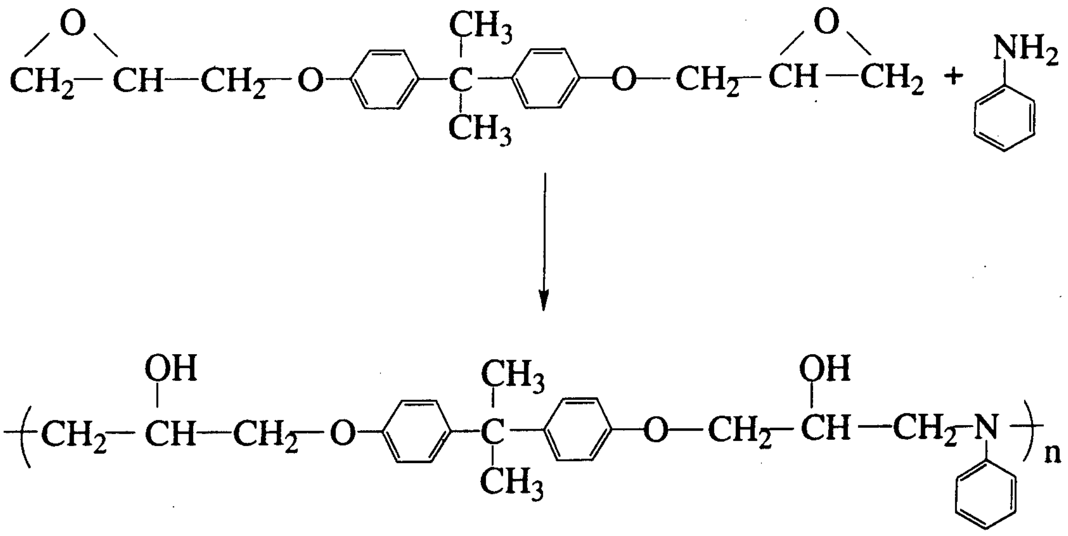
Figure 6. Relationship between the chromophore structure and $\lambda_{max}$ of the polymers.

Figure 7. Temporal behavior of a group of the poled polymers subjected to heat treatment at 80 °C.

| Polymer | Degree of Functionalization (%) | Tg (°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 |

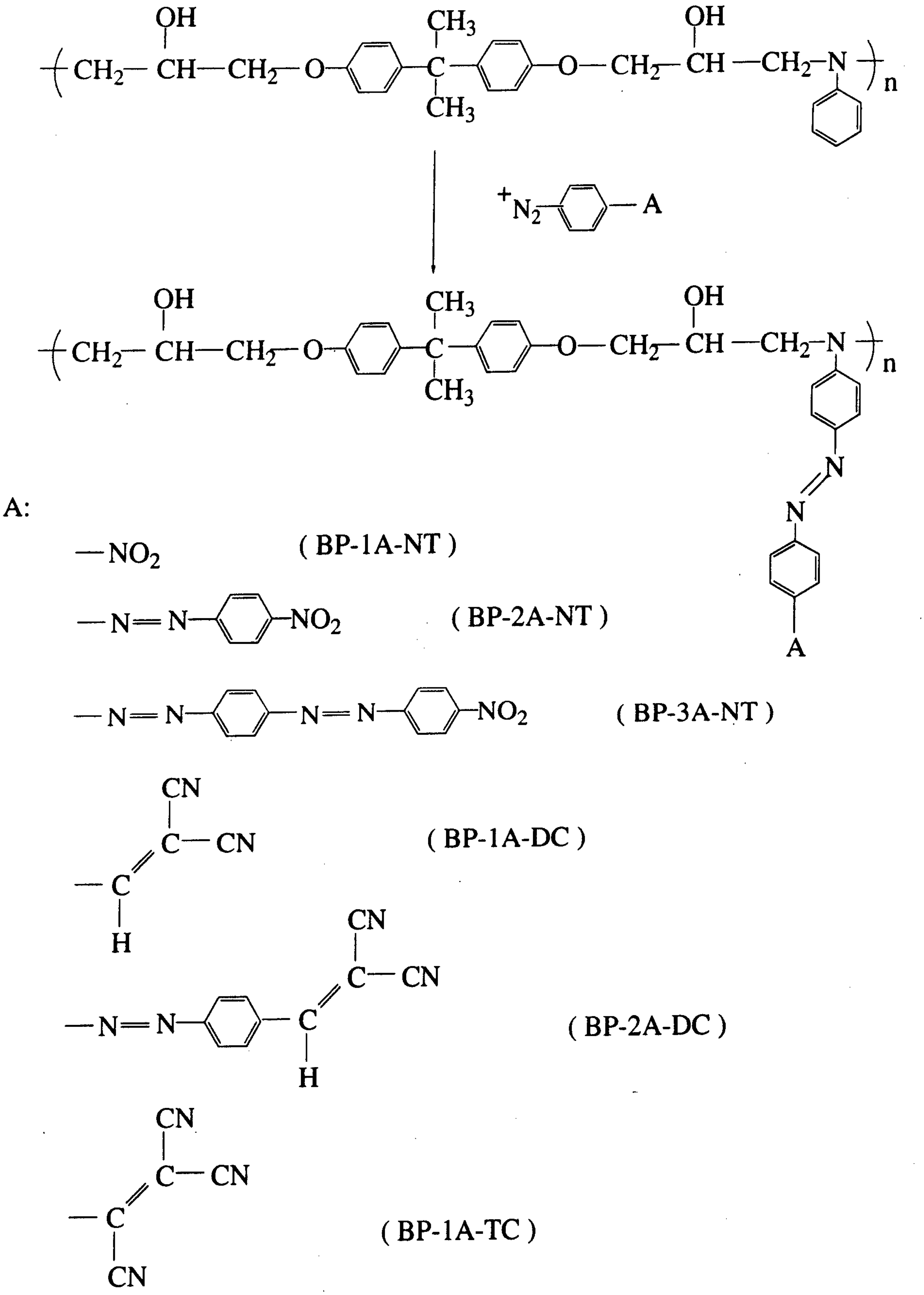
| Polymer | Order Parameter | $d_{33}$ (pm/V) |
|---|---|---|
| BP-1A-NT | 0.18 | 28 |
| BP-2A-NT | 0.26 | 42 |
| BP-1A-DC | 0.16 | 38 |
| BP-AN-TC | 0.18 | 27 |
| BP-1A-TC | 0.11 | 66 |

