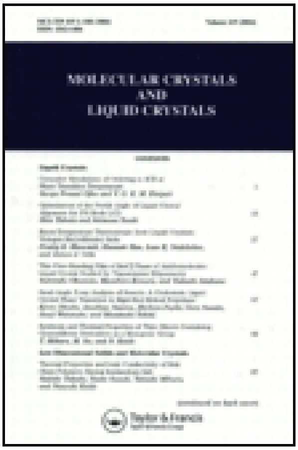

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Thermally Stable Nonlinear Optical Polymers Based on Polyimides Substituted with Chromophores Containing Julolidine Moiety

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We designed and synthesized a NLO chromophore adopting the concept of shape modification as well as possessing high thermal stability. The chromophore was featured by a phenylene ring as a conjugation bridge, a bulky alkyl chain attached on the side of the conjugation bridge, and julolidine moiety as an electron donor. The NLO chromophore was attached to the polyimide as a side chain, resulting in thermally durable NLO polymers. On set decomposition temperature of the NLO chromophore was measured 330°C in TGA analysis. The NLO polymer exhibited high glass transition temperature of 150°C and was thermally stable up to 250°C. The polymer was quite soluble in common solvents and produced an optical quality film by spin-coating. The electro-optic coefficient of the film was measured using 1.55 μm laser source, giving as high as 30 pm/V at the poling condition of 150°C and 1 MV/cm.

Keywords: electro-optic; julolidine donor; nonlinear optical polymer; thermal stability

INTRODUCTION

Organic and polymeric nonlinear optical (NLO) materials have been extensively studied as a viable alternative to the conventional inorganic crystalline materials in the telecommunication applications such as the optical modulators, optical processing devices, etc. In recent research reports, the optical devices incorporating these materials demonstrated broad bandwidth over 150 GHz and low driving voltage less than 1 V [1–4].

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One of the most challenging tasks in this area of research is how to efficiently translate the molecular hyperpolarizability (β) of the chromophores into the macroscopic electro-optic (EO) activities (r_{33}). The concept of shape modification of NLO chromophores by incorporating a bulky side alkyl chain has been introduced to reduce the intermolecular interaction between the chromophore molecules. The electrostatic attraction between the neighboring molecules especially in a high loading density might be a main reason for low poling efficiency because it may act as a strong resistance force against the external poling electric field. The computer simulation and experimental results have proved that the shape modification was an efficient way to enhance the poling efficiency and the macroscopic optical nonlinearity [1(b),3].

Another major quest in the development of device-adaptable NLO polymers is how to secure enough thermal and oxidative stability to endure the harsh condition in the device fabrication and maintain its initial performance through the long-time use over several years [5–7]. For this aim, we need a chromophore with high thermal decomposition stability and also a backbone polymer with high glass transition temperature as well as decomposition stability. Polyene structure has been commonly adopted for the conjugation bridge of the NLO chromophores due to its efficient conjugation. However, such polyene chromophores generally have poor thermal and photo stability, which is a critical drawback in a commercial application. Aromatic rings such as thiophene or phenylene are considered better alternatives, which are efficient and thermally stable conjugation bridge [8]. Among many kinds of polymers, polyimides are well known thermally stable polymers with optical transparency and high T_g. Hence the polymers have been studied for the NLO backbone polymer by many researchers [9].

In this work, we designed a NLO chromophore adopting the concept of shape modification as well as possessing high thermal stability. The chromophore was featured by a phenylene ring as a conjugation bridge, a bulky alkyl chain attached on the side of the conjugation body, and julolidine moiety as an electron donor. Julolidine has a similar chemical structure with aniline with two *N*-alkyl substituents forming rings with aromatic group. The fused ring structure efficiently protects the amine vulnerable to a radical attack and locks the lone electron pair of the nitrogen into the conjugation with the aromatic ring, leading to higher stability and stronger electron donating ability [10]. The NLO chromophore was chemically attached as a side chain to the thermally stable polyimide backbone. The resulting NLO polymer was fully characterized by ^{1}H NMR, UV/Vis absorption spectroscopy, TGA, DSC, and macroscopic optical nonlinearity.

