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High-Performance Polyquinolines with Pendent High-Temperature Chromophores for Second-Order Nonlinear Optics

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High-temperature second-order nonlinear optical (NLO) polymers have evolved as very promising electrooptic (E-O) materials for high-speed E-O modulator and switch applications.[1,2] Recently, delineation of the factors, including dielectric constant, glass transition temperature (T_g), thermal stability, temporal dipole alignment stability, and compatibility with semiconductor processes, that influence the practicality and outcome of different material systems has led to significant improvements of NLO polymer properties. Most notably, extensive studies[3−8] of various polyimide systems have resulted in several prototype devices.[9]

Although preliminary results reported for polyimides are quite encouraging, there are some drawbacks. For example, polyimides, in general, are synthesized via the condensation reaction between very reactive diamines and dianhydrides to afford polyamic acid precursor polymers, followed by a high-temperature imidization process to produce the desired polyimides. These reactive conditions severely limit the selection of usable chromophores. Recently, we have explored a new optical polymer system, polyquinolines, for second-order NLO applications. Polyquinolines, which were first developed by Stille[10] et al., represent a class of high-performance polymers with outstanding thermal stability (>450 °C), low dielectric constants (2.5−3.0), low moisture absorption (0.1−0.15%), very high T_g (250−400 °C), and compatibility with plasma or reactive ion etching. The studies of their electrooptic properties have shown very promising results for both guest/host[11] and side-chain polyquinoline systems.[12] Our previous approach to NLO side-chain polyquinolines includes the synthesis for polyquinoline precursor polymers, and a post-tricyanovinylation of these polyquinolines to activate the side-chain NLO chromophores.[12] However, this approach is limited to the synthesis of side-chain polyquinolines with only tricyanovinyl containing chromophores. Herein, this paper describes a generally applicable synthetic approach to side-chain NLO polyquinolines with several high-temperature NLO chromophores covalently attached onto the polymer backbones. The side-chain polyquinolines were synthesized by the direct polymerization of chromophore-containing bis(ketomethylene) monomers and bis(*o*-amino ketone) monomers. Their physical properties including electrooptic coefficients, inherent thermal stability, temporal stability of the poling-induced polar order, etc. are also reported.

Thermal and chemical stability of the chromophores are critical for the development of high-temperature side-chain NLO polymers. Recently, a new class of high-temperature second-order nonlinear optical chromophores were developed through the replacement of the most reactive cyano-group in the tricyanovinyl-substituted derivatives with donor-substituted aryl units.[13,14] Excellent tradeoffs among optical, chemical, and thermal properties have been achieved in this class of nonlinear optical chromophores. Further functionalization of the chromophores with a hydroxyl group results in chromophores[15] **1**, **2**, and **3** (Scheme 1). The chromophore-containing bis(ketomethylene) monomers **4**, **5**, and **6** for the synthesis of side-chain polyquinolines were prepared by the condensation between the hydroxyl-containing chromophores and 3,5-diacetyl phenol (Scheme 1).[16] The NLO side-chain polyquinolines were synthesized via polymerizations of these monomers (**4**, **5**, **6**) with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether[17] **7**. A fluorinated polyquinoline moiety **9**[18] (Scheme 2) was introduced into the backbone of the side-chain co-polyquinolines in order to achieve the desired physical properties and the

