Heteroaromatic Chromophore Functionalized Epoxy-Based Nonlinear Optical Polymers

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ABSTRACT: A series of epoxy-based second-order nonlinear optical (NLO) polymers containing heteroaromatic chromophores have been designed. Precursor polymers were prepared from the polymerization between the diglycidyl ether of Bisphenol A and aniline or 4-(2-thienyl)aniline. The precursor polymers were postfunctionalized by an azo-coupling reaction as well as tricyanovinylation to form a series of NLO polymers containing heteroaromatic chromophores. We have extended and established the versatility of our earlier reported postmodification strategy to include various heteroaromatic chromophores in the polymers at the final stage of synthesis. The correlation between different heteroaromatic chromophore structures and the NLO properties of the polymers was extensively studied during this work. Polymers containing heteroaromatic chromophores exhibit improved temporal stability and enhanced NLO activity. The d_{33} value of 80 pm/V at 1.550 μm was observed for a representative polymer of the class containing 2-(4-aminophenyl)−(5-tricyanovinyl)thiophene chromophores. NLO properties of the poled polymers exhibit long-term stability at 80 °C.

1. Introduction

Since the first report of an electric field poled guest−host nonlinear optical (NLO) polymer system in 1982,[1,2] new polymer-based second-order NLO materials continue to be actively researched.[3−5] NLO polymers inherit the intrinsic strong points from both the π-electron conjugated chromophoric subunits and the polymers they are tethered to. Large second-order NLO susceptibilities, low dielectric constants, and excellent processability of the NLO polymers make them promising candidates for telecommunication and data processing applications. NLO polymers are especially competitive in the design of high-frequency electrooptical modulators and integrated semiconductor−NLO polymer circuits.[6−9] NLO polymers with significantly improved properties, including NLO activity as well as thermal and temporal stability, have been a topic of active research over the past decade. The polymers include novel chromophores to enhance the capabilities of optical signal manipulation and well-designed polymer structures to improve processability and the temporal stability of the electric field induced NLO effects.[6−14] Concurrently, new theoretical concepts have been proposed to describe the NLO response of individual chromophores and to model the interaction between the chromophores and their environment.[15−19]

Heteroaromatic rings are candidate structures in the design of chromophores with enhanced NLO properties and high thermal stability.[3,20] The aromatized heterocyclic rings are known to provide excellent thermal stability and are used as chain segments of high-temperature resistant polymers.[21,22] Chromophores containing heterocyclic π-electron bridge have been demonstrated to exhibit improved thermal stability.[23,24] The local asymmetric π-electron distribution introduced by the heteroatom in the ring structure is another interesting property, which can be exploited in the design of chromophores. Heteroaromatic rings form both π-electron rich (πEE) and π-electron deficient (πED) compounds and possess either nucleophilic or electrophilic ability, depending on the ring size and the type of heteroatom.[25,26] The electron-releasing and -attracting capabilities of various heteroaromatic rings can be exploited to enhance the donor−acceptor effects in the chromophores or even replace the typical donors and acceptors.[27−30] Marder and co-workers have recently proposed that the lower aromatic stabilization energy of the heteroaromatic rings is favorable in forming the charge transformed state with less energy increase upon polarization.[7,15] Hence, optical nonlinearity can be enhanced by replacing benzene rings in the π-bridged chromophore structure with heterocyclic rings such as thiazole or thiophene in the chromophores.[7,15] However, reports of NLO polymers containing heteroaromatic structures as conjugating bridge are far less numerous than NLO polymers containing benzenoid groups. Systematic study on the relationship between different heteroaromatic structures and NLO polymer properties is needed to completely understand the structure−property correlation in the heteroaromatic chromophore functionalized NLO polymer systems.

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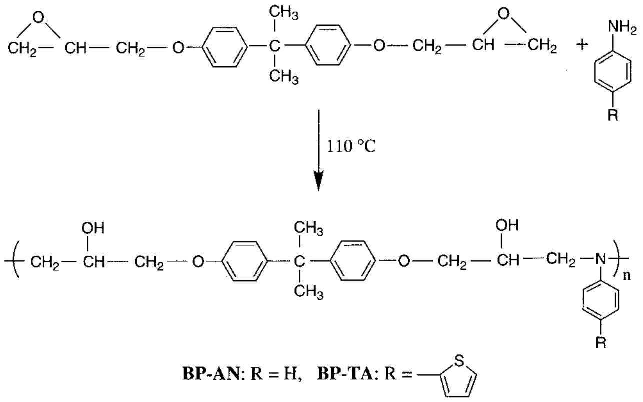
Scheme 1. Scheme for the Synthesis of Precursor Polymers, BP-AN and BP-TA



We have already established an azo-coupling reaction as well as a tricyanovinylation reaction as a viable approach to synthesize a series of epoxy-based NLO polymers containing NLO chromophores with different conjugation lengths and various electron acceptors.[31,32] The effect of the chromophore structure on the bulk NLO and other physical properties were discussed in some detail. The postmodification reactions, especially the post azo-coupling reaction, demonstrate the versatility to form various tethered chromophores at the final stage of NLO polymer preparation. In this study, we have further utilized the postmodification techniques to prepare a series of epoxy-based NLO polymers containing various heteroaromatic chromophores. The structure and properties of the newly synthesized NLO polymers were studied in detail and compared with the epoxy-based NLO polymers containing benzenoid-based chromophores. Appropriately designed heteroaromatic chromophores exhibit improved temporal stability and enhanced NLO response. Most of the synthesized polymers exhibit excellent processability and show large and stable optical nonlinearity. Synthesis of precursor polymers, postfunctionalization of the precursor polymers by azo-coupling and tricyanovinylation reactions, and the structural and thermal properties as well as linear and nonlinear optical properties of the synthesized polymers are discussed in detail in this paper.