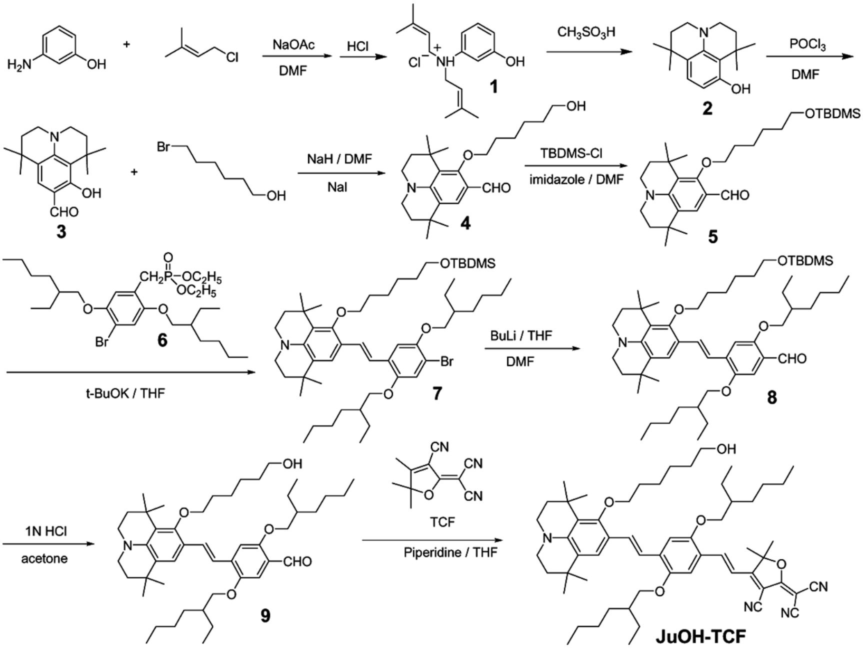
EXPERIMENTAL

Materials

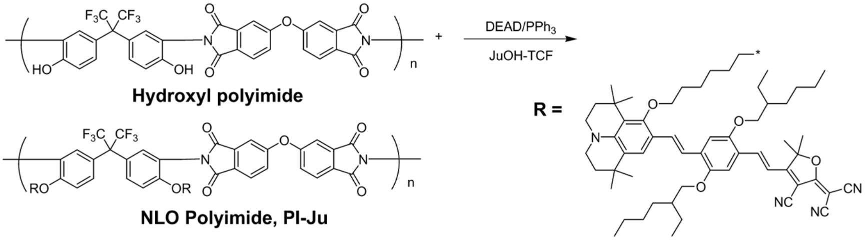
Methanesulfonic acid, phosphorus oxychloride, sodium hydride, sodium iodide, imidazole, *tert*-butyldimethyl-silyl chloride, *n*-butyl lithium in hexane, piperidine, potassium *tert*-butoxide and triethyl amine were purchased from Aldrich and used as received. 3-Aminophenol, 1-chloro-3-methyl-2-butene and 6-bromohexanol were obtained form TCI. The NLO chromophore (JuOH-TCF) and the NLO polyimide (PI-Ju) were synthesized by the routes described in Schemes 1 and 2, respectively.

Synthesis of Compound 1

In a three-necked flask equipped with a nitrogen inlet, a condenser, and a stirrer, 3-aminophenol (30.0 g, 0.27 mol), 1-chloro-3-methyl-2-butene (63.2 g, 0.60 mol), sodium acetate (51.9 g, 0.63 mol) and 80 ml anhydrous DMF were added. The air in the reaction vessel was replaced by nitrogen and the temperature was maintained at 30°C



SCHEME 1 Synthesis of the NLO chromophore JuOH-TCF.



SCHEME 2 Synthesis of the NLO polyimide PI-Ju.

with stirring. After about 12 h, the solution was filtered and the filtrate was collected. An identical volume of conc. HCl (aq) was added at 0°C. The residue was filtered, washed with THF several times and then dried in vacuo at 100°C (yield: 55%). ^{1}H NMR (DMSO, ppm) δ 10.12 (broad, –NH), 7.26-7.17 (m, 3H), 6.84 (s, 1H), 5.24-5.19 (t, $J = 6.75$ Hz, 2H), 4.07 (s, 4H), 3.80 (broad, –OH), 1.60 (s, 6H), 1.53 (s, 6H).

