# Synthesis and Optical Nonlinearity of Thermally Stable Polyimides Incorporated with Electro-Optic Chromophore as Side Chain

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**Summary:** We prepared thermally durable nonlinear optical (NLO) polymers, based on a polyimide attached with a NLO chromophore as a side-chain. The polyimide with two aromatic hydroxyls in the repeat unit was prepared by condensation polymerization between 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane and oxydiphthalic anhydride in DMAc, followed by imidization reaction. Mitsunobu coupling was carried out to incorporate the NLO chromophore into the polyimide backbone, to yield the side-chain polymer with a loading level of the chromophore up to 65 wt%. The thermal characterization of the polymer showed that the NLO polyimide had $T_g$ at 168 °C and was thermally stable up to 370 °C. The polymer solution was spin coated on the ITO glass to produce an optical quality film. The electro-optic coefficient of the film was obtained using 1.55 $\mu$m laser source, giving 31 pm/V with an electrical poling field of 1 MV/cm. The temporal stability of the polymer was confirmed over 330 h at 85 °C under nitrogen condition.

**Keywords:** electro-optic modulator; nonlinear optical polymer; side-chain polyimide; thermal stability

## Introduction

Electro-optic modulator is an indispensable component in the optical communication system, which is featured by converting an electronic signal into an optical one.[1,2] Inorganic crystals based on lithium niobate have been so far dominating the core materials in the device mainly due to their robust stability. But the high production cost and intrinsic large phase mismatch between infrared and millimeter wave frequencies force the researchers to find alternative. Many scientists have recognized nonlinear optical (NLO) organic materials as a promising candidate for such a role due to simple procedure for preparation of the device, easy structure-tailoring for certain purposes and large macroscopic optical nonlinearity.[3–5] In recent days there has been significant progress in development of the organic NLO materials, which have exhibited much higher electro-optic activity than the inorganic materials. Before being introduced into the real market, however there are still several critical hurdles. Thermal stability in the device processing and temporal stability in the real use are the most indispensable requisites, which the NLO materials should acquire.[6,7]

Polyimides have played a key role in the materials for the microelectronics, appliances, and other specialties largely due to their superior thermal stability, chemical resistance, and mechanical durability. Such

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performance has inspired many researchers to utilize the materials for the electro-optic applications.[8–10]

In recent paper, we have reported on a NLO chromophore which is featured by a phenylene ring as a conjugation bridge and a bulky alkyl chain attached on the side of the aromatic ring.[3c] It is thermally robust up to 220 °C and exhibits electro-optic coefficient as high as 24 pm/V. In this paper, as a consecutive work we introduced a terminal hydroxyl group into the NLO chromophore and then covalently bonded it to a thermally reliable polyimide backbone as a side chain. Optical quality films were fabricated by spincoating and their macroscopic optical nonlinearity was also evaluated.

## Experimental Part

### Materials

Diethyl-[2,5-bis(ethylhexyloxy)-4-bromophenyl]methyl phosphonate (compound **4**) and 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) were prepared according to the literatures.[3c,11]

### Synthesis of 2-[(4-{2-[4-Bromo-2,5-bis-(2-*tert*-butyldimethylsiloxyethyl)-phenyl]-vinyl}-phenyl)-methyl-amino]-ethanol (6)

Compound **4** (11 g, 19.55 mmol) was dissolved in dry THF (40 mL) under an atmosphere of dry argon and cooled to −84 °C. 1.5 M lithium diisopropylamide (3.56 g, 33.24 mmol) was added slowly. After 15 min stirring, the solution of compound **5** (6.31 g, 21.50 mmol) in dry THF (15 mL) was added dropwise to the suspension. The resulting reaction mixture was refluxed for 17 h. The crude product was purified by column chromatography (ethyl acetate/hexane = 1/10) to produce a yellow liquid in 63% yield. $^1$H-NMR ($CDCl_3$, ppm): δ 7.37–7.35 (d, 2H), 7.19–7.13 (d, 1H), 7.07 (s, 1H), 7.03–6.98 (d, 1H), 7.03 (s, 1H), 6.67–6.64 (d, 2H), 3.91–3.88 (d, 2H), 3.82–3.80 (d, 2H), 3.76 (t, 2H), 3.47 (t, 2H), 2.99 (s, 3H), 1.75 (q, 2H), 1.54–1.31 (m, 16H), 0.96–0.84 (m, 21), 0.00 (s, 6H).