2. Results and Discussion

2.1. Polymer Synthesis. Precursor polymers were prepared as shown in Scheme 1. Precursor polymer BP-AN was synthesized from diglycidyl ether of Bisphenol A (BP) and aniline (AN). Precursor polymer BP-TA containing 4-(2-thienyl)aniline moieties was synthesized from the diglycidyl ether of Bisphenol A (BP) and 4-(2-thienyl)aniline (TA). All polymerization reactions were carried out at a relatively low temperature (110 °C) in order to avoid the reaction between the hydroxyl groups formed during the polymerization and the unreacted epoxide rings.[33,34] Such a reaction will result in cross-linking and produce intractable network polymers. Low molecular weight oligomers, which are mainly cyclic oligomers,[31] were removed by the fractionation method as described in the experimental part. Number average molecular weights of the polymers, BP-AN and BP-TA, were estimated to be 57 400 and 36 800 with polydispersity indices of 1.56 and 2.71, respectively, using gel permeation chromatography (GPC). The precursor polymers are linear polymers with excellent optical transparency as shown in Figure 1 and exhibit good solubility in polar organic solvents including dimethylformamide and tetrahydrofuran, among others.

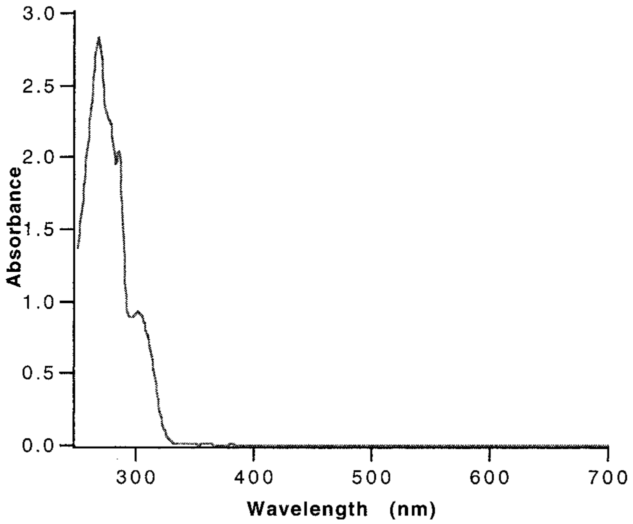
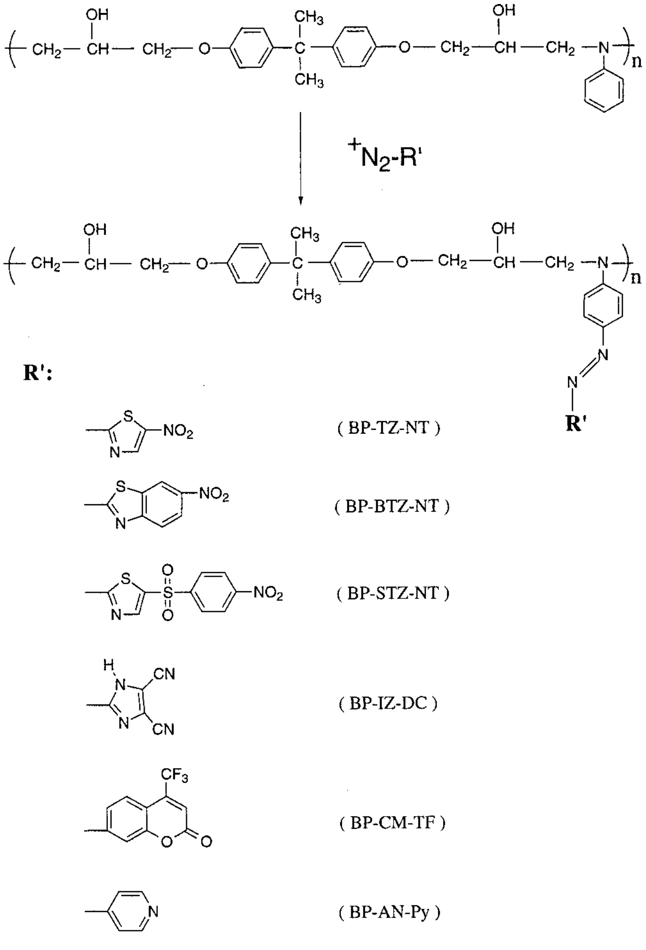


Figure 1. UV–visible absorption spectrum of epoxy-based precursor polymer BP-AN.

Scheme 2. Post Azo Coupling Reaction of the Polymer BP-AN to form NLO Polymers Containing Heteroaromatic Azo Chromophores



The precursor polymers were functionalized to introduce different chromophores at the final stage of the polymer preparation. Two general schemes viz., post azo-coupling reaction (Scheme 2) and post tricyanovinylation (Scheme 3), were employed for the postfunctionalization of the precursor polymers with NLO chromophores. The NLO polymers synthesized in this

Scheme 3. Post Tricyanovinylation of the Polymers, BP-TA, to form BP-TA-TC

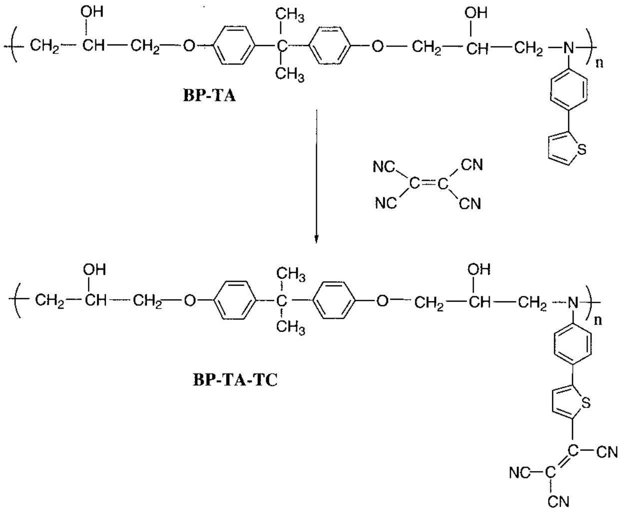


Table 1. Physical Properties of Representative Polymers Prepared by Azo Coupling Reaction and Tricyanovinylation

polymer	DF[a] (% ± 3%)	λ_{max} (nm)	T_g (°C)	T_d (°C)
BP-TZ-NT	77	571	141	210
BP-STZ-NT	70	545	139	222
BP-BTZ-NT	18	549	128	227
BP-IZ-DC	72	489	179	224
BP-CM-TF	85	471	136	242
BP-TA-TC	58	615	126	273
BP-1A-NT[b]	93	477	121	253
BP-AN-TC[c]	90	518	128	283

