Two-Step Synthesis of Side-Chain Aromatic Polyimides for Second-Order Nonlinear Optics

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Received August 25, 1995; Revised Manuscript Received October 18, 1995[⊗]

ABSTRACT: A two-step, generally applicable synthetic approach for NLO side-chain *aromatic* polyimides was developed. This is a one-pot preparation of a preimidized, hydroxyl polyimide, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via a mild post-Mitsunobu reaction. NLO side-chain aromatic polyimides with different polymer backbones and different chromophores were synthesized, and the chromophore loading level in the polyimides was controlled efficiently from 0 to 50% by weight. This facile method provides the synthesis of NLO polyimides with a broad variation of polymer backbone and side-chain chromophores to fine-tune the electrical and structural properties. All the synthesized NLO side-chain polyimides have high glass transition temperatures (T_g > 220 °C) and thermal stability. A large electro-optic (E-O) coefficient (r_{33}) value (11 pm/V measured at 0.83 μm and 34 pm/V at 0.63 μm) and long-term stability (>500 h at 100 °C) of the dipole alignment were observed.

Introduction

Polyimide-based organic materials for second-order nonlinear optics have attracted attention due to their low dielectric constant, high glass transition temperature (T_g), and compatibility with semiconductor processes.[1−5] Guest−host NLO chromophore−polyimide[1] and *aliphatic* NLO side-chain polyimide[6−8] are two material systems of polymides which were developed previously. Although both systems provide encouraging results, their physical properties need to be improved greatly in order to overcome several deficiencies. The guest−host polyimide system, for example, has several problems including low loading levels of effective chromophores, sublimation and diffusion of the chromophores at high processing temperatures and prolonged working periods, plasticization of the polyimide by the chromophores, and erosion of chromophore molecules by organic solvents encountered in fabricating multilayer devices;[6] while the aliphatic side-chain polyimide system suffers low glass transition temperature (T_g), low temperature resistance, poor mechanical properties, and limited structural versatility.[6−8] To overcome these problems, Marks and co-workers[9] achieved a second-order NLO material system of polyfunctional epoxide and diisocyanate cross-linked chromophoric poly(hydroxystyrene)s with high T_g; Dalton and co-workers[10] developed a cross-linkable lattice polyimide with dynamic stability of second harmonic generation (SHG) up to 160 °C; and Burland and co-workers[11,12] synthesized a "donor-embedded" side-chain NLO polyimide with impressive poled order stability at the high temperature of 250 °C. Also, Miller *et al.*,[13] Yu *et al.*,[14] and our group[15] have recently developed a new NLO polyimide system, NLO side-chain *aromatic* polyimides. The side-chain aromatic polyimides exhibit much better properties, including higher temperature alignment stability, better mechanical properties, and lower optical loss, than those of *aliphatic* side-chain and guest−host polyimide systems. However, all these synthetic methods for aromatic side-chain polyimides include a tedious procedure for the synthesis of the chromophore-containing diamine monomers. Moreover, the fact that few chromophores can survive the relatively harsh chemical conditions of the monomer synthesis and the imidization of the polymer severely limits the application of the methodologies.[13−15] We reported[16] recently a facile, generally applicable, two-step approach for the synthesis of NLO side-chain aromatic polyimides. This is a one-pot preparation of a preimidized, hydroxy-containing polyimide,[17] followed by the covalent bonding of a chromophore onto the backbone of the polyimide via a post-Mitsunobu reaction.[18] By introduction of the chromophores at the last stage through the very mild Mitsunobu condensation, the harsh imidization process of the poly(amic acid) is avoided and the synthesis of the chromophore-containing diamine monomers is also not necessary. This allows us to synthesize NLO side-chain aromatic polyimides with a broad variation of polymer backbone and great flexibility in the selection of the chromophores. In this paper, we report detailed studies of the synthesis and the characterization of the polymers, as well as the thermal properties, the second-order nonlinearity, and other physical properties of the synthesized polymeric materials.

Experimental Section

Electronic or polymer grade pyromellitic dianhydride (PMDA), 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF), and 3,3′-dihydroxy-4,4′-diaminobiphenyl (HAB) were purchased from Chriskev Co., Inc. Crude Disperse Red 1 (95%) was from Aldrich Chemical Co. and further purified by silica gel column chromatography before use. Other chemicals were purchased from Aldrich or Lancaster Synthesis Inc. and used as received unless otherwise specified. THF was distilled under argon from sodium benzophenone ketyl. *N,N*-Dimethylacetamide (DMAc), xylenes, and cyclopentanone were purified by distillation over phosphorus pentoxide. Flash column chromatography was carried out on silica gel (grade 9385, 230−400 mesh from Aldrich).