Synthesis of Compound 2

Compound 1 (24.0 g, 0.85 mol) was added to methanesulfonic acid (60 ml) and heated to 95°C. After 2 h at this temperature, the mixture was cooled to 0°C with vigorously stirring. NH_4OH(aq) was added until pH 7–8 was achieved and the solution was filtered. Solid product was collected and dried in vacuo at 100°C (yield: 80%). ^{1}H NMR ($CDCl_3$, ppm) δ 8.70 (–OH), 6.77-6.74 (d, $J = 8.34$ Hz, 1H), 6.08-6.05 (d, $J = 8.34$ Hz, 1H), 2.98-2.94 (t, $J = 5.46$ Hz, 2H), 2.92-2.89 (t, $J = 5.49$ Hz, 2H), 1.67-1.64 (m, 4H), 1.33 (s, 6H), 1.15 (s, 6H).

Synthesis of Compound 3

$POCl_3$ (7.0 ml) was slowly added to 10.0 ml anhydrous DMF under nitrogen at 0°C. The mixture was stirred vigorously for 2 h and then compound 2 (9.7 g, 0.40 mol) dissolved in 10 ml anhydrous DMF was added dropwise. After 12 h at room temperature, the solution was added dropwise to the ice water and then NaOAc(aq) was added until pH 7–8 was achieved. After vigorous stirring overnight, the filtrate was collected and recrystallized from ethyl acetate. The product was filtered and then dried in vacuo at 50°C (yield: 95%). ^{1}H NMR ($CDCl_3$, ppm) δ 9.38 (s, 1H), 7.04 (s, 1H), 3.34-3.30 (t, $J = 6.24$ Hz, 2H), 3.24-3.20 (t, $J = 5.81$ Hz, 2H), 1.75-1.71 (m, 4H), 1.44 (s, 6H), 1.25 (s, 6H).

Synthesis of Compound 4

Compound 3 (16.6 g, 0.06 mol) was dissolved in anhydrous DMF (60 ml) under nitrogen atmosphere. Sodium hydride (1.84 g, 0.073 mol) in DMF (35 ml) was slowly added into the solution. After 15 min stirring, 6-bromohexanol (13.2 g, 0.073 mol) and NaI (0.45 g) was added. The mixture was refluxed at 60°C for 12 h and then cooled to room temperature. The solution was poured into the water. The organic layer was extracted with dichloromethane and dried over anhydrous $MgSO_4$. After the solvent was evaporated, a brown solid was obtained by column chromatography (yield: 77%). ^{1}H NMR ($CDCl_3$, ppm) δ 9.92 (s, 1H), 7.57 (s, 1H), 3.98-3.94 (t, $J = 6.84$ Hz, 2H), 3.69-3.64 (t, $J = 6.43$ Hz, 2H), 3.31-3.27 (t, $J = 5.97$ Hz, 2H), 3.24-3.21 (t, $J = 5.97$ Hz, 2H), 1.94-1.44 (m, 10H), 1.42 (s, 6H), 1.26 (s, 6H).

Synthesis of Compound 5

Compound 4 (17.0 g, 0.046 mol) and imidazole (7.75 g, 0.11 mol) was dissolved in anhydrous DMF (50 ml) under nitrogen atmosphere. A solution of *tert*-butyldimethyl-silyl chloride (8.23 g, 0.055 mol) in DMF (20 ml) was added dropwise to the above solution. The reaction mixture was stirred at room temperature for 3 h. The resulting mixture was poured into the water in a separation funnel and was extracted with hexane. The hexane extract was then dried over $MgSO_4$ and condensed by a rotary evaporator. The residue was purified by column chromatography to produce a green liquid in 83% yield. ^{1}H NMR ($CDCl_3$, ppm) δ 9.89 (s, 1H), 7.53 (s, 1H), 3.92-3.87 (t, $J = 6.72$ Hz, 2H), 3.59-3.54 (t, $J = 6.21$ Hz, 2H), 3.26-3.22 (t, $J = 6.21$ Hz, 2H), 3.19-3.15 (t, $J = 5.76$ Hz, 2H), 1.88-1.37 (m, 12H), 1.35 (s, 6H), 1.21 (s, 6H), 0.84 (s, 9H), 0.00 (s, 6H).