### Synthesis of 2,5-bis-(2-ethylhexyloxy)-4-(2-{4-[(2-*tert*-butyldimethylsiloxyethyl)-methyl-amino]-phenyl}-vinyl)-benzaldehyde (7)

Compound **6** (7.0 g, 9.96 mmol) was dissolved in dry diethyl ether (20 mL). The solution was cooled to −10 °C and 2.5 M *n*-butyl lithium in hexane (1.02 g, 15.93 mmol) was added slowly. After the mixture was stirred for 5 min, dry DMF (8.2 mL) was added dropwise while maintaining the reaction temperature at −10 °C. The mixture was stirred for another 3 h below 0 °C. The organic layer was extracted with ethyl acetate. The extract was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by column chromatography (ethyl acetate/hexane = 1/10) to produce an orange liquid in 70% yield. $^1$H-NMR ($CDCl_3$, ppm): δ 10.40 (s, 1H), 7.41–7.38 (d, 2H), 7.29–7.23 (d, 1H), 7.28 (s, 1H), 7.20–7.14 (d, 2H), 7.13 (s, 1H), 6.69–6.66 (d, 2H), 3.99–3.94 (d, 2H), 3.90–3.88 (d, 2H), 3.77 (t, 2H), 3.49 (t, 2H), 3.01 (s, 3H), 1.79–1.75 (q, 2H), 1.54–1.30 (m, 16H), 0.96–0.85 (m, 21H), 0.00 (s, 6H).

### Synthesis of 2,5-bis-(2-ethylhexyloxy)-4-(2-{4-[(2-hydroxy-ethyl)-methyl-amino]-phenyl}-vinyl)-benzaldehyde (8)

Compound **7** (4.48 g, 6.87 mmol) was dissolved in acetone (30 mL) and 1N HCl (15 mL) was added slowly. The mixture was stirred for 3 h at room temperature. After neutralizing the solution with triethylamine (3 mL), the organic layer was washed with water and extracted with ethyl acetate. The residue was purified by column chromatography (ethyl acetate/hexane=1/2) to produce an orange liquid in 91% yield. $^1$H-NMR ($CDCl_3$, ppm): δ 10.43 (s, 1H), 7.45–7.42 (d, 2H), 7.33–7.28 (d, 1H), 7.31 (s, 1H), 7.22–7.17 (d, 1H), 7.15 (s, 1H), 6.80–6.77 (d, 2H), 4.02–4.00 (d, 2H), 3.92–3.90 (d, 2H), 3.84 (t, 2H), 3.54

(t, 2H), 3.03 (s, 3H), 1.82–1.75 (q, 2H) 1.56–1.23 (m, 16H), 0.99–0.91 (m, 12H).

### Synthesis of 2-(4-{2-[2,5-bis-(2-ethylhexyloxy)-4-(2-{4-[(2-hydroxy-ethyl)-methyl-amino]-phenyl}-vinyl)-phenyl]-vinyl}-3-cyano-5,5-dimethyl-5H-furan-2-ylidene)-malononitrile (StOH-TCF)

