Versatile Synthetic Approach to Nonlinear Optical Side-Chain Aromatic Polyquinolines with Large Second-Order Nonlinearity and Thermal Stability

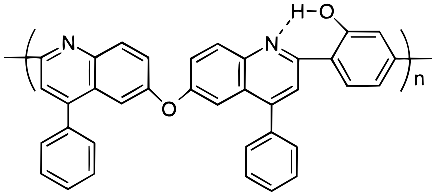
Hong Ma, Xijun Wang, Xiaoming Wu, Sen Liu, and Alex K-Y. Jen*

Department of Chemistry, Northeastern University,
360 Huntington Avenue, Boston, Massachusetts 02115

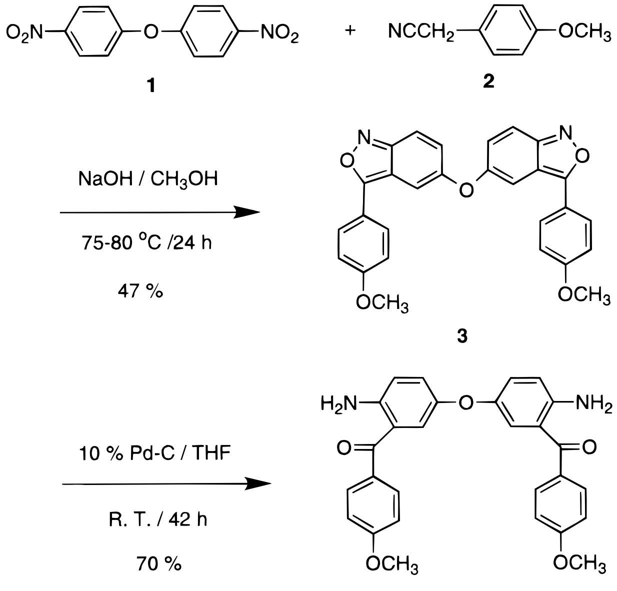
Received February 13, 1998
Revised Manuscript Received April 24, 1998

Organic polymeric second-order nonlinear optical (NLO) materials have been extensively studied due to their potential applications in integrated photonic devices such as high-speed electrooptic (EO) modulators and switches, optical data storage and information processing.[1,2] It is most remarkable that recent improvements in various polyimide systems[3−7] have resulted in several prototype devices based on the second-order NLO polymers.[8] However, to develop practical devices suitable for commercial semiconductor processes, the challenge is to achieve excellent tradeoffs in all the properties of the NLO polymers (i.e., EO coefficients, thermal, chemical, and photochemical stability, temporal dipole alignment stability, optical loss, dielectric constant, and mechanical properties). To date, high T_g polyimides are a leading group of polymers under consideration for use in the production of NLO devices. Although the results reported for these NLO polyimides are quite encouraging, some deficiencies still exist. For example, most polyimides are synthesized via the condensation reaction between very reactive diamines and dianhydrides to afford an amic acid prepolymer, which is then followed by a high-temperature ring-closing thermal conversion reaction to form the final polyimides. The very acidic environment of this imidization process, polar reaction solvents, and byproducts formed at high temperatures severely limit the selection of usable NLO chromophores. Recently, we have explored utilizing polyquinolines as a new optical polymer system for second-order NLO applications. Polyquinolines, which were first developed by Stille et al.[9] during the 1970s in response to the increasing demand for thermally stable materials, represent a class of high-performance polymers with a unique combination of many desirable properties including outstanding thermal stability (>450 °C), low dielectric constant (2.5−3.0), low moisture absorption (0.10−0.15%), low optical loss, good dimensional stability over a wide temperature range, very high T_g (250−400 °C), excellent processibility, and compatibility with plasma or reactive ion etching. Our previous studies of their electrooptic properties have shown very promising results for both guest/host[10,11] and side-chain polyquinoline systems.[12,13] There are two principal routes for attaching chromophores to the polymer backbone to obtain NLO side-chain polyquinolines. One approach involves the synthesis of polyquinoline precursor polymers and then post-tricyanovinylation of these polyquinolines to activate the side-chain NLO chromophores.[12] However, this approach is limited to the synthesis of side-chain NLO polyquinolines with only tricyanovinyl-containing chromophores. The other approach to NLO side-chain polyquinolines involves the synthesis of a NLO chromophore-containing bis(ketomethylene) monomer and a polymerization between the bis(ketomethylene) monomer and a bis(*o*-amino ketone) monomer.[13] Many chromophores, including 4-(dicyanomethylene)-2-methyl-6-(*p*-(dimethylamino)styryl)-4*H*-pyran (DCM) type chromophores, cannot survive the relatively harsh chemical conditions of the acid-catalyzed polymer-forming process. Accordingly, the general applicability of this methodology is severely limited. As a result, it is highly desirable to develop a synthetic method for attaching a variety of hydroxy-containing chromophores onto a polyquinoline backbone. One potential method is to use the similar Mitsunobu condensation reaction that was empolyed previously for postfunctionalization of NLO polyimides to attach a hydroxy-containing chromophore onto a hydroxy-containing polyquinoline backbone. However, this is not a very effective method due to steric hindrance between adjacent aromatic rings and intramolecular hydrogen bonding between the −OH and the nitrogen atom on the quinoline moiety (Chart 1). Herein, we report a versatile approach for the synthesis of NLO side-chain aromatic polyquinolines. This is accomplished through the preparation of a hydroxy-containing polyquinoline by the hydrolysis of a methoxy-containing polyquinoline, followed by the covalent bonding of a chromophore onto the pendent phenyl moieties of the polyquinoline via the Mitsunobu reaction[14] (Scheme 2). By locating the hydroxyl group on the pendent