Synthesis of Compound 7

Compound 5 (18.4 g, 0.038 mol) and compound 6 (25.5 g, 0.045 mol; the synthetic route of the compound 6 was described in our previous paper [4(d)]) was dissolved in anhydrous THF (50 ml) under nitrogen atmosphere. Potassium *tert*-butoxide (5.79 g, 0.049 mol) in THF (20 ml) was transferred into the solution. The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was poured into the saturated $NaHCO_3$. The organic layer was extracted with hexane and then dried over $MgSO_4$. After the solvent was evaporated, the residue was purified by column chromatography to produce a green liquid in 86% yield. ^{1}H NMR ($CDCl_3$, ppm) δ 7.30 (s, 1H), 7.15 (s, 2H), 7.11 (s, 1H), 7.02 (s, 1H), 3.86-3.79 (m, 6H), 3.55-3.51 (t, $J = 6.48$ Hz, 2H), 3.14-3.10 (t, $J = 5.49$ Hz, 2H), 3.07-3.04 (t, $J = 4.74$ Hz, 2H), 1.85-1.23 (m, 38H), 0.95-0.85 (m, 12H), 0.83 (s, 9H), 0.00 (s, 6H).

Synthesis of Compound 8

Compound 7 (18.7 g, 0.021 mol) was dissolved in anhydrous THF (50 ml). The solution was cooled to −84°C and then 2.5 M n-butyl lithium in hexane (2.0 g, 0.031 mol) was added slowly. After the mixture was stirred for 30 min, dry DMF (3.0 g) was added dropwise as the reaction temperature maintained at −84°C. The mixture was stirred for 3 h below 0°C. After the reaction was completed, the organic layer was extracted with hexane. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by column chromatography to produce an orange liquid in 45% yield. ^{1}H NMR ($CDCl_3$, ppm) δ 10.40 (s, 1H), 7.35 (s, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 7.25 (s, 1H), 7.18 (s, 1H), 3.96-3.84 (m, 6H), 3.87-3.52 (t, $J = 6.21$ Hz, 2H), 3.18-3.14 (t, $J = 5.73$ Hz, 2H), 3.11-3.08 (t, $J = 5.49$ Hz, 2H), 1.88-1.24 (m, 38H), 0.96-0.96 (m, 12H), 0.85 (s, 9H), 0.00 (s, 6H).

Synthesis of Compound 9

Compound 8 (7.0 g, 8.27 mmol) was dissolved in acetone (20 ml). 1N HCl (10 ml) was added slowly to the solution. The mixture was stirred for 3 h at room temperature, followed by neutralization with triethylamine (3 ml). The organic layer was washed with water and extracted with hexane. The residue was purified by column chromatography to produce an orange liquid in 75% yield. ^{1}H NMR ($CDCl_3$, ppm) δ 10.42 (s, 1H), 7.36 (s, 1H), 7.33 (s, 1H), 7.30 (s, 2H) 7.20 (s, 1H), 3.98-3.87 (m, 6H), 3.61-3.57 (t, 2H), 3.20-3.16 (t, $J = 5.94$ Hz, 2H), 3.14-3.10 (t, $J = 5.67$ Hz, 2H), 1.91-1.23 (m, 38H), 0.98-0.90 (m, 12H).

Synthesis of JuOH-TCF

Piperidine (0.41 g, 4.85 mmol) was added into the solution of TCF (0.74 g, 3.73 mmol) in dry THF (15 ml) and the solution was stirred at 0°C for 30 min. A solution of compound 9 (2.73 g, 3.73 mmol) in dry THF (60 ml) was added slowly. The reaction mixture was stirred at room temperature for 6 h. The mixture was quenched by adding a small amount of water and THF was removed by a rotary evaporator. The residue was extracted by ethylacetate. The crude product was purified by column chromatography to produce a dark blue solid in 60% yield. ^{1}H NMR ($CDCl_3$, ppm) δ 8.04-7.98 (d, $J = 16.50$ Hz, 1H), 7.44-7.39 (d, $J = 16.20$ Hz, 2H), 7.34-7.28 (d, $J = 16.20$ Hz, 1H), 7.16 (s, 1H), 7.08-7.03 (d, $J = 14.94$ Hz, 2H), 3.98-3.95 (d, $J = 3.45$ Hz, 4H), 3.89-3.84 (t, $J = 6.78$ Hz, 2H), 3.63-3.58 (t, $J = 6.48$ Hz, 2H), 3.24-3.20 (t, $J = 5.82$ Hz, 2H), 3.16-3.13 (t, $J = 5.82$ Hz, 2H), 1.86-1.32 (m, 44H), 1.02-0.90 (m, 12H).