Tab 1, 2

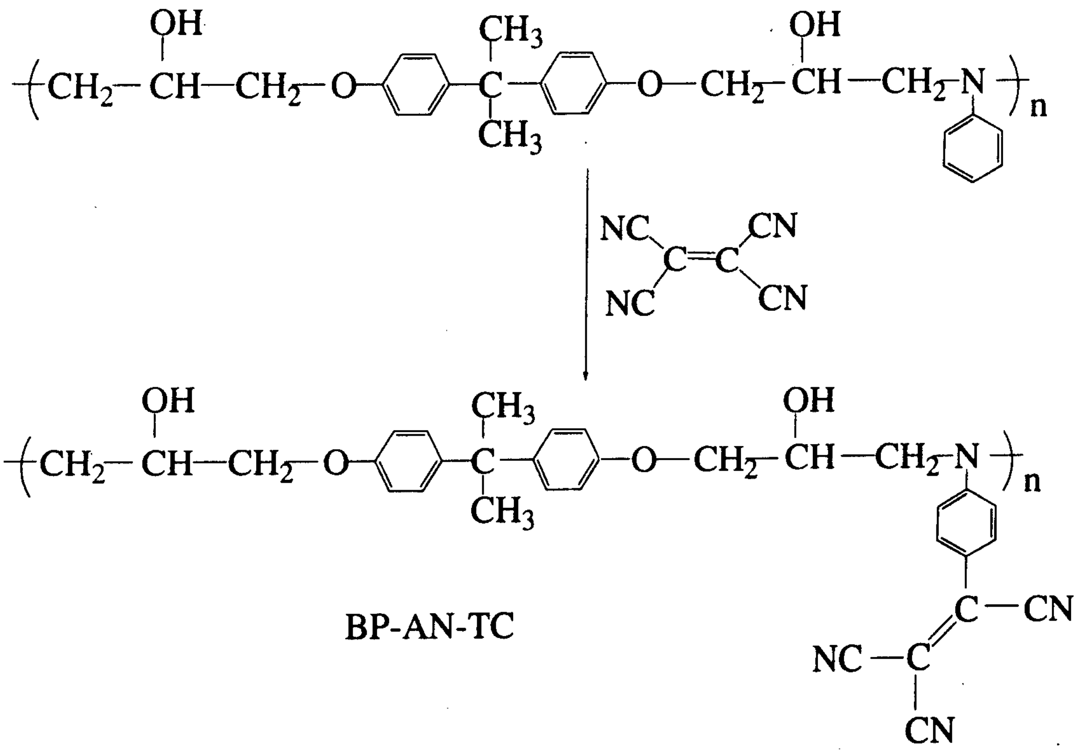


BP-AN

Scheme 1



Scheme 2



BP-AN-TC

Scheme 3 -

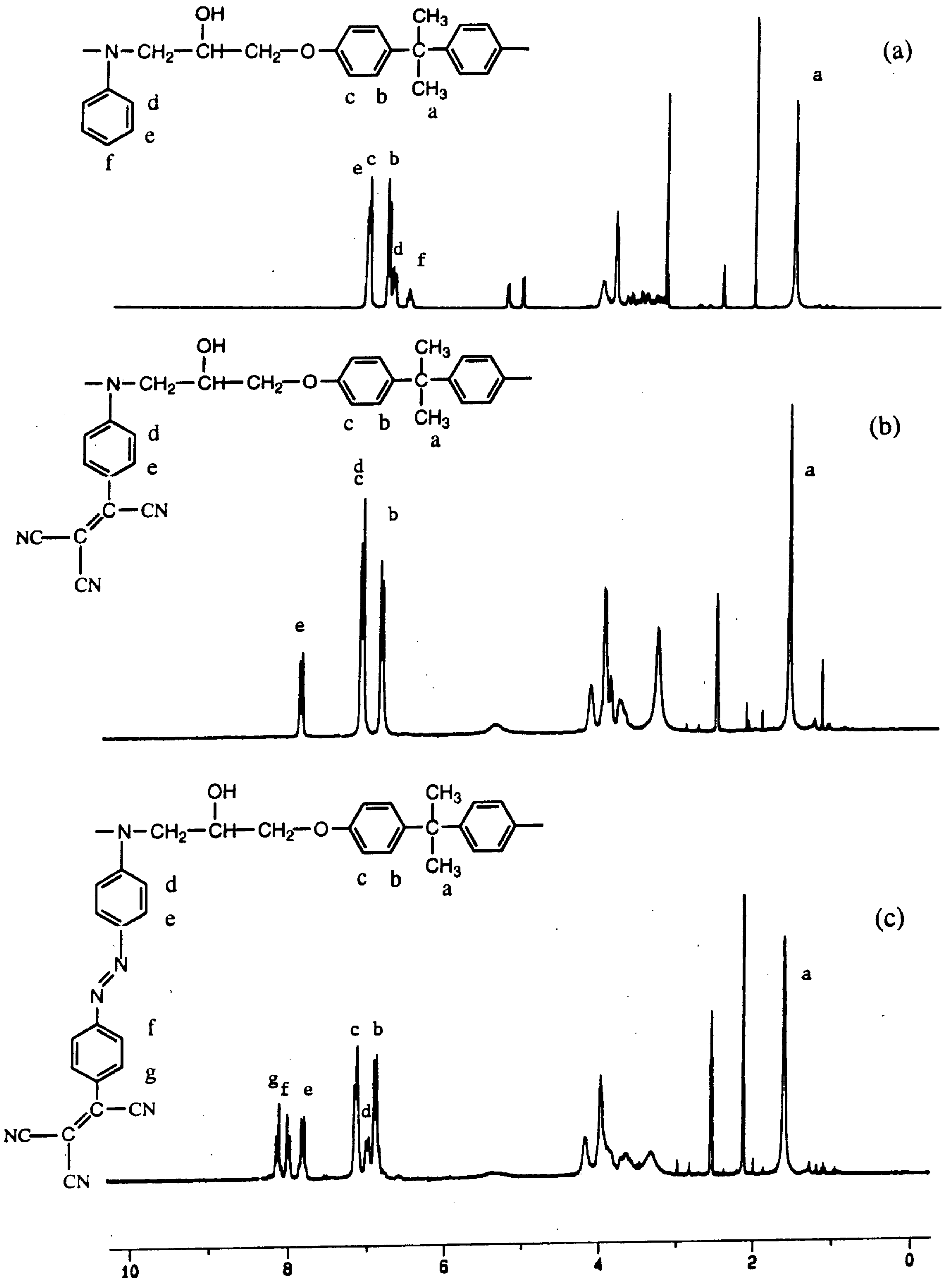

OH
CH3
—N—CH2—CH—CH2—O—
CH3
c b a
d
e
f
(a)
a
e c b
d f
(b)
d
c
b
e
C—CN
NC—C
CN
(c)
N
N
f
g
g f e
c b
d
10
8
6
4
2
0