[a] Degree of functionalization measured by ^{1}H NMR spectroscopy. [b] Epoxy-based polymer containing 4-(4′-nitrophenyl)azoaniline chromophores.[32] [c] Epoxy-based polymer containing 4-tricyanovinylaniline chromophores.[32]

work are listed in Table 1. Properties of two of the epoxy-based polymers with benzenoid chromophores are also shown in Table 1, for comparison purposes. The first part of the polymer nomenclature is an abbreviation to distinguish between precursor polymers from diglycidyl ether of Bisphenol A (BP) and other epoxide compounds. The following parts refer to the different conjugation bridges and electron acceptor moieties of the chromophores.

BP-TZ-NT, BP-STZ-NT, and BP-BTZ-NT are three polymers that contain thiazole based chromophores. The polymers were prepared by post azo-coupling reaction between the precursor polymer BP-AN and the diazonium salts of 2-amino-5-nitrothiazole, 2-amino-6-nitrobenzothiazole, and 2-amino-5-(4-nitrophenylsulfonyl)thiazole. The thiazole-based azo compounds were first reported as blue or violet-colored disperse dyes.[35] Chromophores with thiazole groups exhibit a significant bathochromic effect compared to that with benzenoid structures. From the relationship between absorption maximum (λ_{max}) and molecular hyperpolarizability (β),[36,37] thiazole-containing chromophores are expected to have large $\mu\beta$ values, where μ is the dipole moment of the chromophores. $\mu\beta$ values at 1300 nm ($\mu\beta_{1300}$) of *N*-(ethyl)-*N*′-(6-hydroxyhexyl)-4-(5-nitrothiazole-2-azo)aniline and *N*-(ethyl)-*N*′-(6-hydroxyhexyl)-4-(6-nitrobenzo-thiazole-2-azo)aniline chromophores are reported to be 1310 × 10^{-48} and 1520 × 10^{-48} esu, which are about 2−3 times larger than that for 4-(*N*,*N*′-dimethylamino)-4′-nitrostilbene (DANS) (662 × 10^{-48} esu).[38] BP-CM-TF polymer was prepared from a post azo-coupling reaction between the precursor polymer BP-AN and 7-amino-4-(trifluoromethyl)coumarin. Coumarins, which possess interesting NLO and strong flourescence properties, have been studied for electro-optic,[39] frequency doubling,[40] and photorefractive[41] applications. 7-Amino-4-(trifluoromethyl)coumarin is a laser dye with $\mu\beta$ of 86 × 10^{-48}.[42] In this work, the azo-coupling reaction was used to introduce the coumarin unit to the epoxy-based polymer and enhance the second-order nonlinearity by extending the conjugation length through azo bond. The polymer, BP-IZ-DC, was prepared from post azo-coupling reaction between the precursor polymer BP-AN and 2-amino-4,5-imidazoledicarbonitrile. The polymer, BP-AN-PY, was prepared from post azo-coupling between 4-aminopyridine and the precursor polymer BP-AN. BP-TA-TC was prepared from post tricyanovinylation of the precursor polymer BP-TA containing 4-(2-thienyl)aniline moieties. Tricyanovinyl is a strong electron-withdrawing group and a good candidate for preparing chromophores with large second-order optical nonlinearities.[6,7]

Both diazonium salt and tetracyanoethylene readily attack the aromatic ring at electron-rich positions. The electrophilic substitution (azo-coupling or tricyanovinylation) takes place exclusively at the 4-position of aniline moieties of BP-AN, due to the steric crowding at the 2-position. The tricyanovinylation reaction occurs predominantly at the electron-rich 5-position of thienyl moieties in the case of BP-TA. As the amine becomes more weakly basic, the equilibrium between amine and ammonium salt increasingly favors the former. As a result, diazotization becomes progressively more difficult.[43] The difficulty of forming stable diazonium salts of amino−thiazole compounds was reported earlier, partly due to the nucleophilic substitution of the diazonium group by halogen.[44] In this study, all three amino−thiazole compounds and 4-aminopyridine were diazotized by adding the solid compound directly to the nitrosylsulfuric acid in acetic acid solution. By this method, stable diazonium salt solutions were formed and post azo-coupling reactions were carried out with satisfactory yield. In contrast to the nitrosylsulfuric acid route, post azo-coupling reactions performed by diazotizing the above compounds in the normal method result in a very low degree of functionalization. 2-Amino-4,5-imidazoledicarbonitrile was also diazotized by the nitrosylsulfuric acid method. All the polymers were carefully purified following the procedure given in the experimental part. The structures and purity of the polymers were investigated and confirmed by various spectroscopic methods.

2.2. Structural and Thermal Characterization. The prepolymers and postfunctionalized polymers were characterized using ^{1}H NMR spectroscopy to determine the position of electrophilic substitution and the degree of functionalization. ^{1}H NMR spectra of the two precursor polymers are shown in parts a and b of Figure 2. Strong resonances at 7.10 ppm (doublet) and 6.84 ppm (doublet) correspond to the chemical shift of benzene ring protons in Bisphenol A moieties. Chemical shifts at 7.10 ppm (overlapped), 6.76 ppm (doublet), and 6.55 ppm (multiplet), are attributed to the protons at meta, ortho, and para positions of aniline moieties in the case of precursor polymer BP-AN. The assignment is complex in the case of precursor polymer BP-TA and was solved using a two-dimensional NMR technique (^{1}H−^{1}H correlational spectroscopy−COSY45). The resonance at 7.38 ppm (doublet) has a correlation with the resonance at 6.79 ppm (overlapped) and the two resonances are attributed to the benzenoid protons at meta and ortho positions of the amino groups. The resonance at 7.03 ppm has correlation with resonances at 7.31 and 7.20 ppm and they are assigned to the protons at respective 4-, 5-, and 3-positions of 2-thienyl moieties.