Synthesis of NLO Polyimide Substituted with JuOH-TCF (PI-Ju)

The aromatic polyimide with a hydroxyl functional moiety was prepared according to the literature by carrying out the condensation polymerization between 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoro propane and oxydiphthalic anhydride, followed by imidization reaction [4(f),6]. The synthesized hydroxyl polyimide was characterized by GPC, DSC, and TGA. The average molecular weight was found to be 18,000 and the polydispersity index was 1.6 by GPC. T_g of the polymer was measured 275°C by DSC and the on set degradation was 355°C by TGA.

The NLO chromophore was bonded to the hydroxyl polyimide via Mitsunobu coupling as depicted in Scheme 2. The diethyl azodicarboxylate (DEAD) (1.14 g, 6.57 mmol) was added dropwise for 4–6 h into the solution of hydroxyl polyimide, triphenylphosphine (1.72 g, 6.57 mmol), and JuOH-TCF in THF (64 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 dissolved in THF (60 ml) and reprecipitated from methanol to purify the polymer. The precipitate was filtered and washed with methanol. Finally, the soxhlet extraction was carried out for 3 days to remove any residue of the monomers.

Measurement of Electro-Optic Coefficient

The NLO polyimide was dissolved in cyclopentanone at a concentration of 10–15 wt.%. The solution was spin-coated on ITO glass. The spincoated films were thoroughly dried in the vacuum oven at 100°C for 3 h. The dark blue films were about 1–2 μm thick. 100 nm-thick gold electrodes were deposited on the top of the films in a thermal evaporator. The samples 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 (r_{33}) of the aligned polymer films was measured according to the reflection technique proposed by Teng and Man using 1.55 μm laser source [11].

RESULT AND DISCUSSION

The synthetic procedure for the NLO chromophore was started with build-up of the conjugation bridge consisting of the dialkoxy chain substituted phenyl ring as shown in Scheme 1. 2-Ethylhexyl group was attached to the bridge to keep the chromophore molecule from interacting closely with its neighboring ones and hence minimize its intermolecular electrostatic interaction. The bulky alkyl chains also play a major role in suppressing formation of cis-isomer as well as offering good solubility. 3-Aminophenol and 1-chloro-3-methyl-2-butene reacted to produce compound 1. After cyclization by methansulfonic acid, compound 3 was obtained via Vilsmeier formylation. As a tethering site to the backbone polymer, hydroxyl group was introduced by reacting 6-bromohexanol to the compound 3. After protecting the hydroxyl, the julolidine donor was coupled with the phenylene bridge *via* Wittig-Horner reaction. The terminal bromide of the compound 7 was converted to aldehyde by treatment with *n*-butillithium and DMF according to the Bouveault method. After restoring the hydroxyl, the resulting compound 9 was combined with the electron acceptor, 2-(3-cano-4,5,5-trimethyl-5H-furan-2-ylidene)malononitrile (TCF) in a mild reaction condition using piperidine as a base, to give