Figure 1

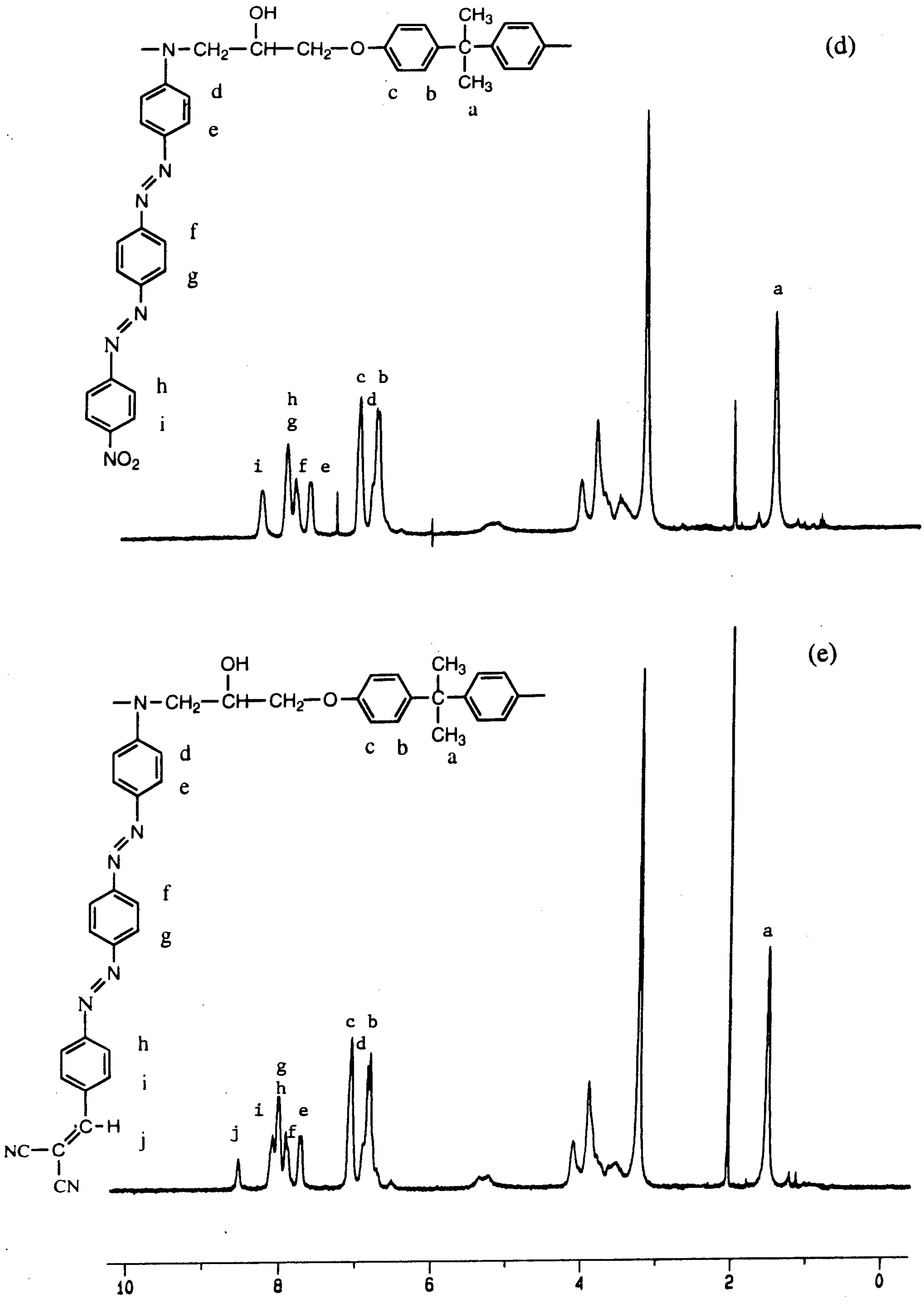

OH
CH3
–N–CH2–CH–CH2–O–
CH3
(d)
c b a
d e f g h i
NO2
a
c b
h g d
i f e
OH
CH3
–N–CH2–CH–CH2–O–
CH3
(e)
c b a
d e f g h i j
C–H
NC–C
CN
a
c b
g d
h
i e
j f
10
8
6
4
2
0