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(15) The chromophore-functionalized bis(ketomethylene) monomers were prepared by Mitsunobu condensation[16] in the yield of >90%, purified through silica gel column, and characterized by ^{1}H NMR spectroscopy and elemental analysis. For example, monomer **5**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.28 (d, J = 2.1 Hz, 1 H), 8.08 (dd, J = 9.0 Hz, 2.4 Hz, 1 H), 7.73 (d, J = 4.2 Hz, 1 H), 7.70 (d, J = 4.2 Hz, 1 H), 7.54 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2 H), 7.27 (d, J = 4.2 Hz, 1 H), 7.25 (d, J = 4.5 Hz, 1 H), 7.00 (d, J = 8.7 Hz, 1 H), 6.73 (d, J = 8.7 Hz, 2 H), 6.66 (d, J = 8.7 Hz, 2 H), 4.32, (t, 2 H), 3.87 (t, 2 H), 3.53 (q, 2 H), 3.40 (q, 4 H), 2.62 (s, 3 H), 2.57 (s, 3 H), 1.22 (t, 3 H), 1.19 (t, 6 H). Anal. Calcd for $C_{42}H_{40}N_4O_3S_2$: C, 70.76; H, 5.66; N, 7.86; S, 8.99. Found: C, 70.58; H, 5.71; N, 7.92; S, 9.21. Monomer **6**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.29 (d, J = 2.7 Hz, 1 H), 8.08 (dd, J = 8.7 Hz, 2.7 Hz, 1 H), 7.66 (d, J = 4.2 Hz, 1 H), 7.64 (d, J = 3.9 Hz, 1 H), 7.39 (d, J = 9.0 Hz, 2 H), 7.36 (d, J = 9.0 Hz, 2 H), 7.00 (d, J = 3.9 Hz, 1 H), 7.07 (d, J = 4.5 Hz, 1 H), 7.02 (m, 3 H), 7.10 (d, J = 15.9 Hz, 1 H), 6.96 (d, J = 15.9 Hz, 1 H), 6.72 (d, J = 9.0 Hz, 2 H), 6.65 (d, J = 9.0 Hz, 2 H), 4.31 (t, 2 H), 3.86 (t, 2 H), 3.52 (q, 2 H), 3.40 (q, 4 H), 2.63 (s, 3 H), 2.58 (s, 3 H), 1.22 (t, 3 H), 1.19 (t, 6 H). Anal. Calcd. for $C_{46}H_{44}N_4O_3S_2$: C, 72.22; H, 5.80; N, 7.32; S, 8.38. Found: C, 71.95; H, 5.93; N, 7.16; S, 8.64.

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(18) ^{1}H NMR ($CDCl_3$, 300 MHz) for pure fluorinated polyquinoline **9**: δ 8.24 (d, J = 9.0 Hz, 2 H), 8.19 (d, J = 8.1 Hz, 4 H), 7.82 (s, 2 H), 7.61 (J = 8.1 Hz, 4 H), 7.53 (br, 2 H), 7.49 (br, 10 H), 7.44 (br, 2 H). Molecular weight: M_w = 47 000 with a polydispersity index of 2.13 determined by GPC.[21]

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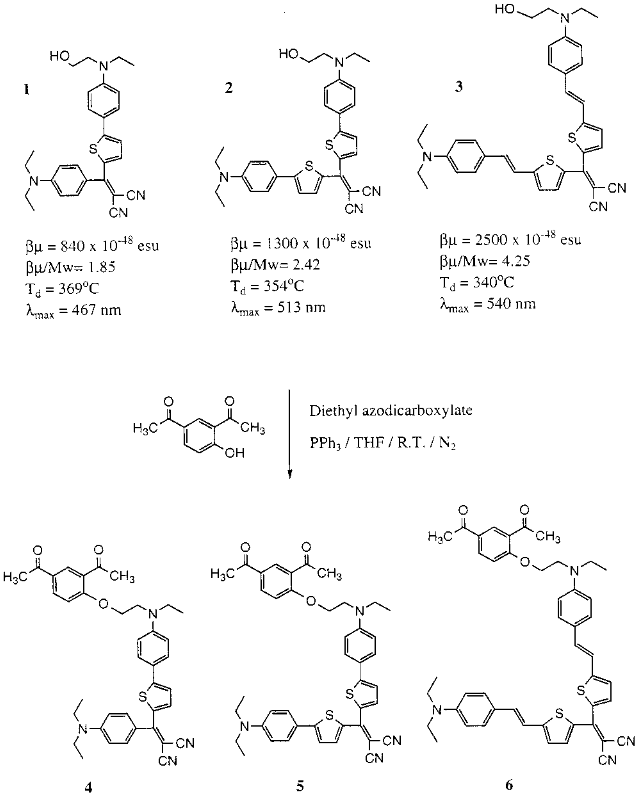
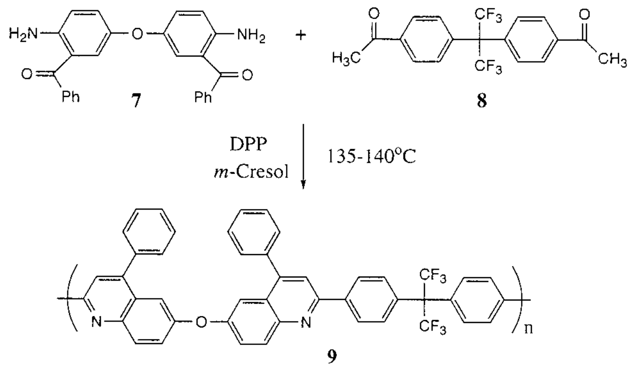
Scheme 1. Preparation of Chromophore-Containing Bis(ketomethylene) Monomers