NMR spectra were obtained on a Varian VXR 300 MHz FT NMR spectrometer. Infrared spectra were taken on a Galaxy FTIR 3000 spectrophotometer with neat polymer films cast from THF solutions on KBr disks. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 UV−vis/near-IR spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere by using the DSC-2910 and TGA-2950 systems from TA instruments. The molecular weights and polydispersities (relative to polystyrene standards) were de-

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

0024-9297/96/2229-0535$12.00/0

termined with a Waters gel permeation chromatograph (GPC) with HR-5E and HR-2 columns at room temperature (THF as the eluant). The melting points (uncorrected) were determined on a Mel-Temp.

The cyclopentanone (or cyclohexanone) solutions of the polymers (10−15% m/m) were filtered through a 0.2 μm syringe filter and then spin-coated onto an indium tin oxide (ITO) glass substrate. The films were kept in a vacuum oven at 200 °C for 1 h to ensure removal of the residual solvent. A thin gold plating (∼80 nm) was sputtered on top of the polymer-coated ITO substrate by plasma. The relevant electro-optic coefficients r_{33} of electrode-poled films were measured by an ellipsometric technique similar to that described by Teng and Man.[19]

2-(*N*-Ethyl-4-(tricyanovinyl)anilino)ethanol (4a). 2-(*N*-Ethylanilino)ethanol (5.0 g, 30 mmol) was reacted with tetracyanoethylene (TCNE, 4.2 g, 33 mmol) in DMF under nitrogen at 0 °C to room temperature for 4 h. The reaction mixture was dissolved in CH_2Cl_2 (100 mL). The solution was then washed with water (3 × 20 mL) and dried with sodium sulfate. The compound was purified on a silica gel column with the eluate 2:1 methylene chloride:ethyl acetate to afford 5.3 g (66% yield) of 2-(*N*-ethyl-4-(tricyanovinyl)anilino)ethanol. The pure compound was a blue needle crystal with mp 154−156 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 8.2 (d, 2 H, J = 8.7 Hz), 6.8 (d, 2 H, J = 8.7 Hz), 3.9 (m, 2 H), 3.7 (m, 4 H), 1.8 (br, 1 H, OH), 1.3 ppm (t, 3 H).

Hydroxyl Aromatic Polyimide 3. The polymerization was conducted in a dry nitrogen-flushed flask at room temperature with a concentration of 15% solids by weight in *N*,*N*-dimethylacetamide (DMAc). A stoichiometric amount of 6FDA (3.332 g, 7.50 mmol) was added to a solution of 3,3′-dihydroxy-4,4′-diaminobiphenyl (1.622 g, 7.50 mmol) in DMAc (30 mL) at 0 °C. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly(amic acid) solution. The viscosity of the solution increased during this period greatly. Dry xylene (30 mL) was added to the flask, and the poly(amic acid) was thermally cyclized at 160 °C for 3 h. Water that was eliminated by the ring-closure reaction was separated as a xylene azeotrope at the same time. The resulting solution was added dropwise into an agitated solution of methanol (500 mL) and 2 N HCl (10 mL) to obtain the brown hydroxyl polyimide. The polymer was redissolved in THF (50 mL) and further purified by reprecipitating into a solution of methanol (500 mL) and 2 N HCl (5 mL) from its THF solution. The polymer was then filtered and dried at 60 °C under vacuum for 24 h to afford 4.26 g (91% yield) of hydroxyl polyimide **3**. ^{1}H NMR (300 MHz, DMSO-d_6) 10.06 (s, 2 H, OH), 8.20 (d, 2 H, J = 7.8 Hz), 8.0 (d, 2 H, J = 7.8 Hz), 7.8 (s, 2 H), 7.4 (d, 2 H, J = 7.8 Hz), 7.21 (s, 2 H), 7.19 ppm (d, 2 H). Molecular weight: M_w = 33 000, M_n = 23 000 with the polydispersity of 1.43. T_g > 360 °C. Thermal stability: <2% weight loss up to 400 °C (20 deg/min, N_2).

Hydroxyl aromatic polyimide 6 was prepared in an analogous manner as above via the polymerization of 2,2-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF) and pyromellitic dianhydride (PMDA) with the yield of 92%. ^{1}H NMR (300 MHz, DMSO-d_6) 10.6 (s, 2 H, OH), 8.3 (s, 2 H), 7.6 (s, 2 H), 7.3 (d, 2 H, J = 8.7 Hz), 7.1 ppm (d, 2 H, J = 8.7 Hz). T_g = 350 °C. Thermal stability: <2% weight loss up to 400 °C (20 deg/min, N_2).