Figure 1

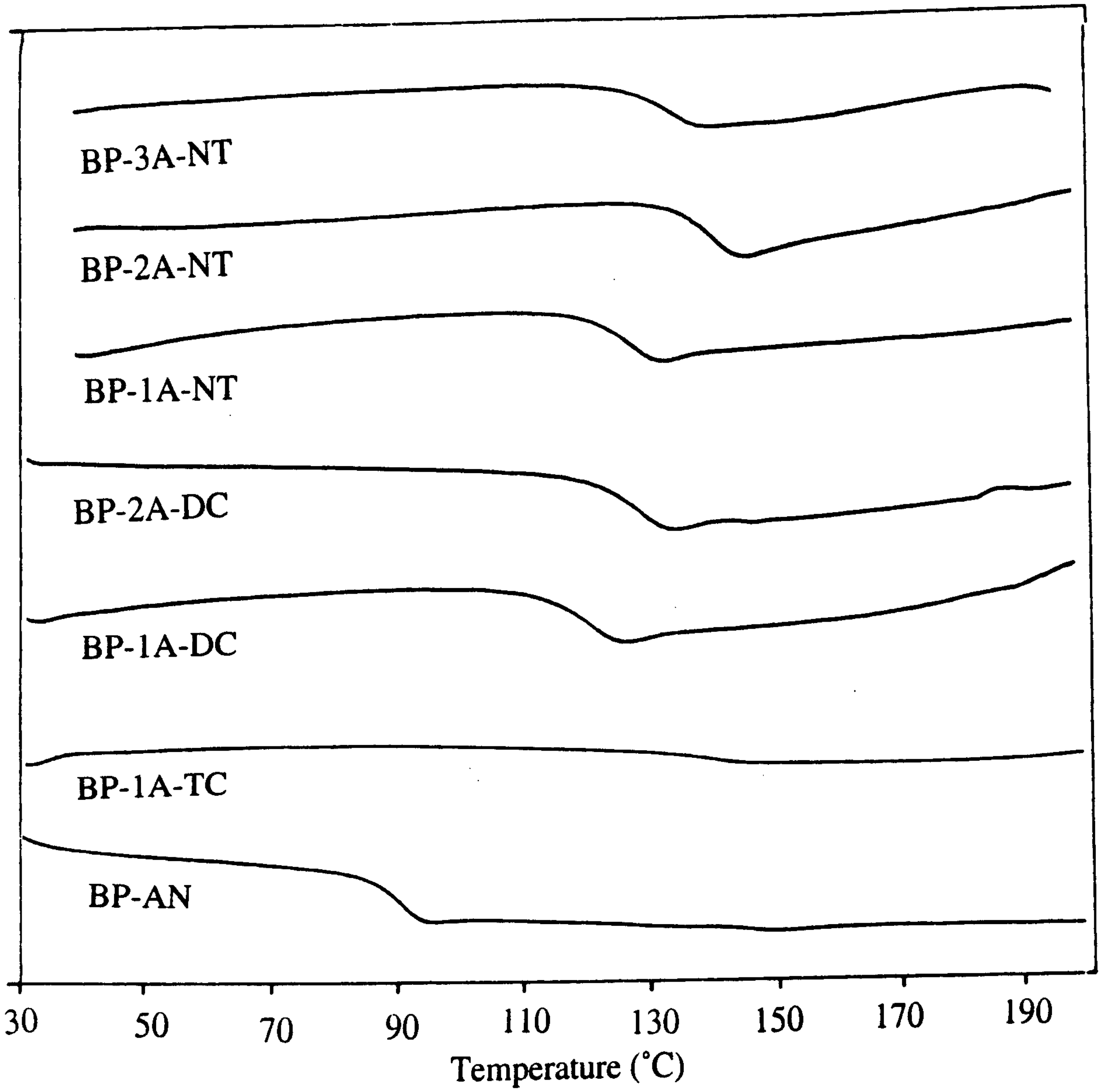

BP-3A-NT
BP-2A-NT
BP-1A-NT
BP-2A-DC
BP-1A-DC
BP-1A-TC
BP-AN
30
50
70
90
110
130
150
170
190
Temperature (˚C)

Figure 2

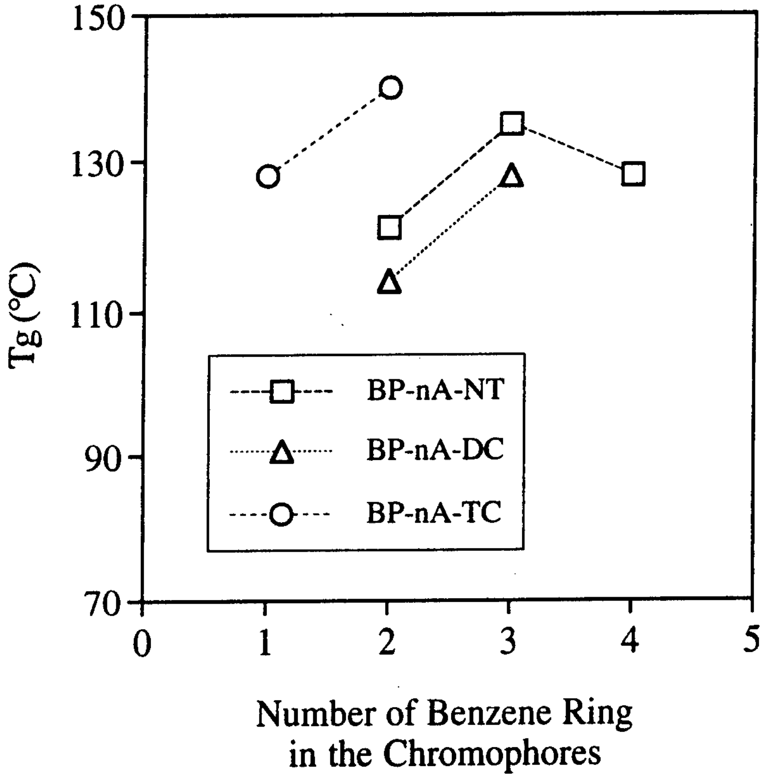

150
130
110
90
70
Tg (°C)
0
1
2
3
4
5
Number of Benzene Ring
in the Chromophores
BP-nA-NT
BP-nA-DC
BP-nA-TC