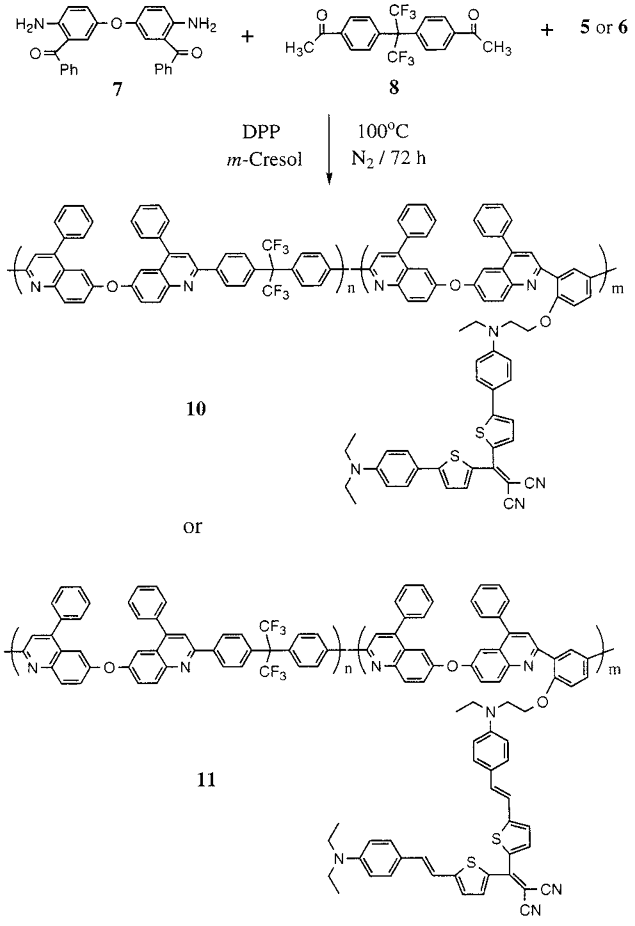


Scheme 2. Synthesis of Fluorinated Polyquinoline



Glass Transition Temperature (Tg): 260°C
Dielectric Constant: 2.50 (1 MHz)
Optical Loss: < 1 dB/cm (0.83 μm), measured by the prism-coupled streak method on a slab waveguide
Thermal Stability: < 1% weight loss up to 500°C

Scheme 3. Synthesis of Side-Chain NLO Polyquinolines



flexibility of adjusting the chromophore contents. Side-chain polyquinolines **10** and **11**, for example, were synthesized by the polymerization of 1:0.5:0.5 equiv of bis(*o*-amino ketone), **7**, 2,2-bis(4-acetylphenyl) hexafluoropropane, **8**, chromophore-containing bis(ketomethylene) monomer **5** or **6** in 11.5 equiv of *m*-cresol and 25.0 equiv of diphenyl phosphate (DPP) at 100 °C for 72 h under nitrogen. The resulting viscous polymer solutions were precipitated into a large amount of agitating solution of methanol containing 10% (v/v) of triethylamine. The polymers were collected through filtration and purified by Soxhlet extraction with methanol (containing 10% triethylamine) for 24 h. The polymers were then redissolved in $CHCl_3$ and reprecipitated into the methanol solution (10% triethylamine), followed by drying under vacuum at 80 °C for 24 h. The structures and the purities of the side-chain polyquinolines were verified by ^{1}H NMR spectroscopy[19] and elemental analysis. This simple synthesis is applicable not only to NLO polyquinolines with the side-chain chromophores described above but also to the side-chain polyquinolines with many different chromophores, such as disperse red and DCM type of chromophores.[15] Moreover, this methodology may allow us to synthesize NLO side-chain polyquinolines with broad variations of polymer backbone[20] to fine-tune the physical properties of the polymeric materials for device applications.