Piperidine (0.69 g, 8.1 mmol) was added into the solution of **TCF** (1.37 g, 6.85 mmol) in dry THF (50 mL) and the solution was stirred at 0 °C for 20 min. The solution of compound **8** (3.35 g, 6.23 mmol) in dry THF (30 mL) was added slowly. The reaction mixture was stirred at room temperature for 3 h. The mixture was quenched with water and excess of the solvent was removed by a rotary evaporator. The residue was extracted by dichloromethane. The crude product was purified by column chromatography (ethyl acetate/hexane = 2/3) to produce a dark blue solid in 62% yield. $^1$H-NMR ($CDCl_3$, ppm): δ 8.01–7.95 (d, $J = 16.4$ Hz, 1H), 7.47–7.44 (d, $J = 8.6$ Hz, 2H), 7.34–7.29 (d, $J = 16.4$ Hz, 1H), 7.27–7.22 (d, $J = 16.1$ Hz, 1H), 7.13 (s, 1H), 7.06–7.00 (d, $J = 18$ Hz, 1H), 7.00 (s, 1H), 6.81–3.78 (d, $J = 8.7$ Hz, 2H), 4.02 (t, 2H), 3.95–3.93 (d, $J = 5.2$ Hz, 2H), 3.87 (t, 2H), 3.6 (t, 2H), 3.07 (s, 3H), 1.80 (m, 8H), 1.61–1.36 (m, 16H), 1.02–0.90 (m, 12H).

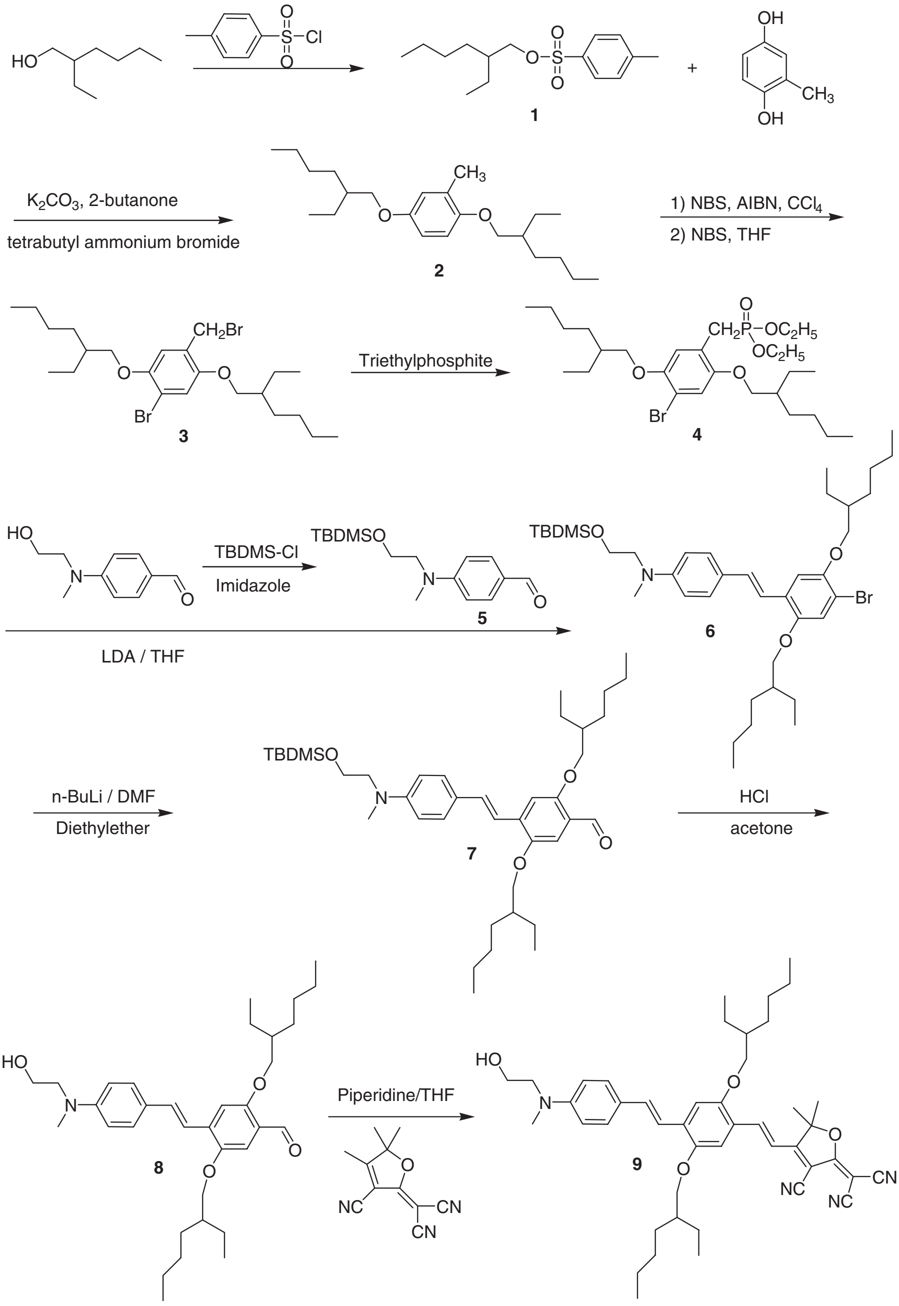
### Synthesis of NLO Polyimide (PI-StTCF)