Figure 3

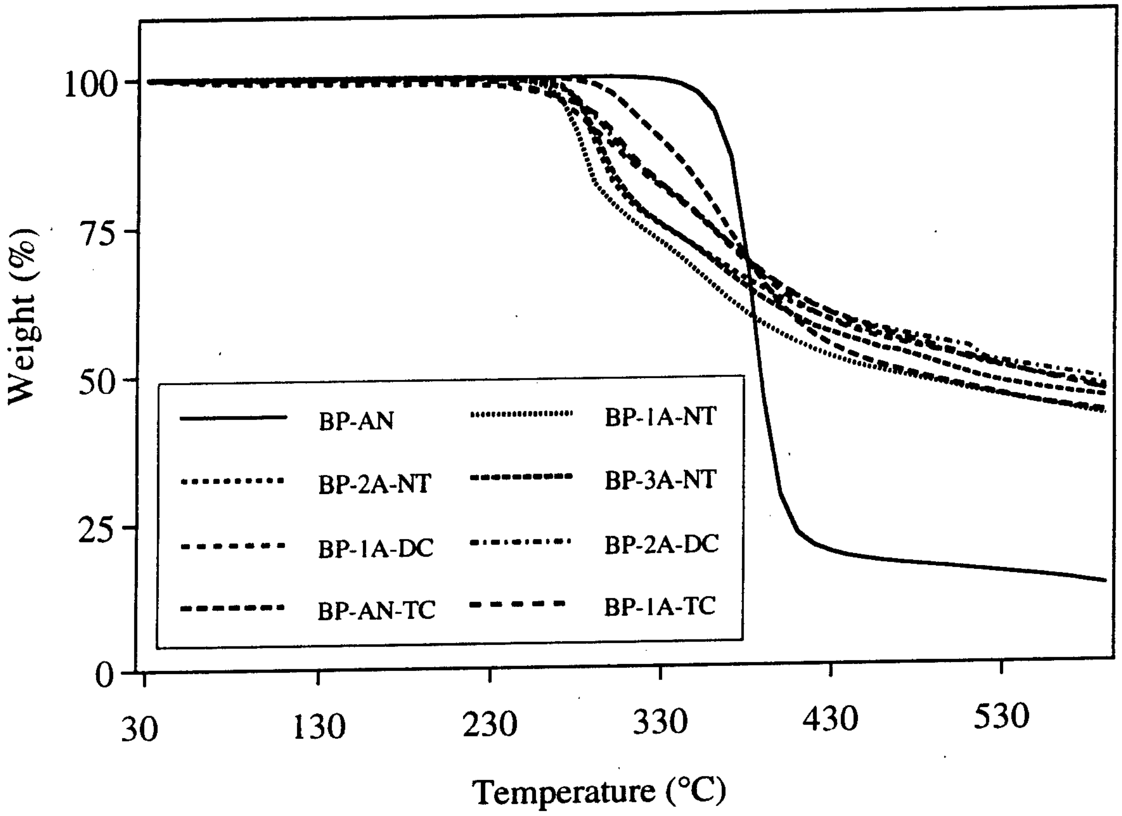

100
75
50
25
0
Weight (%)
30
130
230
330
430
530
Temperature (°C)
BP-AN
BP-1A-NT
BP-2A-NT
BP-3A-NT
BP-1A-DC
BP-2A-DC
BP-AN-TC
BP-1A-TC

