Facile Approach to Nonlinear Optical Side-Chain Aromatic Polyimides with Large Second-Order Nonlinearity and Thermal Stability

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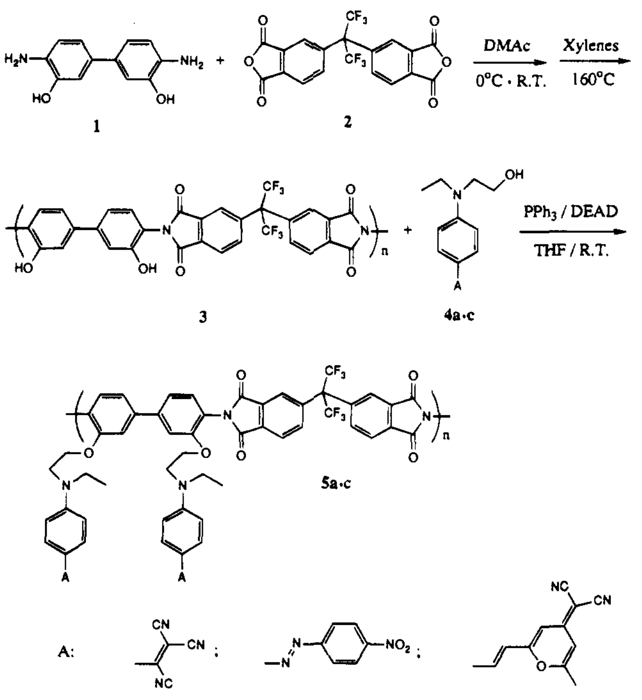
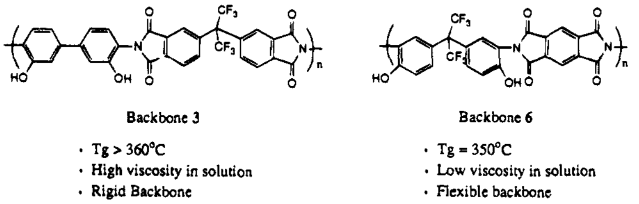
Nonlinear optical (NLO) side-chain *aromatic* polyimides with large second-order nonlinearity and good thermal stability of poled films were recently developed by ROI Technology[1] and other labs.[2,3] These NLO side-chain aromatic polyimides have several advantages, including higher temperature alignment stability, better mechanical properties, and lower optical loss, over *aliphatic* side-chain polyimide and guest−host NLO chromophore−polyimide systems.[1−4] The method we reported for the synthesis of NLO side-chain aromatic polyimides includes the polymerization of a preimidized side-chain polyimide precursor and a post-tricyanovinylation for the activation of the NLO side-chain chromophore.[1] Both the approaches developed by Yu *et al.*[2] and by Miller *et al.*[3] involve the synthesis of a NLO chromophore containing diamine compound and a polymerization between the diamine monomer and a dianhydride monomer. All of these methods 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.[1−3] We have recently developed 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,[5] followed by the covalent bonding of a chromophore onto the backbone of the polyimide via a post-Mitsunobu reaction[6] (Scheme 1). By the introduction of the chromophores at the last stage through the very mild Mitsunobu condensation, the harsh imidization process of the polyamic 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 broad variation of polymer backbone (Scheme 2) and great flexibility in the selection of the chromophores (Scheme 1). In this paper, we also report the preliminary results of E-O coefficient, thermal stability, and other physical properties of the polymeric materials.

Scheme 1. Two-Step Synthesis of NLO Side-Chain Aromatic Polyimide[a]



[a] DEAD: diethyl azodicarboxylate. DMAc: *N,N*-dimethylacetamide.