Hydroxyl polyimide (PI-OH) was synthesized by condensation polymerization between 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane and oxydiphthalic anhydride in DMAc, followed by imidization reaction. To prepare NLO polyimide, diethyl azodicarboxylate (DEAD, 0.82 g, 4.69 mmol) was added dropwise for 4–6 h into a solution of PI-OH (1.04 g, 1.56 mmol), triphenylphosphine (1.23 g, 4.69 mmol), and the NLO chromophore StOH-TCF (2.81 g, 3.91 mmol) in THF (50 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 48 h. The resulting reaction mixture was precipitated into an agitated solution of methanol. The collected precipitate was purified by repeated reprecipitation several times. We characterized it by $^1$H NMR spectroscopy to figure out how many hydroxyls were remained in the polyimide backbone after the Mitsunobu reaction. We blocked the remaining hydroxyl groups in the polymer by coupling them with 2-(*N*-methyl-*N*-phenylamino)ethanol via Mitsunobu reaction using diethyl azodicarboxylate and triphenylphosphine.

## Results and Discussion

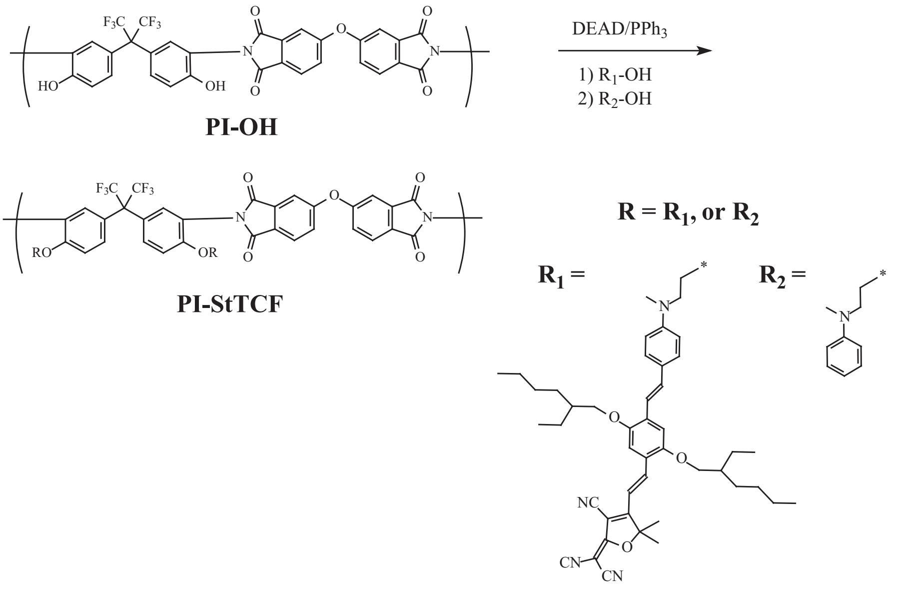
Synthetic procedure for the NLO chromophore was started with build-up of the conjugation bridge consisting of dialkoxy-substituted phenyl ring as shown in Scheme 1. 2-Ethylhexyl group was attached to the phenyl so as to keep the chromophore molecule from contacting closely its neighbor chromophores and hence to minimize the intermolecular electrostatic interaction. The alkyl chains may also play a major role in suppressing formation of cis-isomer as well as offering good solubility in solvents and polymer medium. Wittig-Horner reaction is an efficient coupling way between an aldehyde and a phosphonate compound. Knoevenagel condensation is a simple and high yield coupling method to produce an ethylene unit from an aldehyde and an activated methyl moiety. So the phenyl ring was designed to have not only the phosphonate functionality for coupling with the donor (aminobenzaldehyde), but also the bromide terminal which is inert in the Wittig-Horner coupling but is able to easily transform to an aldehyde for Knoevenagel condensation with the activated methyl of the acceptor (TCF).