Side-Chain Aromatic Polyimide 5a. Hydroxyl polyimide **3** (0.312 g, 0.50 mmol of repeat unit), PPh_3 (0.393 g, 1.50 mmol), and 2-(*N*-ethyl-4-(tricyanovinyl)anilino)ethanol (**4a**, 0.293 g, 1.10 mmol) were dissolved in dry THF (15 mL) successively. The flask was flushed with dry nitrogen. Diethyl azodicarboxylate (DEAD, 0.26 g, 1.50 mmol) was added dropwise to the solution. A red precipitate formed immediately and dissolved into the solution after stirring at room temperature for 2 h. The reaction mixture was further stirred at room temperature for 48 h and was then added dropwise into an agitated solution of methanol (300 mL) and 2 N HCl (5 mL). The collected precipitate was redissolved in THF (30 mL) and reprecipitated into the solution of methanol and HCl. The precipitate was filtered and washed with methanol. The polymer was further purified by Soxhlet extraction with methanol for 24 h and dried at 60 °C under vacuum for 24 h to afford 0.50 g (89% yield) of the red side-chain polyimide **5a**. ^{1}H NMR (300 MHz, DMSO-d_6) 8.14 (d, 2 H, J = 8.1 Hz), 8.0 (br, 2 H), 7.8 (d, 4 H, J = 8.7 Hz), 7.7 (s, 2 H), 7.6 (br, 2 H), 7.5 (br, 4 H), 6.9 (d, 4 H, J = 8.1 Hz), 4.5, 4.3 (br, 4 H, CH_2), 3.9 (br, 4 H, CH_2), 3.4 (br, 4 H, CH_2), 0.9 ppm (t, 6 H, CH_3). UV−vis: λ_{max} = 520 nm. Molecular weight: M_w = 57 000 with a polydispersity index of 1.51. T_g = 222 °C. Thermal stability: <1% weight loss up to 300 °C.

Side-chain aromatic polyimide 5b was synthesized by a procedure similar to that for polyimide **5a** by using Disperse Red 1 (**4b**) instead of **4a**. ^{1}H NMR (DMSO-d_6) 8.4−6.6 (m, 28 H, aromatic H), 4.4, 4.3 (br, 4 H, CH_2), 3.7 (br, 4 H, CH_2), 3.3 (br, 4 H, CH_2), 0.9 ppm (br, 6 H, CH_3).

Side-chain aromatic polyimide 5c was synthesized by a procedure similar to that for **5a** by using 4-(dicyanomethylene)-2-methyl-6-[4-(ethyl(2-hydroxyethyl)amino)styryl]-4*H*-pyran[20] (hydroxyl DCM, **4c**) instead of **4a**. ^{1}H NMR (DMSO-d_6) 8.4 −6.4 (m, 28 H, aromatic H), 4.1 (br, 4 H, CH_2), 3.7 (br, 4 H, CH_2), 3.2 (br, 4 H, CH_2), 2.4 (br, 6 H, CH_3 on pyran ring), 0.8 ppm (br, 6 H, CH_3).