Scheme 2. Adjustment of the Backbone Rigidity



The polymerization of the hydroxy-containing preimidized polyimides and the Mitsunobu condensation for covalent bonding of the chromophores onto the polymer backbone were monitored by proton NMR spectroscopy. The ^{1}H NMR spectrum of polymer **3** shows a completely imidized polyimide structure with the aromatic hydroxy resonance at 10.06 ppm (Figure 1a). Polymer **3** was reacted with 1.1 equiv (relative to the equivalent of the repeat units of the polymer) of hydroxy chromophores, such as **4a**, at room temperature under nitrogen for 48 h to produce a side-chain polyimide[7] with an average polymer structure of **7** (Figure 1b), in which 50% of the hydroxy groups reacted with chromophores and the other 50% remained intact.[8] Also polymer **3** was reacted with 2.2 equiv of the chromophores under the same conditions to yield side-chain polyimide **5** with <2% intact hydroxy group. The reaction extent was determined by ^{1}H NMR integration of the disappearance of the hydroxyl proton on the polymer backbone vs the appearance of aromatic proton 8 (Figure 1) on the side-chain chromophore and the original aromatic protons on the polymer backbone. The post-Mitsunobu condensation between

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(2) (a) Yu, D.; Gharavi, A.; Yu, L. *Macromolecules* **1995**, *28*, 784−786. (b) Yu, D.; Yu, L. *Macromolecules* **1994**, *27*, 6718−6721.

(3) (a) Miller, R. D.; Burland, D. M.; Dawson, D.; Hedrick, J.; Lee, V. Y.; Moylan, C. R.; Twieg, R. J.; Volksen, W.; Walsh, C. A. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1994**, *35*, 122−123. (b) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Miller, R. D.; Volksen, W.; Thackara, J. I.; Walsh, C. A. *Proc. SPIE—Int. Soc. Opt. Eng.* **1994**, *2285*, 17−30. (c) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Macromolecules* **1995**, *28*, 3005−3007.

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(7) (a) Workup procedure for the postpolymeric Mitsunubo reaction: The resulting reaction mixture was added dropwise into an agitated solution of methanol (500 mL) and 2 N HCl (10 mL). The collected precipitate was dissolved in THF (50 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 80 °C under vacuum for 24 h. (b) The purity of the resulting NLO side-chain polyimide was confirmed by proton NMR spectroscopy.

(8) Structure **7** represents only an average structure of the polymer with approximately 50% of the hydroxy groups reacted and the other 50% intact. The actual structure of polymer 7 is a mixture of the repeat unit in polymers **3**, **5**, and **7**. The symmetric phenol group OH (as shown in structure **3**) shows a proton NMR signal at 10.06 ppm and the unsymmetric OH (as shown in structure **7**) at 10.02 ppm (Figure 1).

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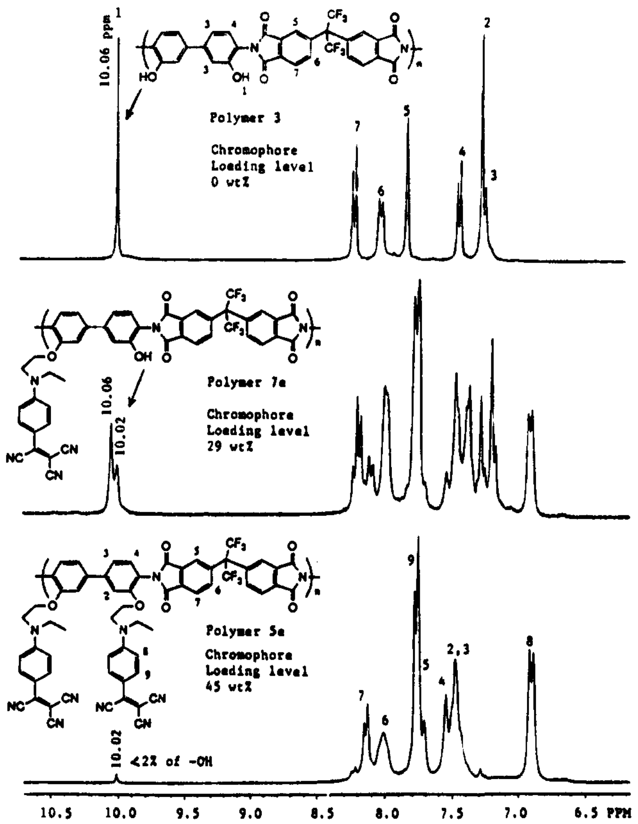