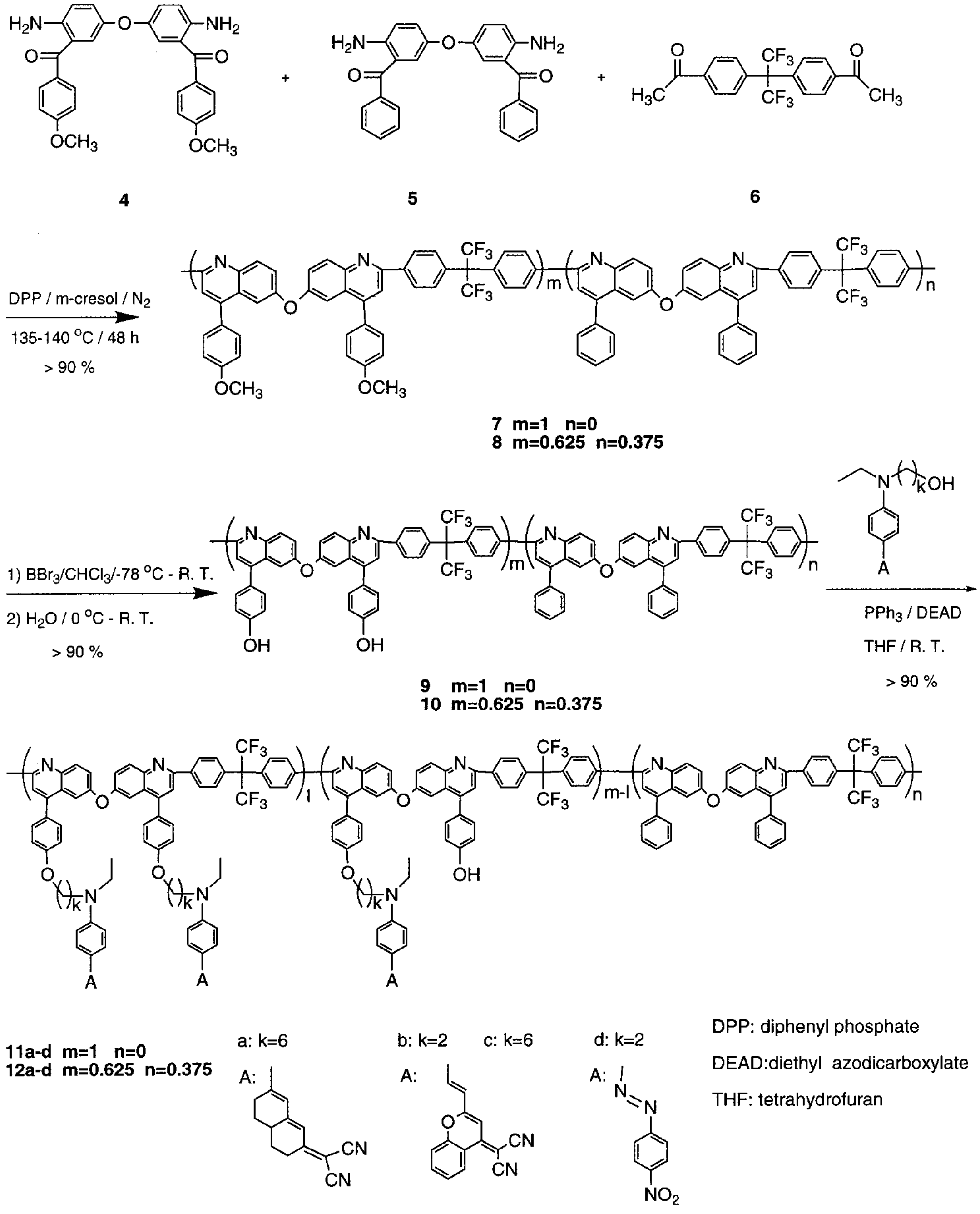
Chart 1. Intramolecular Hydrogen Bonding between the Hydroxy Group on the Polymer Backbone and the Nitrogen Atom on the Quinoline Moiety