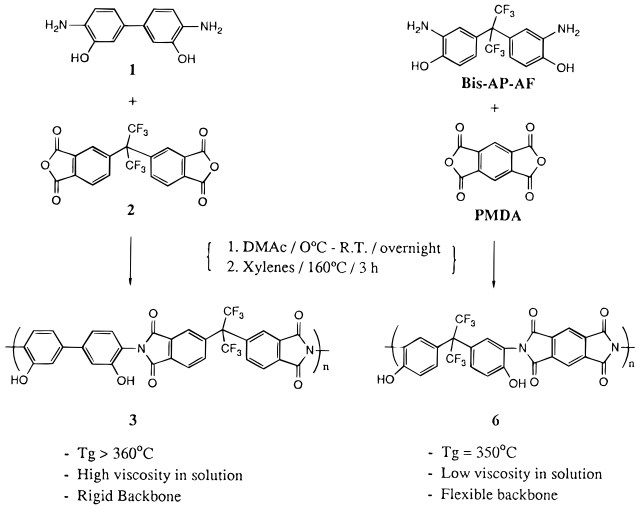
Side-Chain Aromatic Polyimide 7a. Polyimide **3** (0.312 g, 0.50 mmol of repeat unit), PPh_3 (0.184 g, 0.70 mmol), and **4a** (0.160 g, 0.60 mmol) were dissolved in dry THF (20 mL) successively. The flask was flushed with dry nitrogen. DEAD (0.13 g, 0.75 mmol) was added dropwise into the solution. A red precipitate formed immediately and redissolved into the solution after stirring at room temperature for 2 h. The reaction solution was further stirred at this temperature for 48 h and was then added dropwise into an agitated solution of methanol (400 mL) and 2 N HCl (5 mL). The collected precipitate was redissolved in THF (30 mL) and reprecipitated into the solution of methanol and HCl. The polymer was further purified by Soxhlet extraction with methanol for 24 h and dried at 60 °C under vacuum for 24 h to afford 0.38 g (88% yield) of a red solid of polyimide **7a**. ^{1}H NMR (DMSO-d_6) 10.06 and 10.02 (s, 1 H, OH), 8.2−8.1 (m, 2 H), 8.0 (br, 2 H), 7.8 (m, 4 H), 7.6−7.2 (m, 6 H), 6.9 (d, 2 H, J = 8.4 Hz), 4.5, 4.3 (br, 2 H), 3.8 (br, 2 H), 0.9 ppm (t, 3 H). UV−vis: λ_{max} = 518 nm. Molecular weight: M_w = 41 000 with a polydispersity of 1.77. T_g = 235 °C. Thermal stability: <1% weight loss up to 300 °C.

Side-chain aromatic polyimide 7b was synthesized by a procedure similar to that above. Polyimide **3** (0.624 g, 1.00 mmol of repeat unit), PPh_3 (0.367 g, 1.40 mmol), and Disperse Red 1 (**4b**, 0.346 g, 1.10 mmol) were dissolved in dry THF (25 mL) successively. DEAD (0.24 g, 1.4 mmol) was added dropwise into the solution. The solution was stirred at room temperature under nitrogen for 48 h. The polymer was worked up with the same procedure as above to afford 0.85 g (92% yield) of the red side-chain polyimide **7b**. ^{1}H NMR (DMSO-d_6) 10.08 and 10.03 (s, 1 H, OH), 8.4−6.6 (m, 20 H, aromatic H), 4.4 (br, 2 H, CH_2), 3.8 (br, 2 H, CH_2), 3.3 (br, 2 H, CH_2), 0.9 ppm (br, 3 H, CH_3). UV−vis: λ_{max} = 480 nm. Molecular weight: M_w = 48 000 with a polydispersity of 1.41. T_g = 228 °C. Thermal stability: <1% weight loss up to 300 °C.

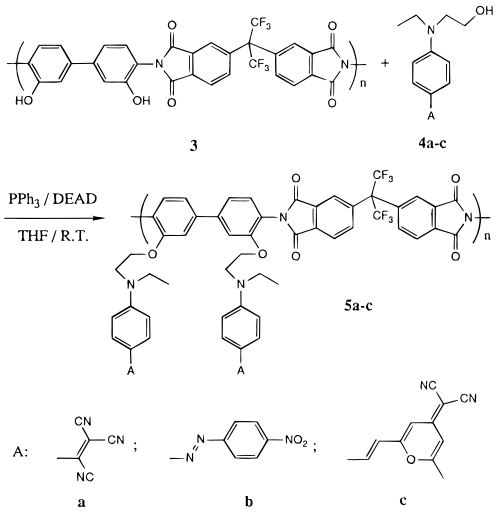
Side-chain aromatic polyimide 7c was synthesized by a procedure similar to that above. Polyimide **3** (0.187 g, 0.30 mmol of repeat unit), PPh_3 (0.105 g, 0.40 mmol), and hydroxyl DCM (**4c**, 0.122 g, 0.35 mmol) were dissolved in dry THF (15 mL) successively. DEAD (0.07 g, 0.4 mmol) was added dropwise into the solution. The solution was stirred at room temperature under nitrogen for 48 h. The polymer was worked up with the same procedure as above to yield 0.27 g (95% yield) of red polyimide **7c**. ^{1}H NMR (DMSO-d_6) 9.85 and 9.90 (s, 1 H, OH), 8.5−6.3 (m, 20 H, aromatic H), 4.2 (br, 2 H, CH_2), 3.7 (br, 2 H, CH_2), 3.2 (br, 2 H, CH_2), 2.5 (br, 3 H, CH_3), 0.9 ppm (br, 3 H, CH_3). UV−vis: λ_{max} = 473 nm. T_g = 220 °C. Thermal stability: <1% weight loss up to 320 °C.