Figure 1. ^{1}H NMR (DMSO-d_6, 300 MHz) spectra of the polymers and the control of the chromophore loading level.

hydroxy polyimides and hydroxy chromophores was surprisingly quantitative, which allowed us to control the loading level of the side-chain chromophores efficiently from 0 up to 50 wt % and to fine-tune the structural and electrical properties of the polymer materials. The hydroxy-containing side-chain polyimide, such as **7**, can be further cross-linked in order to improve the mechanical properties, solvent resistance, and thermal alignment stability of the materials.[9]

Polyimides **5** and **7** were all soluble in polar solvents such as cyclohexanone, methyl sulfoxide, dimethylformamide, *N*-methylpyrrolidinone, and tetrahydrofuran. Optical-quality films can be prepared by spin-coating on glass substrates from the polymer solutions. The molecular weights of the polymers can be estimated by gel permeation chromatography (GPC). Polymer **5a**, for example, has a M_w of 57 000 with a polydispersity index of 1.51.[10] These results imply that a much higher molecular weight polymer with a narrower molecular weight distribution can be obtained by this method compared to other procedures.[2] All the resulting side-chain polyimides have a high glass transition temperature (T_g) and good thermal stability. Polyimide **5a** (with a chromophore loading level up to 45%), for example, has a T_g of 222 °C by differential scanning calorimetry (DSC) analysis and a thermal stability of <1% weight loss up to 300 °C by thermogravimetric analysis (TGA). The UV−vis spectrum of a thin film of **5a** exhibited a strong absorption pattern (λ_{max} = 520 nm) due to the $\pi-\pi^*$ charge-transfer band of the NLO chromophore.

Thin films (1−3 μm) of polyimides **5** and **7** were spin-coated onto an indium tin oxide (ITO) glass substrate by using a 10−15% m/m solution (filtered through a 0.2 μm syringe filter) of the polymer in cyclohexanone. The films were kept in a vacuum oven at 200 °C for 1 h to ensure the removal of the residual solvent. The dipole alignments in the NLO polymers could be achieved and the second-order nonlinearity could be induced either by contact poling or corona poling. Preliminary tests showed that the synthesized NLO side-chain polyimides exhibited a large E-O coefficient (r_{33}) value and good thermal stability of dipole alignment. The r_{33} value was measured with an experimental setup similar to that described by Teng *et al.*[11] Polyimide **5a**, for example, exibited a preliminary r_{33} value of 11 pm/V measured at 0.83 μm, and 34 pm/V at 0.63 μm with a poling field of 0.8 MV/cm. The r_{33} value retained >90% of the original value at 100 °C for more than 400 h. The optimization of the E-O coefficient and thermal alignment stability of this polyimide system and its cross-linking system are currently under investigation.

In conclusion, we have developed a two-step facile synthesis for NLO side-chain aromatic polyimides. A series of aromatic polyimides functionalized with different types of NLO chromophores were synthesized. The resulting NLO polyimides possess excellent solubility, processibility, large E-O coefficients, and good alignment thermal stability. The obvious advantages of this method over others include a wide variety for the selection of the chromophores, easy control for the loading level of the chromophore, and great flexibility for the adjustment of the polymer backbone rigidity. The hydroxy-containing NLO side-chain aromatic polyimides can be further cross-linked through the intact OH groups in the polymer backbone. We are continuing to examine many aspects which may further improve the properties of the resultant NLO polymeric materials.

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Supporting Information Available: Typical procedure for the synthesis of NLO side-chain aromatic polyimides and ^{1}H NMR spectra of polyimides **3**, **5**, and **7** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(9) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155−173.

(10) The molecular weight and polydispersity (relative to polystyrene standard) were determined by a Waters GPC with HR-5E and HR-2 columns at room temperature (THF as the eluant).

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