^{1}H NMR spectra of the postfunctionalized NLO polymers are shown in parts c−g of Figure 2. Azo-coupling substitution preferentially occurs at the para positions of aniline moieties in the precursor polymers with high yield, as inferred from NMR spectra. The resonance at 6.55 ppm, which corresponds to the protons at the para position of the amino group in aniline moieties nearly disappears upon the azo-coupling reaction. Moreover, the chemical shifts of protons that are ortho and meta to the amino groups shift to lower magnetic field, due to the presence of strong electron-withdrawing groups introduced by the azo-coupling reaction. Additional resonances corresponding to chemical shifts of the introduced heteroaromatic ring protons appear upon post azo-coupling reaction. The resonances of polymer BP-TZ-NT, BP-STZ-NT and BP-BTZ-NT are well separated and are easily assigned. A chemical resonance appears at 8.77 ppm for thiazole ring protons of BP-TZ-NT. Chemical resonances appear at 8.56 ppm for thiazole protons and at 8.40 ppm and 8.27 ppm for benzenoid protons in 2-amino-5-(4-nitrophenyl-sulfonyl)-thiazole moieties in BP-STZ-NT. The resonances are overlapped in BP-CM-TF and were deconvulated using two-dimensional COSY NMR spectroscopy. The resonances at 8.23 and 6.97 ppm are attributed to the protons at 5, 6, 8 and 3 positions of coumarin moieties. The resonances of benzenoid protons of substituted aniline moieties appear at 7.70 and 6.92 ppm. BP-IZ-DC has one resonance at 7.77 ppm. 2D NMR indicates that these protons are correlated with protons with a resonance at 7.00 ppm, which indicates both to be from substituted benzenoid protons of aniline moieties.

The degrees of functionalization for BP-TZ-NT, BP-BTZ-NT, BP-STZ-NT, and BP-IM-DC were 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 isopropylidine protons of Bisphenol A moieties. Chemical shifts at 7.79, 7.75, 7.81, and 7.77 ppm correspond to the meta protons of BP-TZ-NT, BP-STZ-NT, BP-BTZ-NT, and BP-IZ-DC polymers, respectively. The degrees of functionalization for the polymers BP-TZ-NT, BP-STZ-NT, and BP-IZ-DC were estimated to be between 70 and 80% (Table 1). The degree of functionalization of BP-BTZ-NT is extremely low (18%). The chemical resonances from aniline and coumarin moieties of 4-(4′-(trifluoromethyl)coumarinazo)aniline chromophores in BP-CM-TF are overlapped. The degree of functionalization in BP-CM-TF is estimated to be 85% by comparing the peak areas in the range 7.79−7.68 ppm (5H) and the peak area at 1.58 ppm.

BP-TA-TCV was synthesized from the precursor polymer BP-TA by a post tricyanovinylation reaction. New resonances at 8.02 and 7.67 ppm (overlapped) appear upon tricyanovinylation and correspond to protons of tricyanovinylated thienyl moieties. The resonances of remaining unsubstituted thienyl protons appear between 7.32 and 7.23 ppm. The degree of functionalization for BP-TA-TC was estimated to be around 60%, from the ratio between peaks at 8.02 and 1.58 ppm.

The processability of some of the synthesized polymers was dramatically affected upon functionalization. All the polymers discussed above were able to form homogeneous solutions in DMF, during the postfunctionalization process. However, the polymers collected by precipitating in water after the reaction exhibited different solubility characteristics. Polymers BP-TA-TC, BP-CM-TF, BP-IZ-DC, and BP-STZ-NT are highly soluble in polar solvents. The solubility of BP-TZ-NT is poor compared to that of BP-STZ-NT in DMF. BP-BTZ-NT exhibits poor solubility even in polar solvents such as DMF, due to the presence of rigid benzothioazole units in the chromophore structure. BP-AN-Py-containing 4(4′-pyridylazo)aniline chromophores are not soluble in any solvent tested in our laboratory. The insolubility of BP-AN-Py is ascribed to the presence of a strong hydrogen-bonding interaction between the pyridine nitrogen and the hydroxyl groups on the main chain, causing physical cross-links. A similar phenomenon has been reported for low molecular weight pyridine derivatives.[25]

The phase transition behavior of the precursor and the NLO polymers was studied using differential scanning calorimetry (DSC). All the polymers including precursor polymers and NLO polymers containing different heteroaromatic bridges or acceptors exhibit thermal behavior typical of the amorphous state. The glass transition temperatures (T_g's) for various polymers determined by DSC are listed in Table 1. The T_g's of precursor polymers BP-AN and BP-TA are 91 and 103 °C, respectively. The T_g's of the functionalized polymers are much higher than those for the precursor polymers, and the increase in T_g is attributed to significant increase both in the size and the dipole moment of the side groups. The T_g's of BP-TZ-NT, BP-STZ-NT and BP-CM-TF are determined to be in the range 130−140 °C, which are about 10−20 °C higher than those for the epoxy-based polymers with the same main chain containing 4-(4′-nitrophenylazo)aniline chromophores. The T_g of BP-AN-Py is 160 °C and the high T_g is attributed to possible presence of intermolecular hydrogen bonds between pyridine and hydroxyl groups, causing physical networks. BP-IM-DC exhibit the highest T_g of 179 °C among the series, and the reason for this high T_g could be attributed to possible intermolecular hydrogen bonding between imidazole units of the chromophores and the secondary hydroxyl groups present in the polymer. The T_g of BP-TA-TC is 126 °C, which is almost the same as that for the polymer having the same main chain and containing 4-tricyanovinylaniline chromophores.