The chemical structure and purity of the chromophore were verified by $^1$H NMR spectroscopy. $^1$H NMR spectrum in Figure 1 shows that all the relevant peaks are present with the exact integration ratios and no impurities are seen. We could recognize the protons attached with the double bond connecting the phenylene bridge and the acceptor in the $^1$H-$^1$H COSY spectrum (not shown), in which



***Scheme 1.***
Synthesis of the NLO chromophore StOH-TCF.

the proton at 8.0 ppm was correlated to one at 7.05 ppm. As large as 16 Hz coupling constant indicates that the ethenyl moiety has a trans-conformation. Another ethenyl protons in the double bond connecting the donor and the phenylene bridge showed peaks centered at 7.26 ppm with as large as 16 Hz coupling constant. The NMR



***Scheme 2.***
Synthesis of the NLO polyimide PI-StTCF.

data showed that the chromophore was obtained in a trans conformation. The UV/Vis absorption spectrum of the chromophore in chloroform exhibited a strong absorption band centered at 612 nm due to the π-π* charge transfer in the molecule. Differential scanning calorimeter (DSC) result pointed out that the chromophore has a melting point at 156 °C with a sharp endothermic peak. The onset decomposition temperature was also evaluated by TGA. The chromophore was remained thermally durable up to 280 °C.

The aromatic polyimide with a hydroxyl functional moiety was prepared by carrying out the condensation polymerization