Figure 4

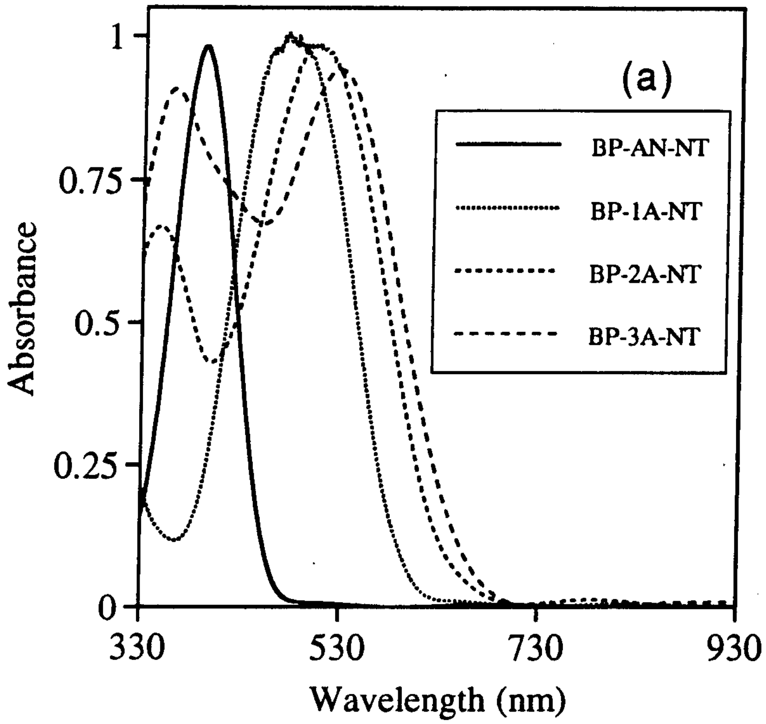

(a)
BP-AN-NT
BP-1A-NT
BP-2A-NT
BP-3A-NT
Absorbance
1
0.75
0.5
0.25
0
330
530
730
930
Wavelength (nm)

Figure 5

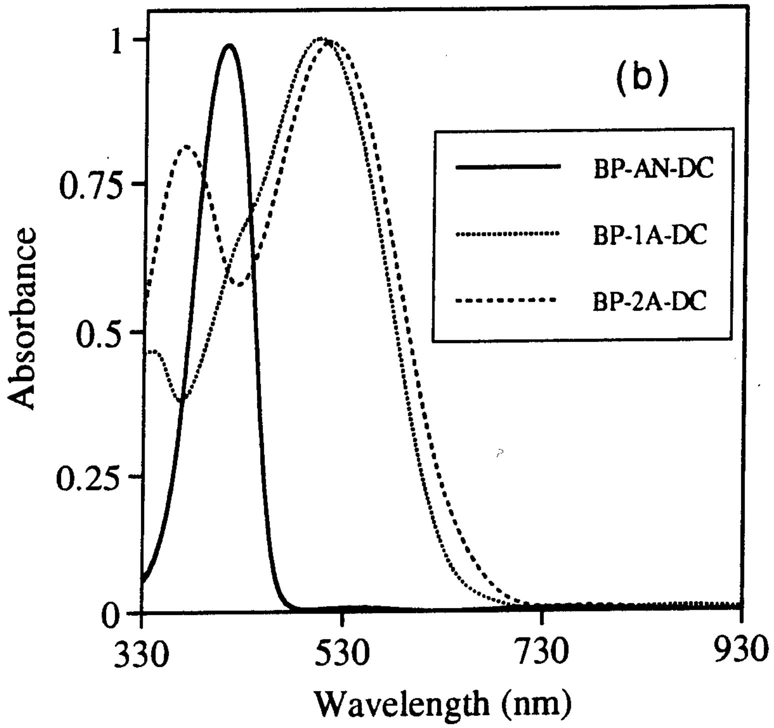

(b)
BP-AN-DC
BP-1A-DC
BP-2A-DC
Absorbance
1
0.75
0.5
0.25
0
330
530
730
930
Wavelength (nm)

Figure 5

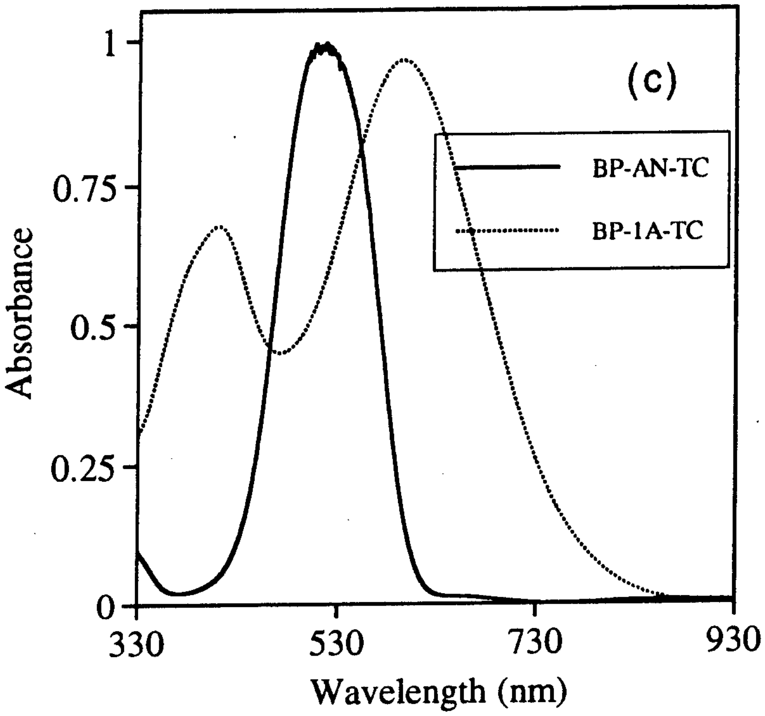

(c)
BP-AN-TC
BP-1A-TC
Absorbance
0
0.25
0.5
0.75
1
330
530
730
930
Wavelength (nm)