Thermal stability of the polymers was characterized by thermogravimetric analysis (TGA). TGA curves of both precursor and NLO polymers are shown in Figure 3. The precursor polymers BP-AN and BP-TA have very similar thermal stabilities and are thermally stable up to 330 °C under nitrogen atmosphere. Thermal stability of the formed NLO polymers declines, upon functionalization. The magnitude of the decrease depends on the type of heteroaromatic chromophores present in the polymer. Most of the NLO polymers derived from precursor BP-AN start to lose weight in the temperature range between 220 and 230 °C. BP-CM-TF possesses a higher thermal stability and starts to lose weight in the range between 240 and 250 °C. BP-TA-TC starts to decompose in the temperature range between 270 and 280 °C, which is as stable as the epoxy-based polymer-containing 4-tricyanovinylaniline chromophores. Most

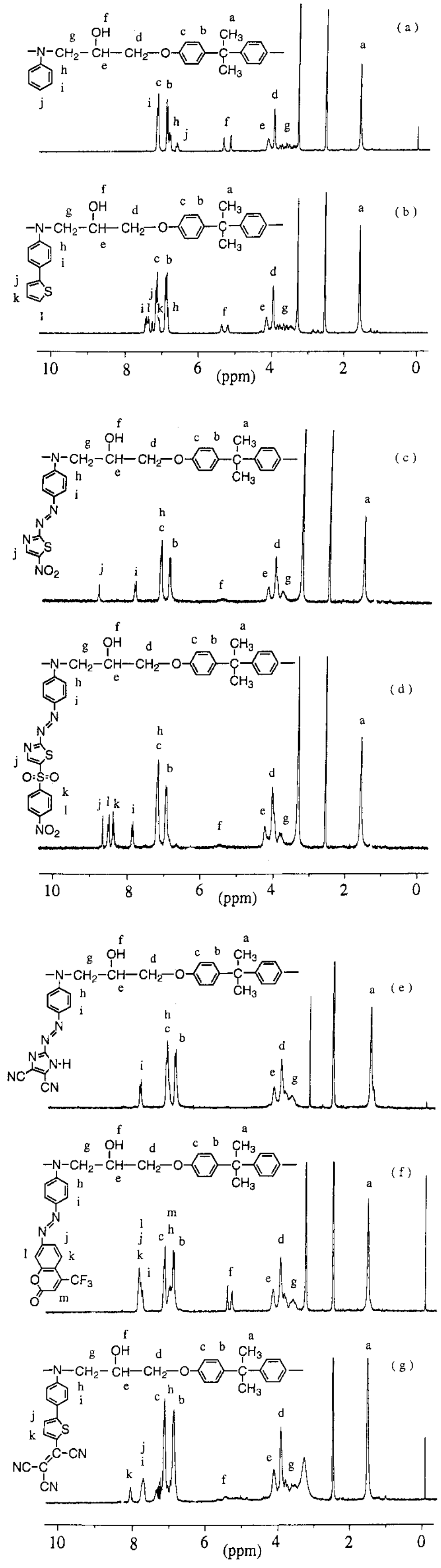


Figure 2. ^{1}H NMR spectra of (a) BP-AN, (b) BP-TA, and (c) BP-TZ-NT, (d) BP-STZ-NT, (e) BP-IZ-DC, (f) BP-CM-TF, and (g) BP-TA-TC in dimethyl-d_6 sulfoxide.

of the polymers with heteroaromatic azo chromophores studied in this work do not show improved thermal stability over the epoxy-based polymers with azobenzene-type chromophores. However, the BP-TA-TC polymer, with highly enhanced NLO activity due to the presence of 2-(4-aminophenyl)(5-tricyanovinyl)thiophene chromophores, was developed during this work, while maintaining thermal stability.

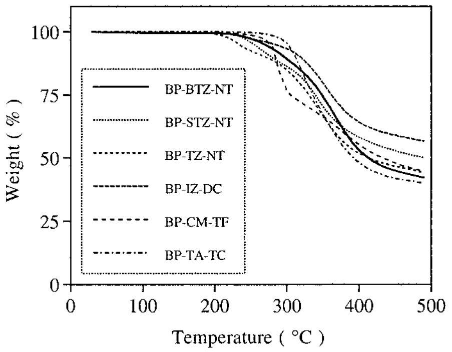


Figure 3. TGA curves of the epoxy-based precursor polymers and polymers containing heteroaromatic chromophores.

2.3. Linear and Nonlinear Optical Properties. The UV−vis spectra of the thin films of the heteroaromatic chromophores functionalized epoxy-based polymers are shown in parts a and b of Figure 4. Absorption maxima of the polymers are given in Table 1. All the polymers exhibit strong absorption in the visible region. The polymers show color ranging from red to blue. Polymers, BP-CM-TF and BP-IZ-DC, exhibit absorption maxima at 476 and 490 nm, respectively. Polymers BP-TZ-NT, BP-STZ-NT, and BP-BTZ-NT have λ_{max} respectively at 571, 545, and 549 nm, compared to the absorption maximum of 480 nm shown for the epoxy-polymer-containing 4-(4′-nitrophenylazo)aniline. Thioazole units demonstrate a strong bathochromic effect in the absorption behavior in the test systems. BP-TA-TC has the longest λ_{max}, 615 nm, in the series. Polymers BP-IZ-DC, BP-CM-TF and BP-STZ-NT exhibit a single electronic transition due to the $\pi-\pi^*$ charge-transfer in the visible range. Polymers BP-TA-TC and BP-TZ-NT exhibit a second weak absorption band respectively at 400 and 388 nm in addition to their strong $\pi-\pi^*$ transition bands. Absorption spectrum of the polymer BP-BTZ-NT is more complicated. In addition to an absorption maximum at 549 nm, a strong absorption band at 430 nm and a broad band in the range from 600 to 800 nm were seen for this polymer. As pointed out by a number of authors, it is important to have the optical band edge away from the operating wavelength of the electrooptical devices in selecting a suitable material.[4,6]