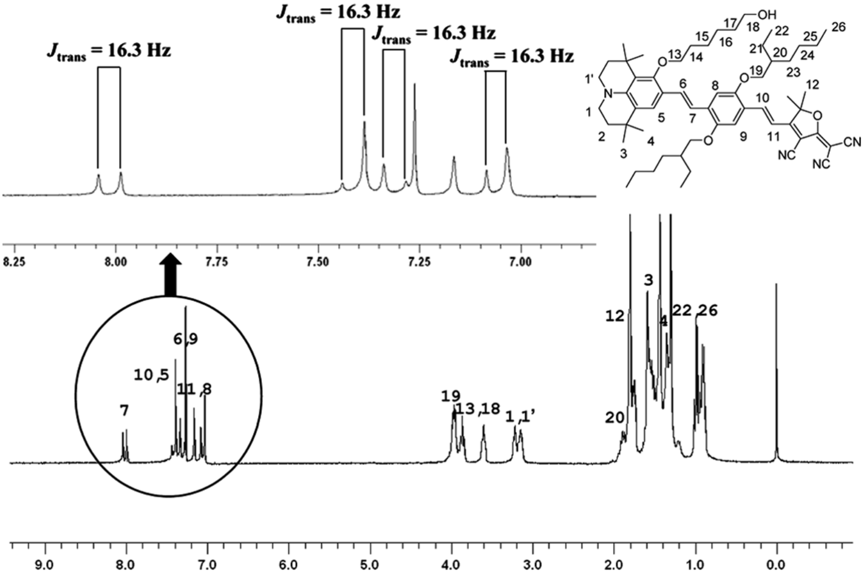
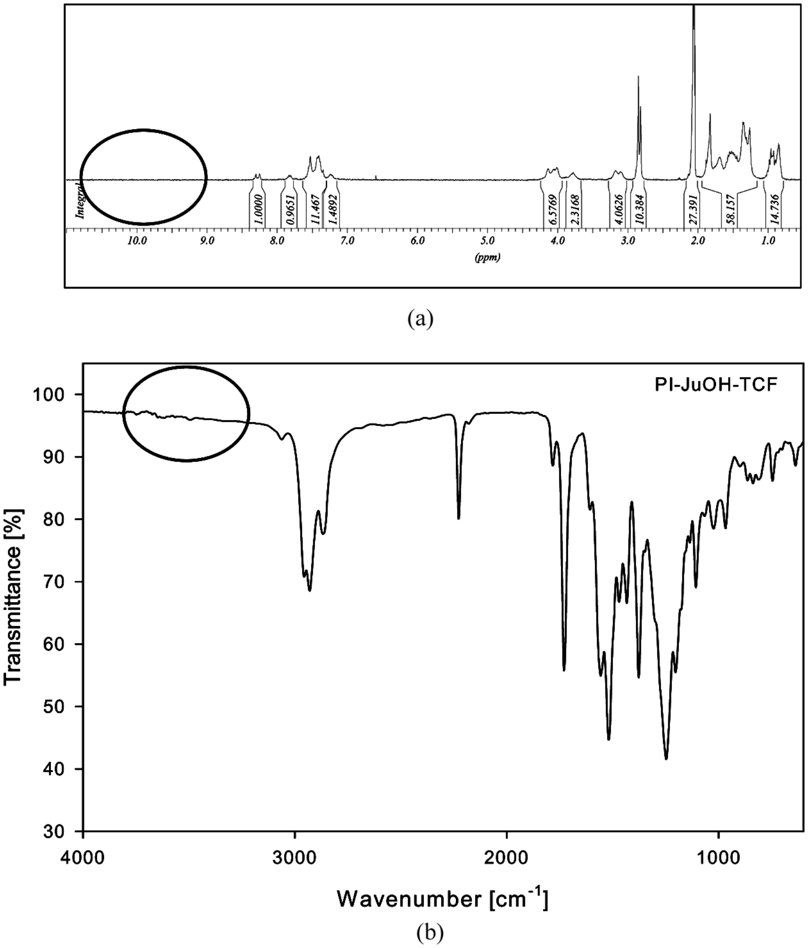


FIGURE 1 ^{1}H NMR spectrum of JuOH-TCF.

the final product JuOH-TCF. The chromophore was purified by column chromatography to yield a dark blue powder.

The NLO chromophore was characterized by ^{1}H NMR, UV/Vis absorption spectroscopy, DSC, and TGA. The NMR spectrum in Figure 1 clearly indicated that JuOH-TCF was successfully synthesized in a high purity. In addition, the coupling constants as large as 16 Hz at 8.02, 7.41, 7.31, and 7.05 ppm clearly indicated that the ethenyl moieties in the conjugation body had a trans conformation. There was seen no peak due to cis-conformation as the bulky alkyl chain may suppress