Scheme 1. Synthesis of Methoxy-Containing Bis(*o*-amino ketone) Monomer



Scheme 2. Synthesis of Aromatic NLO Side-Chain Polyquinolines



phenyl side group instead of on the polyquinoline backbone, a higher efficiency of chromophore attachment is achieved. In addition, by introducing the chromophores at the last stage through the very mild Mitsunobu condensation, NLO chromophore decomposition during the high-temperature, acidic polymer-forming reaction is avoided. This methodology allows us to synthesize NLO side-chain aromatic polyquinolines with a broad variety of polymer backbones and flexibility in selecting NLO chromophores. It is also noteworthy that a phenyl spacer between the polymer backbone and the NLO chromophores facilitates the process for high electric field poling of the NLO polyquinoline **11** or **12** compared to polyquinolines with chromophores directly attached on the polymer backbone. The preliminary results of EO activity has demonstrated the advantage of this molecular design approach.

The methoxy-containing bis(*o*-amino ketone) monomer **4**[15] was prepared as shown in Scheme 1. Compounds 4,4′-dinitrodiphenyl ether **1** and bis(*o*-amino ketone) **5** were synthesized according to the literature method.[16] The methoxy-containing polyquinoline homopolymer **7** ($m = 1$, $n = 0$) was obtained in high yield (>90%) via the polymerization of a fluorinated ketomethylene monomer **6** and an amino ketone monomer **4** in diphenyl phosphate/*m*-cresol at 135−140 °C for 48 h under nitrogen[17] according to the modified literature procedures.[9,18] The hydroxy-containing polyquinoline homopolymer **9** ($m = 1$, $n = 0$) was then prepared by the hydrolysis of the precursor methoxy-containing polyquinoline **7** with BBr_3/H_2O in chloroform with a yield of >90%.[19] The NLO side-chain polyquinoline homopolymer **11** was obtained through the Mitsunobu condensation between hydroxy-containing chromophores[20] and hydroxy polyquinoline precursor **9**.[21] The polymerization of a methoxy-containing polyquinoline, the deprotection of the methoxy group to generate the hydroxy-containing polyquinoline, and the covalent attachment of the chromophores onto the polymer pendent phenyl moieties were monitored by ^{1}H NMR spectroscopy.[22] The extent of deprotection was determined by the integration of the residual methoxy proton vs the intensity of the phenol proton on the polymer phenyl side group. Accordingly, the extent of the Mitsunobu condensation was obtained by the ^{1}H NMR integration of residual phenol proton on the polymer. Very surprisingly, the yields of the deprotection step and the Mitsunobu condensation step were both quantitative. This observation allowed us to adjust the loading level of the side-chain chomophores to fine-tune electrooptic and thermal properties of the polymers. The chromophore loading levels of these polyquinolines were controlled in the range 20−30 wt % in order to prevent chromophore aggregation, which may lead to the increase of optical loss in the polymer materials due to light scattering. The hydroxy-containing NLO side-chain polyqunolines, such as **11**, can be further cross-linked in order to improve the mechanical properties, solvent resistance, and thermal alignment stability of the materials.[2b]