Side-chain aromatic polyimide 8 was prepared by the post-Mitsunobu reaction of **3** with Disperse Red 1 (**4b**, 1.6 equiv relative to the repeat unit of polymer **3**) in 92% yield. ^{1}H NMR (DMSO-d_6) 10.03 (s, 1 H), 8.4−6.4 (m, 48 H), 4.4 and 4.3 (br, 6 H), 3.8 (br, 6 H), 3.3 (br, 6 H), 0.9 ppm (br, 9 H).

Scheme 1. Synthesis of Hydroxyl Aromatic Polyimides and Adjustment of the Backbone Rigidity



Scheme 2. Synthesis of NLO Side-Chain Aromatic Polyimides

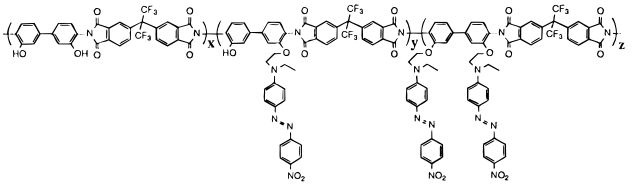


Results and Discussion

Synthesis of NLO Side-Chain Aromatic Polyimides. Previously, in order to achieve NLO side-chain aromatic polyimides, it was necessary to prepare the chromophore-containing diamine monomers by multistep syntheses and to carry the chromophore all the way through the processes of polymerization and imidization of the poly(amic acid)s. The conditions of both the monomer syntheses and the polymerization may destroy the chromophore, which strongly limits the application of the techniques. Our strategy for the synthesis of NLO side-chain aromatic polyimides was to covalently bond the chromophores directly onto the backbone of a preformed polyimide, by which the troublesome synthesis of diamine monomer and the harsh imidization processes were avoided.

The synthesis was a two-step process. The first step was for the synthesis of hydroxyl polyimides (Scheme 1) and the second for the incorporation of the chromophores to the polymer backbone (Scheme 2). The synthesis of hydroxyl polyimides was quite straightforward via the direct polymerization of hydroxyl diamine and dianhydride monomers. Moreover, the fact that most of the dianhydride and hydroxyl diamine monomers are commercially available makes the synthesis even more facile. A great variety of polymer backbones (see Scheme 1 for example) can be achieved by applying

Scheme 3. Control of the Chromophore Loading level and the Density of the Intact OH Group



Polyimides	Chromophore Loading Level	x	y	z
3	0 wt%	n	0	0
7b	32 wt%	n/3	n/3	n/3
8	42 wt%	0	n/2	n/2
5b	49 wt%	0	0	n

different hydroxyl diamine and/or dianhydride monomers in the polymerization to fine-tune the rigidity of the backbone and the physical properties of the final NLO polymers. Polyimide **3**, for example, with *p*-diphenyldiamine and hexafluoropropyl dianhydride moieties in the backbone, has a higher T_g and a much higher viscosity in solution than that of polyimide **6**, in which the backbone contains a hexafluoropropyl *m*-diphenyldiamine moiety. Some of the hydroxyl polyimides, such as **6**, are well known as precursors for photoreactive or photoimagable polyimides.[17] The hydroxyl groups on the backbones of the imidized polyimides were important to ensure the solubility and the reactive sites for postcondensation with functional chromophore molecules.

The covalent bonding of the chromophore to the backbone of the polymer can be effected easily via Mitsunobu condensation[18] between the pendant hydroxy group on the chromophores and the phenol group on the polyimides. The very mild conditions of the condensation provided us great flexibility in the choice of the chromophores (see Scheme 2 for examples). Many chromophores with a pendant hydroxy group, such as 2-(*N*-ethyl-4-(tricyanovinyl)anilino)ethanol (**4a**) ($\beta\mu$ = 700 × 10^{-48} esu at 1.9 μm), Disperse Red 1 (**4b**) ($\beta\mu$ = 550 × 10^{-48} esu), and hydroxyl DCM (**4c**) ($\beta\mu$ = 800 × 10^{-48} esu), can now be incorporated directly onto the polyimide backbone to creat different NLO side-chain aromatic polyimides. Moreover, the post-Mitsunobu condensation between hydroxy polyimides and hydroxy chromophores was rather efficient, which allowed us to control the loading level of the side-chain chromophores efficiently from 0 up to 50 wt % and the density of the intact hydroxy group from 0 to 0.5 equiv (Scheme 3). Polymer **3**, for example, was reacted with 1.1 equiv (relative to the equivalents of the repeat units of the polymer) of hydroxy chromophores, such as **4b**, at room temperature for 48 h to produce a side-chain polyimide **7b** (Scheme 3), in which 50% of the hydroxy groups reacted with chromophores and the other 50% remained intact, while **3** reacted with 2.2 equiv of the chromophores under the same conditions to yield side-chain polyimide **5b** (Scheme 3) with <2% intact hydroxy groups. The reaction extents were determined by ^{1}H NMR integration of the disappearance of the hydroxyl proton on the polymer backbone vs the appearance of the aromatic proton (Figure 1) on the side-chain chromophore and the original aromatic protons on the polymer backbone. The hydroxy-containing side-chain polymides, such as **7**, can be further cross-linked to improve the mechanical properties, solvent resistance, and thermal alignment stability of the materials.[20,21]