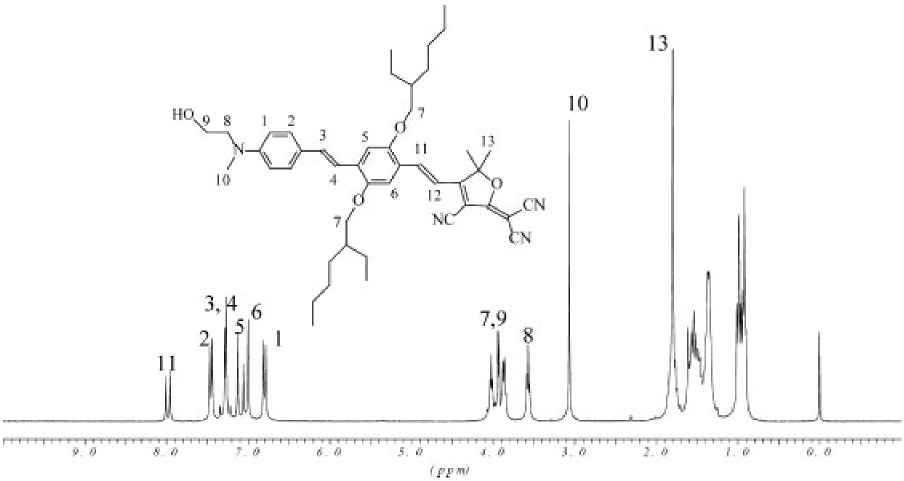


***Figure 1.***
$^1$H NMR spectrum of the hydroxyl NLO chromophore StOH-TCF.

between 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoro propane and oxydiphthalic anhydride, followed by imidization reaction. The $^1$H NMR spectrum of the polyimide (Figure 2a) shows an imidized polymer structure with the peak due to the two aromatic hydroxyl groups at 10.42 ppm. We also confirmed the complete imidization by the FT-IR spectrum, showing the strong peaks due to the symmetric and asymmetric stretching vibration absorptions of aromatic imides at 1782 and 1724 cm$^{-1}$. The average molecular weight of the resulting hydroxyl polyimides was 15,000 g/mol with a polydispersity of 1.56, which were estimated by GPC analysis based on a polystyrene standard.

The polyimide has the two hydroxyls in the repeat unit, which would be bonded to the NLO chromophore. The Mitsunobu coupling was performed in the presence of triphenyl phosphine and diethyl azodicarboxylate in THF solvent at room temperature to yield side-chain polyimide, in which 90% of the hydroxyl groups was reacted with the chromophores and the other 10% remained intact. The reaction extent was determined by comparing the relative integration of the remained hydroxyl peak at 10.42 ppm and that of methyl peak attached to amine at 2.69 ppm in the $^1$H NMR spectrum. The intact hydroxyls were reacted with 2-(*N*-methyl-*N*-phenylamino)ethanol via another Mitsunobu reaction to give the NLO polyimide PI-StTCF. The complete disappearance of the aromatic hydroxyl groups was confirmed by the $^1$H NMR spectrum as shown in Figure 2(b). The loading level of the NLO chromophore in the polyimide was estimated to be 65 wt%.

The thermal features of the NLO polyimide were investigated by DSC and TGA. The NLO polymer exhibited fairly high glass transition temperature of 168 °C as determined by DSC. TGA analysis in Figure 3 clearly shows that the NLO polyimide was remained thermally durable