Corona poling was carried out at temperatures 10−15 °C higher than the glass transition temperatures of the polymers, to achieve noncentrosymmetric alignment of the chromophores in the polymer films.[46,47] Second-order NLO coefficients (d_{33}) were measured by a second harmonic generation (SHG) technique. The measurement was carried out at 1.064 and 1.550 μm. Second-order NLO coefficients measured at 1.550 μm are reported in this communication, since significant resonant enhancement is anticipated for most of the polymers at 1.064 μm. The measured d_{33} values are given in Table 2. Polymers with absorption maximum closer to 532 nm exhibit highly enhanced second-order NLO activity at 1.064 μm compared to polymers with absorption maximum further away from 532 nm as shown in Table 2. The polymer BP-TA-TC, containing 2-(4′-

Table 2. Second-Order NLO Properties of Representative NLO Polymers

polymer	d_{33} (pm/V, 1.064 μm)	d_{33} (pm/V, 1.550 μm)
BP-TZ-NT	104.5	24.5
BP-STZ-NT	108.4	14.1
BP-BTZ-NT	19.0	
BP-CM-TF	59.5	6.2
BP-IZ-DC	24.3	
BP-TA-TC	76.0	80.0
BP-AN-TC[a]	178.0	27.0
BP-1A-NT[b]	124.0	28.0

[a] Epoxy-based polymer containing 4-tricyanovinylaniline chromophores.[32] [b] Epoxy-based polymer containing 4-(4-nitrophenyl)-azoaniline chromophores.[32]

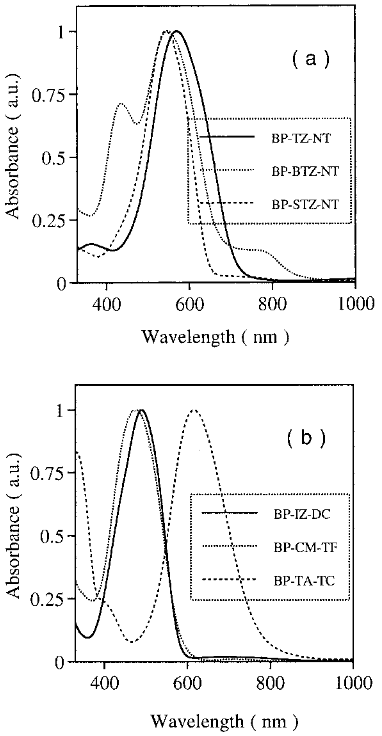


Figure 4. UV−Vis absorption spectra of (a) BP-TZ-NT, BP-STZ-NT, and BP-BTZ-NT and (b) BP-IZ-DC, BP-CM-TF, BP-TA-TC spin cast films.

aminophenyl)-5-(tricyanovinyl) thiophene chromophores, exhibited significantly larger optical nonlinearities due to the presence of a strong electron-withdrawing tricyanovinyl group. The extremely small d_{33} of BP-BTZ-NT is attributed to the small degree of functionalization for the polymer.

The long-term stability of the electric field induced NLO property is a critical requirement for practical applications. In this study, the SHG signal decay as a function of time was measured both at room temperature and at 80 °C. No SHG intensity decay was observed at room temperature for the polymers prepared in this work during our measurement period (1000 h). The temporal stability of the NLO properties at 80 °C is shown in Figure 5. For comparison, the temporal stability of BP-AN-TC and BP-1A-NT reported earlier are also shown on the same figure. For all the polymers, after an initial decay, the NLO response of the polymers tends to be stable. The rate of initial decay of the SHG signal and percentage of final retention depends on the chromophore structures. The polymer BP-AN-TC where the chromophore contains a single benzenoid ring as conjugating bridge shows poorest temporal stability among the series and 31% decay was observed after 200 h. BP-1A-NT shows a higher stability (28% decay) due to a longer conjugation length. Compared with polymers containing benzenoid-based chromophores, the polymers prepared in this work, containing heteroaromatic chromophores, show improved temporal stability. After a small and short initial decay, the NLO response of the latter polymers tends to be stable with time. For most of the polymers, 80−90% of the NLO signal was retained after 1000 h at 80 °C. BP-STZ-NT shows the highest retention of 93% among the series. It appears that the presence of extended chromophores in the polymers improves the temporal stability. Temporal stability of the optical nonlinearity of the polymers is not directly correlated with T_g's of the polymers. The optical nonlinearities of polymers with an almost similar glass transition temperature show significantly different temporal behaviors. BP-IZ-DC, possessing the highest T_g among the series, does not show the highest temporal stability of the second harmonic generation intensity. Although most of the polymers containing heteroaromatic chromophores synthesized in this work exhibit glass transition temperatures similar to those for the polymers containing benzenoid-based chromophores, they demonstrate superior temporal stability than the latter.[31,32] It is believed that at temperatures below T_g, the SHG signal decay is strongly dependent on the local mobility of the chromophore instead of the chain segmental motion. The heteroaromatic chromophores have a stronger interaction between chromophores and the surrounding molecules.

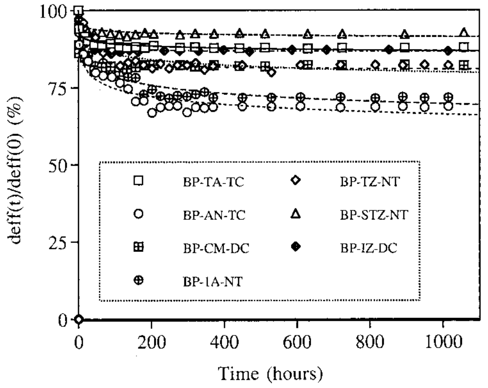


Figure 5. Temporal behavior of poled polymers at 80 °C.

In summary, two epoxy-based precursor polymers have been functionalized to form a series of NLO polymers containing heteroaromatic chromophores. The physical properties of the polymers depend on chromophore structure. The polymers containing heteroaromatic chromophore show an enhanced second-order optical nonlinearity and an improved temporal stability. The polymer containing 2-(4′-aminophenyl)−(5-tricyanovinyl)thiophene chromophores exhibits the largest second-order optical nonlinearity (80 pm/V at 1.550 μm) among the series of heteroaromatic chromophore containing epoxy polymers.