Characterization of the Polyimides. The polymerization of polyimide **3** and **6** and the Mitsunobu

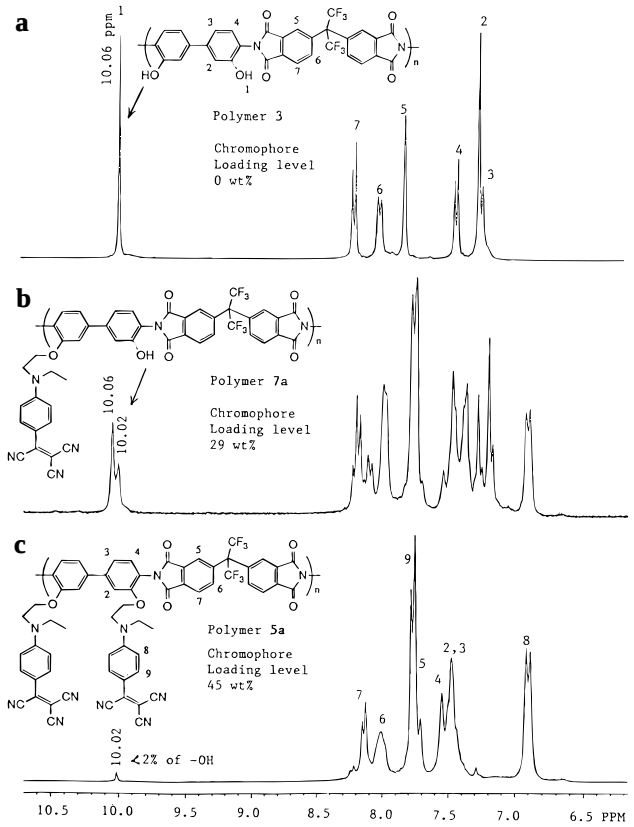


Figure 1. ^{1}H NMR (DMSO-d_6, 300 MHz) spectra of the polymers and the control of the chromophore loading level.

condensation between **3** and hydroxyl chromophores were monitored by proton NMR spectroscopy and FTIR. The ^{1}H NMR spectrum of **3** shows a completely imidized polyimide structure with the aromatic hydroxy resonance at 10.06 ppm. The three sets of resonance peaks at 8.20, 8.00, and 7.80 ppm were assigned to the aromatic protons of the 6F-dianhydride moieties. Another three sets of peaks at 7.39, 7.21, and 7.18 ppm were attributed to the aromatic protons of the dihydroxybiphenyl moieties (Figure 1a). The ^{1}H NMR spectrum of **6** also shows a completely imidized structure with aromatic OH resonance at 10.6 ppm, three sets of peaks at 7.6, 7.3, and 7.1 ppm for Bis-AP-AF moieties, and one peak at 8.3 ppm for PMDA moieties. The proposed structures of all side-chain polyimides, **5**, **7**, and **8**, are also clearly supported by NMR spectral analysis (Figure 1b,c). For example, the ^{1}H NMR spectrum of polymer **5a** was consistent with a fully functionalized (*N*,*N*-diethylamino)-4-(tricyanovinyl)benzene side-chain aromatic polyimide (functionality of OH group >98%). The chemical shifts due to the 6F-dianhydride moieties (protons 5, 6, and 7 at 7.7, 8.0, and 8.1 ppm) are similar to that of the parent polyimide **3**. The peaks for protons 2, 3, and 4 of the dihydroxybiphenyl moieties are shifted downfield to 7.5, 7.5, and 7.6 ppm due to the effect of the side-chain chromophore as compared to that of the parent hydroxyl polyimide **3**. Two doublet peaks at 6.9 and 7.8 ppm are attributed to the NLO chromophore of (*N*,*N*-diethylamino)-4-(tricyanovinyl)benzene. Structure **7a** in Figure 1 represents only an average structure of the polymer with approximately 50% of the hydroxy groups condensed with hydroxyl chromophores and the other 50% intact. The actual structure of polymer **7a** is a mixture of the repeat units of **3**, **5a**, and **7a** and is similar to that of polymer **7b** in Scheme 3. The symmetric phenol group, OH (as shown in **3**), shows a proton NMR signal at 10.06 ppm and the unsymmetric OH (as shown in **7a**) a signal at 10.02 ppm. The ^{1}H NMR analysis of polyimide **8** shows that approximately 75% of the hydroxy groups in polymer **3** reacted with Disperse Red and the other 25% were intact (Scheme 3). The chemical shift of the intact OH protons was observed at 10.02 ppm. The resonances between 6.6 and 8.4 ppm belong to all the aromatic protons of the backbone and the side-chain Disperse Red 1. The resonances of the side-chain aliphatic protons in polymer **8** appear at 4.37, 3.75, 3.26, and 0.88 ppm.