Figure 5

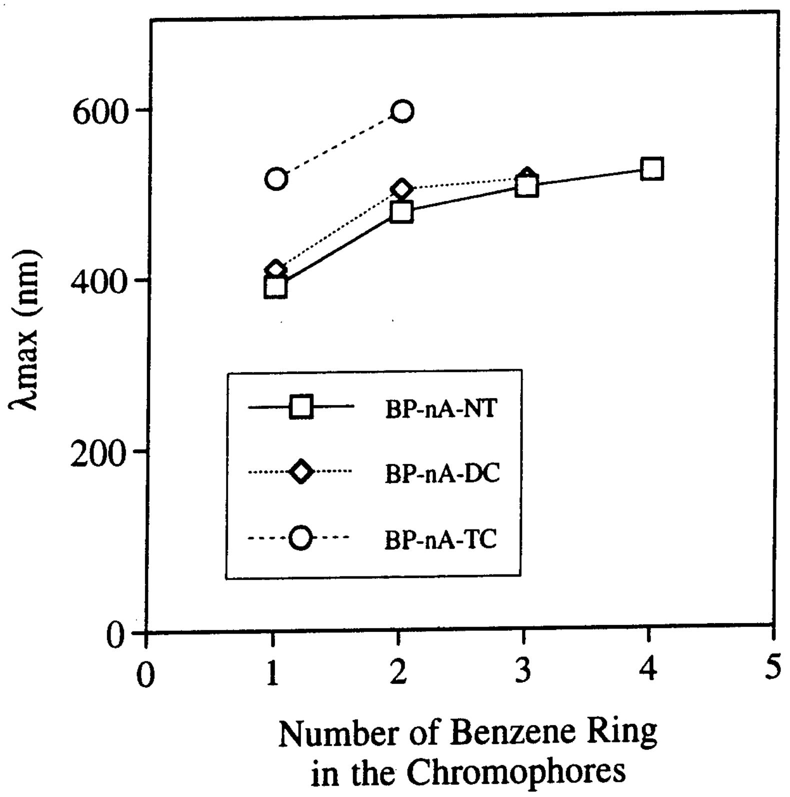
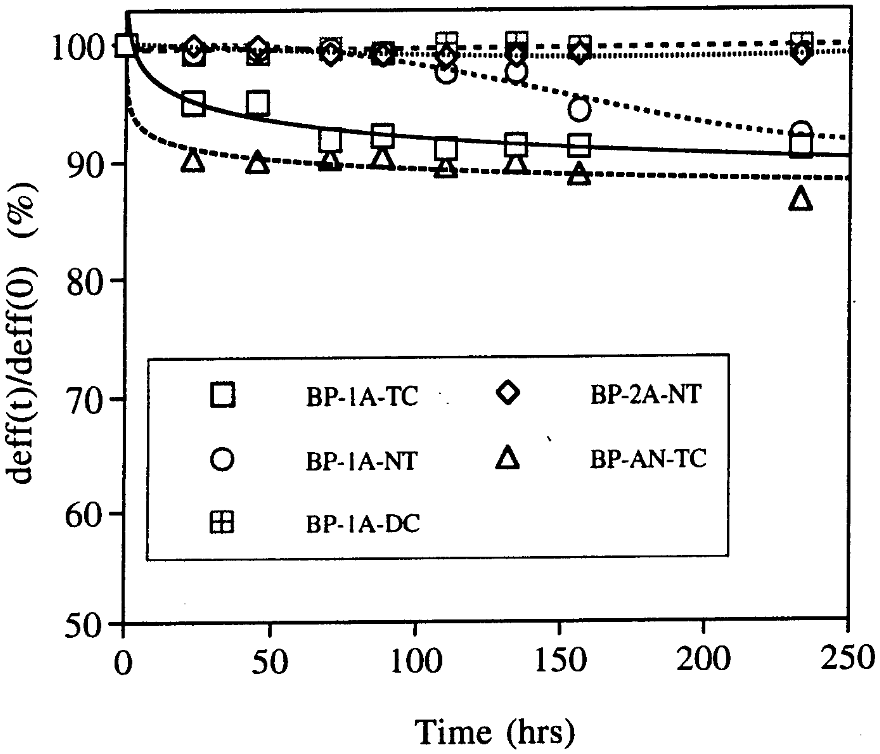

λmax (nm)
600
400
200
0
0
1
2
3
4
5
Number of Benzene Ring in the Chromophores
BP-nA-NT
BP-nA-DC
BP-nA-TC

Figure 6



100
90
80
70
60
50
deff(t)/deff(0) (%)
0
50
100
150
200
250
Time (hrs)
□ BP-1A-TC
◇ BP-2A-NT
○ BP-1A-NT
△ BP-AN-TC
⊞ BP-1A-DC

Figure 7