The precursor polyquinolines **7**−**10** and the NLO side-chain polyquinolines **11** and **12** were all soluble in polar solvents, such as cyclopentanone, cyclohexanone, and *N*,*N*-dimethylacetamide. All of the resulting side-chain polyquinolines have high T_g's and good thermal stabilities. For example, homopolymer **11a** (chromophore loading level of 23 wt %) has a T_g of 203 °C, and the copolymer **12a** (loading level of 27 wt %) has a T_g of 250 °C, respectively, by differential scanning calorimetry (DSC) analysis. They all possess high thermal stability (<3% weight loss up to 300 °C) by thermogravimetric analysis (TGA). Linear optical measurements by using the prism-coupled streak method on a slab waveguide show that the copolymer **12a** possesses refractive indices (TE = 1.6905, TM = 1.6183) and optical loss (2.1 dB/cm) at 0.83 μm laser wavelength. The UV−vis spectra of the thin films of the NLO polyquinolines also exhibited a strong absorption pattern ($\lambda_{\max}$ of 535 nm for polymer **11a** and **12a**) due to the $\pi-\pi^*$ charge-transfer band of the NLO chromophore.

Thin films (1−3 μm) of the polyquinolines **11** and **12** were prepared by spin-coating of the polymer solution in cyclopentanone (15% w/w solution, filtered through a 0.2 μm syringe filter) onto an indium tin oxide (ITO) glass substrate. The films were kept in a vaccum oven at 80 °C overnight to ensure the removal of the residual solvent. Preliminary poling results showed that the synthesized NLO side-chain polyquinolines exhibited a large electrooptic coefficient (r_{33}) value and good temporal stability. The r_{33} value was measured with an experimental setup similar to that described by Teng et al.[23] Polyquinoline **12a**, for example, exhibited an r_{33} value of 17 pm/V at 0.83 μm with a poling field of 1.0 MV/cm. The r_{33} value of polymer **12a** retained ~90% of the original value at 80 °C for more than 1000 h.

In conclusion, we have developed a versatile, generally applicable synthetic methodology for NLO side-chain aromatic polyquinolines. The resulting polyquinolines possess excellent solubility, processibility, large EO coefficients, and good temporal stability. The obvious advantages of this method over others include flexibility in selecting NLO chromophores, ease in controlling the chromophore loading level, and the ability to adjust the polymer backbone structures in order to fine-tune their physical properties for device applications. The obtained NLO side-chain aromatic polyquinolines could be efficiently poled by taking advantage of a pendent phenyl spacer. Further cross-linking of the poled polymers through the intact OH groups on the polymer with polyepoxide at high temperature may further enhance both their mechanical properties and temporal stability.

Acknowledgment. This research was supported by the Air Force Office of Scientific Research (AFOSR) under Grant F49620-97-1-0240 and Office of Naval Research (ONR) through the MURI Center CAMP.

References and Notes

(1) (a) Marder, S. R.; Kippelen, B.; Jen, A. K-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845. (b) Lindsay, G. A., Singer, K. D., Eds. *Polymers for Second-order Nonlinear Optics*; ACS Symposium Series No. 601; American Chemical Society: Washington, DC, 1995. (c) Chemala, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987.

(2) (a) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, H. W.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060. (b) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. (c) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.*, **1994,** *94*, 31.

(3) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. *Appl. Phys. Lett.* **1991**, *58*, 225.

(4) (a) Becker, M.; Sapochak, L.; Ghosen, R.; Dalton, L. R.; Shi, Y.; Steier, W. H.; Jen, A. K-Y. *Chem. Mater.* **1994**, *6*, 104. (b) Liang, Z.; Dalton, L. R.; Garner, S. M.; Kalluri, S.; Chen, A.; Steier, W. H. *Chem. Mater.* **1995**, *7*, 941.

(5) (a) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Science* **1995**, *268*, 1604. (b) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Macromolecules* **1995**, *28*, 3005.

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

(7) (a) Chen, T.-A.; Jen, A. K-Y.; Cai, Y. M. *J. Am. Chem. Soc.* **1995**, *117*, 7295. (b) Jen, A. K-Y.; Liu, Y.-J.; Cai, Y.; Rao, V. P.; Dalton, L. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2711.

(8) Dagani, R. *Chem. Eng. News* **1996**, March 4, 22.

(9) Stille, J. K. *Macromolecules* **1981**, *14*, 870 and references therein.

(10) Cai, Y. M.; Jen, A. K-Y. *Appl. Phys. Lett.* **1995**, *117*, 7295.