3. Experimental Section

3.1. Characterization. Infrared spectra were recorded 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 recorded 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 weights were determined by gel permeation chromatography (GPC) utilizing a Waters Model 510 pump and 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.

3.2. Materials. Commercially available tetracyanoethylene was purified by recrystallization in dry toluene prior to reaction. 4-(2-Thienyl)aniline was synthesized in our laboratory by reacting 4-bromonitrobenzene with 2-(tributylstannyl)thiophene in the presence of catalytic amounts of tetrakis(triphenylphosphino)palladium(0) followed by the reduction of the nitro group in the resulting compound with tin and hydrochloric acid.[45] All other starting materials, reagents, and solvents, purchased from Aldrich, VWR, and Shell, were used without further purification unless otherwise mentioned. The polymers were synthesized according to the schemes shown in Schemes 1−3. The details of the syntheses are described in the following sections.

3.3. Preparation of BP-AN. Equimolar quantities of diglycidyl ether of Bisphenol A (7.6 g, 0.02 mol) and aniline (1.86 g, 0.02 mol) were homogeneously mixed under gradual heating and polymerized at 110 °C for 48 h. The product (10 g) was dissolved in a $CHCl_3/CH_3OH$ solvent mixture (4:1, 50 mL) followed by precipitation in 500 mL of acetone. The polymer was collected by filtration and dried under vacuum for at least 24 h. 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 91 °C. Number average molecular weight of the polymer was estimated to be 57 400, with a polydispersity index of 1.56 using gel permeation chromatography (GPC). ^1H NMR (δ, in ppm): 7.08 (CH, 6H, d), 6.82 (CH, 4H, d), 6.74 (CH, 2H, d), 6.55 (CH, 1H, m), 5.27 (OH, 1H, d), 5.08 (OH, 1H, d), 4.06 (CH, 2H, m), 3.89 (CH_2, 4H, s), 3.75−3.34 (CH_2, 4H, m), 1.56 (CH_3, 6H, s).

3.4. Preparation of BP-TA. Equimolar quantities of diglycidyl ether of Bisphenol A (3.8 g, 0.01 mol) and 4-(2-thienyl)aniline (1.75 g, 0.01 mol) were homogeneously mixed under gradual heating and polymerized at 110 °C for 48 h. The product (5 g) was dissolved in DMF (10 mL), followed by reprecipitation in excess methanol to remove low molecular weight oligomers. The polymer was collected by filtration and dried under vacuum for at least 24 h. 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 103 °C. The number average molecular weight of the polymer was estimated to be 36 800 with a polydispersity index of 2.71 using gel permeation chromatography (GPC). ^1H NMR (δ, in ppm): 7.38 (CH, 2H, d), 7.31 (thienyl CH, 1H, br), 7.20 (thienyl CH, 1H, br), 7.10 (CH, 4H, d), 7.03 (thienyl CH, 1H, br), 6.84 (CH, 4H, d), 6.80 (CH, 2H, d), 5.30 (OH, 1H, br), 5.14 (OH, 1H, br), 4.09 (CH, 2H, br), 3.92 (CH_2, 4H, br), 3.80−3.36 (CH_2, 4H, m), 1.57 (CH_3, 6H, s).

3.5. Preparation of BP-TZ-NT. Nitrososulfuric acid was prepared by carefully adding sodium nitrite (0.04 g, 0.578 mmol) to 0.08 mL of sulfuric acid at 70 °C while stirring. The temperature was strictly controlled not to exceed 75 °C during the addition. The resulting solution was cooled in an ice bath and diluted with 1 mL of glacial acetic acid. A diazonium salt of 2-amino-5-nitrothiazole was prepared by adding the solid of 2-amino-5-nitrothiazole (0.0726 g, 0.5 mmol) directly into the above nitrososulfuric acid solution. The mixture was stirred at 5 °C for 5 min before the excess nitrous acid was decomposed by the 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 *N*,*N*′-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-TZ-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 repeated washing with acetone and subsequently dried under vacuum at least for 24 h. IR (KBr, cm^{-1}): 3387, 2964, 2937, 2867, 1600, 1510, 1482, 1422, 1339, 1302, 1235, 1198, 1138, 1123, 1048, 898, 827, 793, 744, 664, 644, 570, 535, 485, 422. ^1H NMR (δ, in ppm): 8.77 (CH, 1H, s), 7.80 (CH, 2H, d), 7.10 (CH, 6H, d), 6.86 (CH, 4H, d), 5.38 (OH, 2H, br), 4.17 (CH, 2H, m), 3.97 (CH_2, 4H, s), 3.95 (CH_2, 2H, m), 3.78 (CH_2, 2H, m), 1.57 (CH_3, 6H, s).

3.6. Preparation of BP-STZ-NT. The diazonium salt of 2-amino-5-(4-nitrophenylsulfonyl)thiazole (0.1426 g, 0.5 mmol) was prepared via a procedure similar to that described above for 2-amino-5-nitrothiazole. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 50 mL of *N*,*N*′-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-STZ-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 repeated extraction with acetone and dried under vacuum at least for 24 h. IR (KBr, cm^{-1}): 3387, 2965, 2937, 2877, 1600, 1531, 1505, 1481, 1413, 1347, 1310, 1240, 1182, 1138, 1086, 1040, 1016, 903, 863, 826, 797, 737, 683, 662, 639, 614, 578, 535, 458, 422. ^1H NMR (δ, in ppm): 8.77 (CH, 1H, s), 7.79 (CH, 2H, br), 7.10 (CH, 6H, d), 6.86 (CH, 4H, d), 5.38 (OH, 2H, br), 4.17 (CH, 2H, m), 3.97 (CH_2, 4H, s), 3.95 (CH_2, 2H, m), 3.78 (CH_2, 2H, m), 1.57 (CH_3, 6H, s).