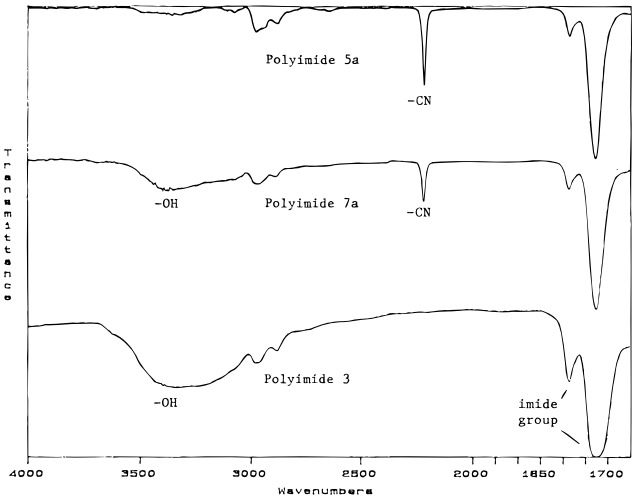


Figure 2. FTIR spectra of side-chain polyimides **7a** and **5a** and their parent hydroxylpolyimide **3**.

The FTIR spectra of all the side-chain aromatic polyimides (**5**, **7**, and **8**) and their parent hydroxyl polyimides (**3** and **6**) showed clearly the characteristic imide group bands at 1786 and 1725 cm^{-1}, which were consistent with the fully imidized structure as proposed. The post-Mitsunobu condensation process between hydroxyl chromophores and hydroxyl polyimides was also monitored by FTIR. The FTIR spectrum of **3** showed a fully imidized hydroxyl polyimide structure with a strong and broad absorption around 3400 cm^{-1} for hydroxy groups (Figure 2a). The strength of the OH absorption was significantly reduced and the characteristic CN band appeared at 2216 cm^{-1} after approximately 50% of the OH groups in polymer **3** reacted with the chromophore of hydroxyl (*N*,*N*-diethylamino)-4-(tricyanovinyl)benzene (polymer **7a**, Figure 2b). The OH absorption almost disappeared and the CN band became much more intense in the spectrum of polymer **5a** (Figure 2c), which corresponded to a more complete condensation between the OH groups in **3** and the hydroxyl chromophores.

The NLO polyimides described above are all soluble in polar solvents such as cyclohexanone, DMSO, DMF, DMAc, NMP, and THF. The molecular weights of the polymers can thus be estimated by gel permeation chromatography (GPC). Polymer **5a**, for example, has a weight-average molecular weight (relative to polystyrene standards) M_w of 57 000 with a polydispersity index of 1.51. The parent hydroxyl polyimide **3** has a M_w of 33 000, a M_n of 23 000, and a polydispersity of 1.43. All the resulting side-chain polyimides have a high glass transition temperature (T_g > 220 °C) and excellent thermal stability. Although the chromophore loading level is as high as 42% by weight, polymer **8** still has a T_g of 228 °C and a thermal stability of <1% weight loss up to 300 °C, which are also the case for polyimides **5** and **7** (Figure 3). The parent hydroxyl polyimides have a higher T_g (>360 °C for **3** and 350 °C