(11) Jen, A. K-Y.; Cai, Y. M. U.S. Patent No. 5,679,763.

(12) Chen, T.-A.; Jen, A. K-Y.; Cai, Y. M. *Chem. Mater.* **1996**, *8*, 607.

(13) Jen, A. K-Y.; Wu, X.-M.; Ma, H. *Chem. Mater.* **1998**, *10*, 471.

(14) Mitsunobu, O. *Synthesis* **1981**, January, 1.

(15) ^{1}H NMR (CDCl$_3$, 300 MHz) for monomer **4**: δ 7.63 (d, J = 8.7 Hz, 4H), 7.07 (d, J = 2.6 Hz, 2H), 6.96 (dd, J = 8.8 Hz, 2.6 Hz, 2H), 6.89 (d, 8.7 Hz, 4H), 6.68 (d, J = 8.8 Hz, 2H), 5.35 (br, 4H), 3.85 (s, 6H).

(16) Norris, S. O.; Stille, J. K. *Macromolecules* **1976**, *9*, 496.

(17) The methoxy-containing polyquinoline homopolymer **7** was prepared by the polymerization of 1:1 equivalent of the bis(*o*-amino ketone) monomer **4** and bis(ketomethylene) monomer **6** in 11.5 equiv of *m*-cresol and 25.0 equiv of DPP at 135−140 °C under N$_2$ for 48 h. The resulting polymer was precipitated into a large, agitated solution of methanol containing 10% (V/V) triethylamine. The polymer was redissolved in CHCl$_3$, and reprecipitated into the methanol solution (10% triethylamine). The collected polymer was purified by Soxhlet extraction with methanol solution (10% triethylamine) and dried under vacuum at 100 °C for 24 h. The structure and the purity of the polymer were verified by ^{1}H NMR spectroscopy and by elemental analysis.

(18) (a) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895. (b) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 633.

(19) The hydrolysis of methoxy-containing polyquinoline was carried out with 1:7 equiv of the polymer methoxy group vs BBr$_3$ in the solution of chloroform at −78 °C for 0.5 h and

at room temperature for 12 h under a nitrogen atmosphere, followed by the reaction with water at 0 °C for 15 min then at room temperature for 30 min. The resulting reaction mixture was neutralized with 2 N sodium hydroxide solution, filtered, and washed with a large amount of water and methanol. The obtained hydroxy-containing polyquinoline was redissolved in THF and reprecipitated into methanol. The collected polymer was dried under vacuum at 60 °C for 24 h. The complete hydrolysis of methoxy-containing polyquinoline was confirmed by ^{1}H NMR spectroscopy.

(20) Jen, A. K-Y.; Marder, S. R. Manuscript in preparation.

(21) Workup procedure for the Mitsunubo reaction: The resulting reaction mixture was added dropwise into a large, agitated amount of methanol. The collected precipitate was redissolved in THF, reprecipitated into methanol, 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. The purity of the resulting NLO side-chain polyquinoline was confirmed by ^{1}H NMR spectroscopy and elemental analysis.

(22) ^{1}H NMR (pyridine-d_5, 300 MHz), δ: for polyquinoline **7**, 8.65 (d, 4H), 8.60 (d, 2H), 8.16 (s, 2H), 7.94 (d, 2H), 7.90 (d, 4H), 7.84 (dd, 2H), 7.65 (d, 4H), 7.16 (d, 4H), 3.71 (s, 6H); for **9** 12.12 (s, 2H), 8.64 (d, 4H), 8.57 (d, 2H), 8.17 (s, 2H), 8.07 (d, 2H), 7.90 (d, 4H), 7.85 (dd, 2H), 7.67 (d, 4H), 7.35 (d, 4H); for **11a** (chromophore loading level of 23 wt % or 28 mol %) polymer backbone 12.05 (s, 0.72 × 2H), 8.64 (d, 4H), 8.58 (d, 2H), 8.17 (s, 2H), 8.06 (d, 2H), 7.90 (d, 4H), 7.83 (dd, 2H), 7.67 (d, 4H), 7.35 (d, 4H), NLO chromophore 6.6−7.1 (m, 0.28 × 8H), 4.1−4.5 (br, 0.28 × 4H), 4.0 (br, 0.28 × 4H), 3.1−3.5 (br, 0.28 × 8H), 1.0−3.0 (m, 0.28 × 40H).

(23) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990,** *56*, 1734.

MA980233Z