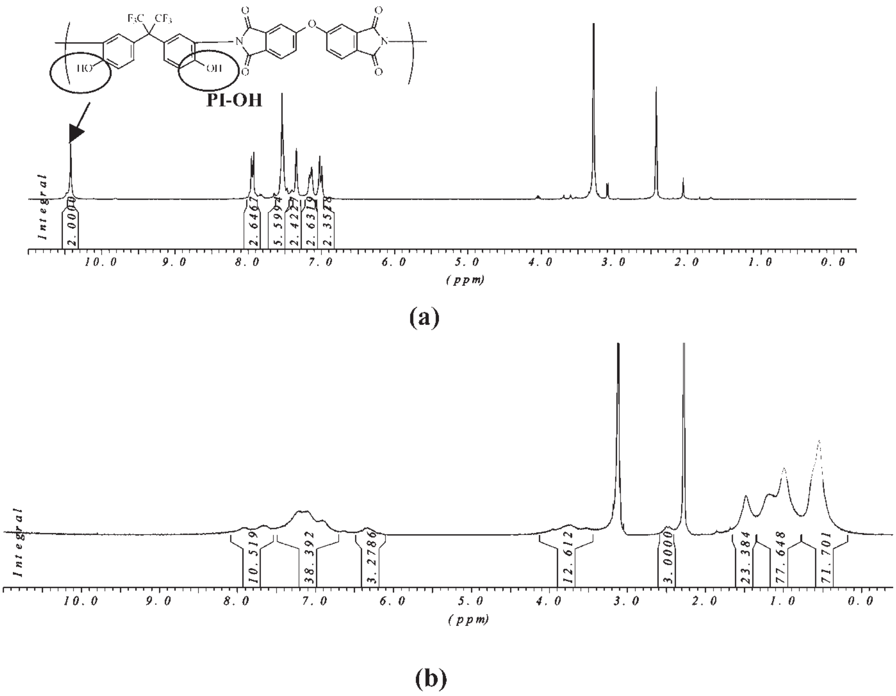


**Figure 2.**
$^1$H NMR spectra of (a) the hydroxyl polyimide PI-OH and (b) the NLO polyimide PI-StTCF.

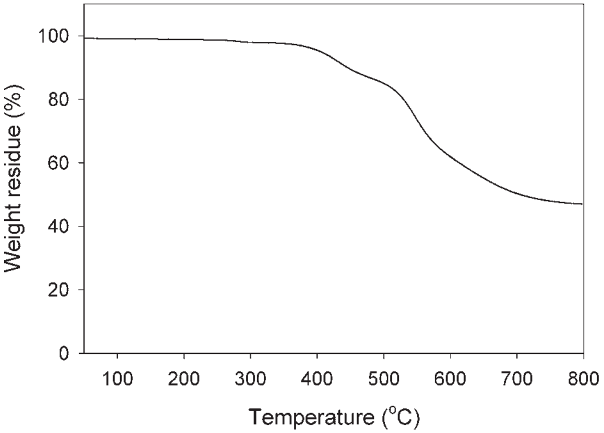


***Figure 3.***
Thermal degradation behavior observed by TGA thermogram of the NLO polyimide PI-StTCF.

up to 370 °C, until then there was very little weight loss less than 1%.

We fabricated optical quality films by spincoating the solution of PI-StTCF in cyclopentanone on the ITO glass. The films were thoroughly dried in the vacuum oven at 100 °C for 3 h. A gold electrodes were deposited on the top of the films by a thermal evaporation. Then the films were heated on a hot plate with a temperature controller to around the glass transition temperature of the polymer films, remained in the temperature for 5–30 min, and cooled down to room temperature under the electric field. Electro-optic coefficient of the poled polymer films was measured according to the reflection technique proposed by Teng and Man.[12] To find out optimum poling condition, we measured the electro-optic coefficients ($r_{33}$) of the films poled at different several temperatures in the range of 170~185 °C. The NLO polyimide showed the highest $r_{33}$ of 31 pm/V at 175 °C with a poling field of 1 MV/cm. We also invesigated the temporal stability of the poled polymer films by measuring the

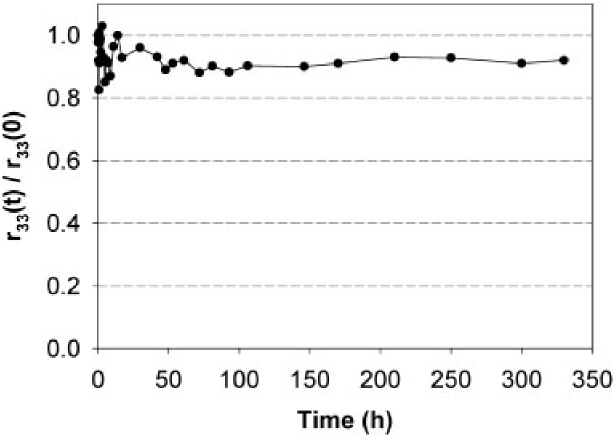


***Figure 4.***
Temporal stability of the electro-optic coefficient of the NLO polyimide at 85 °C.

decay tendency of the EO value at an elevated temperature. EO coefficient of the polymer was found to remain fairly stable even at longer periods. The initial value of EO coefficient was maintained up to 90% at an elevated temperature of 85 °C over 330 h as shown in Figure 4.

## Conclusion

In this work we successfully prepared a thermally stable NLO polymer by incorporating a NLO chromophore into a polyimide as a side chain by the Mitsunobu coupling with a loading density of the chromophore up to 65 wt%. The NLO polymer exhibited fairly high glass transition temperature of 168 °C and was thermally durable up to 370 °C. We obtained optical quality films as well by spincoating its solution. Its macroscopic optical nonlinearity was measured to be 31 pm/V by using simple reflection technique at 1.55 μm laser source. Its electro-optic coefficient was remained stable up to 330 h at an elevated temperature of 85 °C.

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