3.7. Preparation of BP-BTZ-NT. The diazonium salt of 2-amino-6-nitrobenzothiazole (0.0976 g, 0.5 mmol) was prepared via a procedure similar to that described above for 2-amino-5-nitrothiazole. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 50 mL of *N*,*N*′-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-STZ-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 repeated extraction with acetone and dried under vacuum at least for 24 h. IR (KBr, cm^{-1}): 3387, 2964, 2937, 2897, 1600, 1555, 1505, 1471, 1422, 1377, 1342, 1317, 1286, 1236, 1182, 1153, 1110, 1043, 918, 826, 747, 699, 572, 555, 420. ^1H NMR (δ, in ppm): 8.96 (CH, 1H, br), 8.24 (CH, 1H, br), 8.08 (CH, 1H, br), 7.81 (CH, 2H, br), 7.08 (CH, 4H, d), 6.97 (CH, 2H, d), 6.85 (CH, 4H, d), 5.33 (OH, 2H, br), 4.15 (CH, 2H, m), 3.97 (CH_2, 4H, s), 3.95 (CH_2, 2H, m), 3.69 (CH_2, 2H, m), 1.57 (CH_3, 6H, s).

3.8. Preparation of BP-CM-TF. A diazonium salt of 7-amino-4-(trifluoromethyl)coumarin 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 7-amino-4-(trifluoromethyl)coumarin (0.1146 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 30 mL of *N*,*N*′-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-CM-TF was obtained by precipitation of the above solution in water and was washed with plenty of water until the neutral stage was achieved. The polymer was further purified by repeated extraction with acetone and dried under vacuum at least for 24 h. IR (KBr, cm^{-1}): 3446, 2965, 2937, 2877, 1742, 1596, 1566, 1510, 1472, 1436, 1396, 1362, 1322, 1285, 1234, 1192, 1167, 1143, 1096, 1048, 998, 968, 928, 875, 826, 722, 653, 634, 573, 554, 403. ^1H NMR (δ, in ppm): 7.79 (CH, 3H, br), 7.70 (CH, 2H, d), 7.10 (CH, 4H, br), 6.97 (CH, 1H, s), 6.92 (CH, 2H, d), 6.85 (CH, 4H, d), 5.37 (OH, 1H, d), 5.25 (OH, 1H, d), 4.13 (CH, 2H, m), 3.94 (CH_2, 4H, br), 3.82 (CH_2, 2H, br), 3.58 (CH_2, 2H, m), 1.57 (CH_3, 6H, s).

3.9. Preparation of BP-IZ-DC. The diazonium salt of 2-amino-4,5-imidazoledicarbonitrile (0.0666 g, 0.5 mmol) was prepared via a procedure similar to that described above for 2-amino-5-nitrothiazole. The diazonium salt solution was added dropwise into a solution of BP-AN (0.1892 g, 0.4 mmol) in 50 mL of *N*,*N*′-dimethylformamide at 0 °C. The solution was stirred at 0 °C for 12 h. BP-IZ-DC 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 repeated extraction with acetone and dried under vacuum at least for 24 h. IR (KBr, cm^{-1}): 3447, 2977, 2937, 2867, 2239, 1598, 1561, 1510, 1472, 1417, 1362, 1302, 1235, 1198, 1149, 1118, 1043, 1023, 825, 674, 564, 519. ^{1}H NMR (δ, in ppm): 7.80 (CH, 2H, d), 7.09 (CH, 4H, br), 7.02 (CH, 2H, br), 6.86 (CH, 4H, br), 5.44 (OH, 2H, br), 4.16 (CH, 2H, br), 3.96 (CH_2, 4H, br), 3.86 (CH_2, 2H, br), 3.69 (CH_2, 2H, m), 1.57 (CH_3, 6H, s).

3.10. Preparation of BP-TA-TC. BP-TA (0.555 g, 1 mmol) was dissolved in dimethylformamide (50 mL) at room temperature. Recrystallized tetracyanoethylene (0.512 g, 4 mmol) was added slowly into the polymer solution in small portions with 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, dried, and further purified by repeated extraction with toluene. The polymer was dried under vacuum at least for 24 h before use. IR (KBr, cm^{-1}): 3426, 2965, 2937, 2877, 2217, 1602, 1536, 1510, 1486, 1419, 1367, 1312, 1257, 1198, 1087, 1039, 998, 963, 928, 829, 779, 739, 670, 574, 530, 505. ^{1}H NMR (δ, in ppm): 8.02 (thienyl CH, 1H, d), 7.72 (thienyl CH, 1H, br), 7.67 (CH, 2H, br), 7.10 (CH, 4H, d), 6.93 (CH, 2H, d), 6.85 (CH, 4H, d), 5.44 (OH, 2H, br), 4.12 (CH, 2H, br), 3.92 (CH_2, 4H, m), 3.78 (CH_2, 2H, br), 3.29 (CH_2, 4H, br), 1.57 (CH_3, 6H, s).

3.11. Polymer Film Preparation and Poling. The homogeneous solutions of polymers in spectroscopic grade *N*,*N*′-dimethylformamide were filtered through 0.2 μm membranes. The solutions were spin-coated onto glass slides. The film thickness was controlled to be between 0.4 and 0.5 μm by adjusting the solution concentration (about 10 wt %) and the spin speed (800−900 rpm). The spin-coated films were dried under vacuum for 48 h at 40−50 °C and were stored in a desiccator for further measurements.

Poling was performed by the corona poling technique in a wire to plane arrangement.[46,47] The corona discharge was generated from a tungsten wire that 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 110 °C. The sample was then slowly heated to a temperature 15 °C above the T_g of the polymer. The sample was poled at this temperature for an additional 20 min. before cooling.

3.12. Nonlinear Optical Property Measurement. The second-order NLO coefficients (d_{33}) of the poled films were measured by the second harmonic generation (SHG) technique. The measurements were carried out with a lase radiation at 1.550 or 1.064 μm from an optical parametric oscillator pumped with a Q switched Nd:YAG laser at 355 nm (Spectra-Physics). The SHG signal selected with an IR blocking colored glass filter and an appropriate interference filter, was detected by a photomultiplier tube and measured with a boxcar integrator (Stanford Research System). 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 indices and thicknesses of the polymer films were measured with an ellipsometer (Rudolph Research) and a profilometer (Dektak IIA), respectively.

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