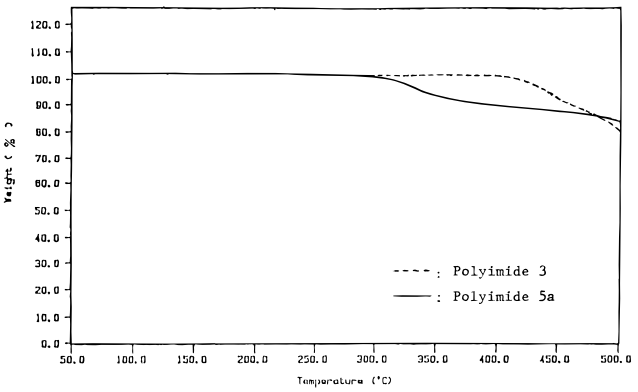


Figure 3. Thermogravimetric analysis (TGA) of side-chain polyimide **5a** and the parent hydroxyl polyimide **3**.

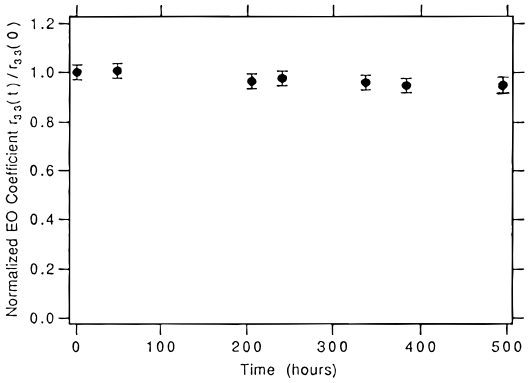


Figure 4. Temporal stability of the poled side-chain polyimide **8** at 100 °C in air. Normalized r_{33} as a function of baking time.

for **6**) and an even better thermal stability of <2% weight loss up to 400 °C for both **3** and **6** (Figure 3). The UV−vis spectra of thin films of side-chain polyimides exhibited a strong absorption pattern due to the $\pi-\pi^*$ charge-transfer band of the side-chain chromophores ($\lambda_{max} = 520$ nm for "a" chromophore, 480 nm for "b" chromophore, and 473 nm for "c" chromophore).

Physical Characterization. Optical-quality thin films (2−3 μm) of the side-chain polyimides were prepared by spin-coating of the polymer solutions in cyclohexanone (15% m/m, filtered through a 0.2 μm syringe filter) onto an indium tin oxide (ITO) glass substrate. Dipole alignment of the NLO polymers can be achieved and the second-order nonlinearity can be induced by either contact poling or corona poling. The tests showed that the synthesized NLO side-chain polyimides exhibited a large E-O coefficient (r_{33}) and good thermal stability of dipole alignment. The E-O coefficient, r_{33}, was measured with an experimental setup similar to that described by Teng *et al.*[19] The films were kept in a vacuum oven at 120 °C over a weekend and briefly heated in a hot stage at 200 °C under nitrogen for 30 min to ensure the removal of residual solvent. A thin layer of gold was vacuum evaporated on the polyimide films to serve as the top electrode for poling. The samples were poled at 200−220 °C with an applied dc electric field of 0.5−0.8 MV/cm and cooled to room temperature, and the poling field was subsequently removed. The optimized r_{33} value for polyimide **5a**, for example, was 34 pm/V measured at 0.63 μm and 11 pm/V at 0.83 μm. The r_{33} for polyimide **8** was 30 pm/V at 0.63 μm and 10 pm/V at 0.83 μm. The r_{33} value was also predicted to be 7 pm/V at 1.33 μm by using a two-level model.[22] The r_{33} values retained >95% of the original value at 85 °C and >90% at 100 °C for more than 500 h (Figure 4). The losses of the r_{33} values at these temperatures were primarily due to the orientational relaxation of the poled polymer films.[23]

Conclusion

NLO side-chain aromatic polyimides can now be prepared using a facile, two-step synthetic method. Moreover, the synthesis provides a generally applicable approach to NLO side-chain polyimides with a wide variety of pendant nonlinear optical chromophores, great flexibility of the polymeric backbone rigidity, and easy control of the chromophore loading level to fine-tune the desired physical properties of the polymeric materials. The resulting NLO polyimides possess high glass transition temperatures (T_g > 220 °C), excellent solubility, and processibility even though the loading level of the side-chain chromophore is up to ~50% by weight. Large E-O coefficient values (up to 34 pm/V at 0.63 μm and 11 pm/V at 0.83 μm) were achieved, and high thermal stability of the poled films at 100 °C was observed.

Acknowledgment. We gratefully thank Dr. K. J. Drost for help with DSC and TGA experiments and Dr. R. M. Mininni for his helpful discussions, continuing support, and encouragement.

References and Notes

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MA9512566