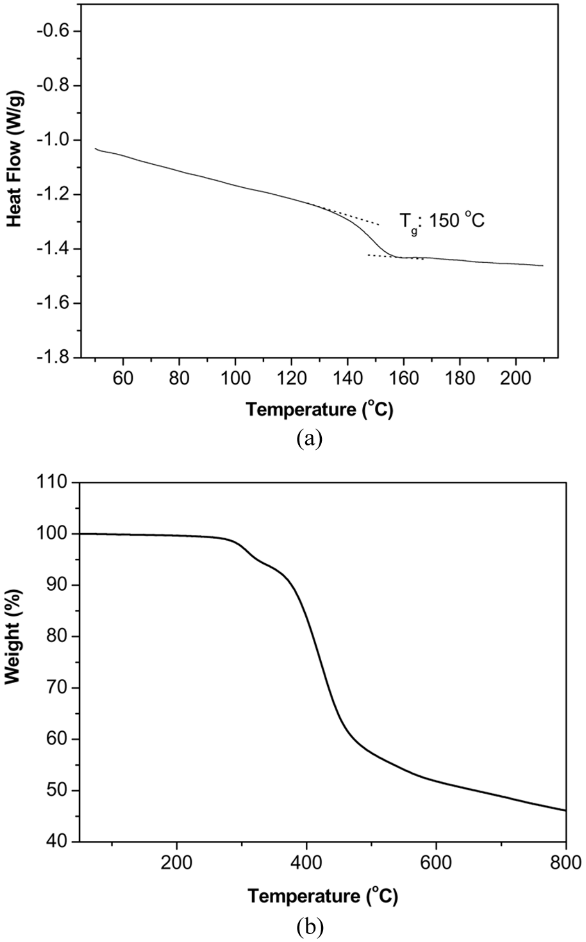
(a)

(b)

FIGURE 2 (a) ^{1}H NMR spectrum and (b) FT–IR spectrum of the NLO polyimide PI-Ju.

the formation of the cis-isomer. The UV/Vis absorption spectrum of the chromophore in chloroform exhibited a strong absorption band centered at 665 nm due to the π-π charge transfer in the molecule. The DSC data of the chromophores exhibited sharp melting peaks at 128°C, indicating that it was crystalline and highly pure compound. The onset decomposition temperature was also evaluated by TGA. JuOH-TCF was remained thermally stable up to 330°C.

The hydroxyl polyimide has two hydroxyl groups in the repeat unit, which would be bonded to the NLO chromophore through Mitsunobu



(a)

(b)

FIGURE 3 (a) DSC thermogram and (b) TGA thermogram of NLO polyimide PI-Ju.

coupling in the presence of triphenyl phosphine and diethyl azodisscarboxylate. The resulting NLO polyimide was purified by repeated reprecipitation from THF to methanol and soxhlet extraction. The NLO polyimide was thoroughly characterized by ^{1}H NMR, FT-IR, DSC, and TGA. The NLO polyimide showed no peak around 10 ppm in ^{1}H NMR spectrum of Figure 2(a), while the hydroxyl polyimide had a peak at 10.42 ppm due to the hydroxyl groups, confirming that all hydroxyls in the backbone were bonded with the NLO chromophore. FT-IR in Figure 2(b) also verified the full conversion since there was no absorption band around 3300 cm^{-1} due to the hydroxyl group. The thermal features of the NLO polyimide were investigated by DSC and TGA as shown in Figure 3. The NLO polymer exhibited fairly high glass transition temperature of 150°C as determined by DSC. The TGA analysis clearly shows that the NLO polyimide was remained thermally durable up to 250°C.

We fabricated optical quality films by spin-coating the solution of the NLO polyimide in cyclopentanone on the ITO glass. The films were thoroughly dried in the vacuum oven at 100°C for 3 h. After gold electrodes were deposited, 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 by the reflective technique using 1.55 μm laser source. The NLO polyimide showed as high as 30 pm/V of electro-optic coefficient at the poling condition of 150°C and 1 MV/cm.

CONCLUSION

In this work, we prepared a NLO chromophore adopting the concept of shape modification as well as possessing high thermal stability and also incorporated the NLO chromophore into the hydroxyl polyimide, resulting thermally durable NLO polymers. The NLO polymer exhibited high glass transition temperature of 150°C and was thermally stable up to 250°C in the DSC and TGA analysis. The optical quality films obtained from the polymer showed as high as 30 pm/V of macroscopic optical nonlinearity at 1.55 μm.

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