The synthesized side-chain polyquinolines were all soluble in common polar solvents, such as *N*,*N*-dimethylacetamide, chloroform, cyclohexanone, and tetrahydrofuran (THF). The molecular weights of the side-chain polyquinolines can be estimated by gel permeation chromatography (GPC).[21] Polyquinoline **4**, for example,

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[19] ^{1}H NMR ($CDCl_3$, 300 MHz) for side-chain polyquinoline **10**: δ 8.60 (br, 1 H), 8.34 (d, 2 H), 8.20 (m, 7 H), 7.83 (m, 4 H), 7.68 (t, 2 H), 7.62 (d, 4 H), 7.50 (br, 31 H), 7.20 (d, 2 H), 7.17 (d, 2 H), 6.62 (d, 2 H), 6.54 (d, 2 H), 4.31 (br, 2 H), 3.71 (br, 2 H), 3.38 (q, br, 4 H), 3.20 (br, 2 H), 1.18 (t, 6 H), 0.94 (t, 3 H). For **11**: δ 8.6 (br, 1 H), 8.0 (br, 9 H), 7.8 (br, 4 H), 7.5 (br, 37 H), 7.0 (br, 4 H), 6.5 (br, 4 H), 4.2 (br, 2 H), 3.6 (br, 2 H), 3.4 (br, 4 H), 3.1 (br, 2 H), 1.1 (br, 6 H), 0.9 (br, 3 H).

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[21] The molecular weights and the polydispersities (relative to polystyrene standard) were determined by a Waters GPC with HR-5E and HR-2 columns at room temperature (THF as the eluant).

has a weight average molecular weight M_w = 53 000 with a polydispersity index of 1.81; polyquinoline **5**, M_w = 55 000 with a polydispersity index of 1.97. The UV–vis spectra of thin films of the side-chain polyquinolines exhibited a strong absorption pattern (λ_{max} of 530 nm for polymer **4** and of 546 nm for polymer **5**) due to the $\pi-\pi^*$ charge-transfer band of the NLO chromophores. These side-chain polyquinolines also possess high glass transition temperature (T_g) and excellent thermal stability. Polymer **4** (chromophore content: 30 wt %) has a T_g of 215 °C determined by differential scanning calorimetry (DSC) analysis and a <1% weight loss up to 360 °C determined by thermogravimetric analysis (TGA); while polymer **5** (chromophore content: 32 wt %) has a T_g of 205 °C and a <1% weight loss up to 330 °C.[22]

Very uniform thin films (2–3 μm) of side-chain polyquinoline **4** or **5** were prepared by spin-coating the polymer solution (20% m/m, filtered through a 0.2 μm syringe filter) in cyclohexanone/DMAc (1:1 mixture) onto an indium tin oxide (ITO) glass substrate. The films were kept in a vacuum oven at 180 °C overnight to ensure the removal of residual solvents. The dipole alignment of the NLO chromophores in the polymer film were achieved by contact poling. Preliminary tests showed that the synthesized NLO side-chain polyquinolines exhibited a large electrooptic coefficient (r_{33}) value and good temporal stability of dipole alignment at elevated temperature. The r_{33} values were measured with an experiment that was described by Teng and Man.[23] Polyquinoline **4**, for example, exhibited an r_{33} value of 12 pm/V measured at 0.83 μm, polyquinoline **5**, 17 pm/V also at 0.83 μm with a poling field of 0.9 MV/cm. The r_{33} value remained at ~80% of the original value at 100 °C in air for more than 3000 h (Figure 1).

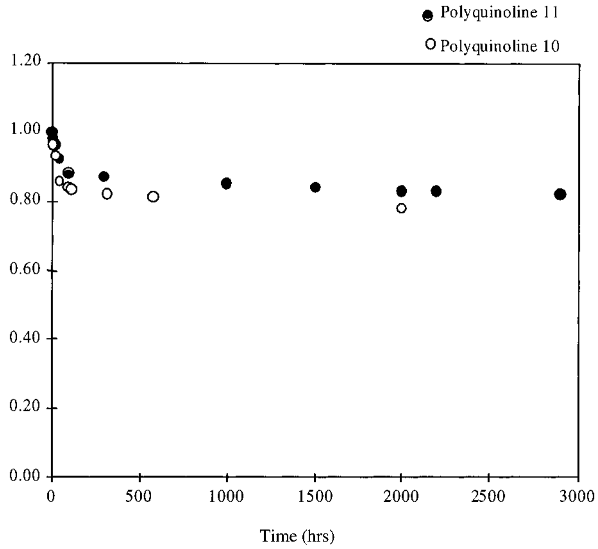

Figure 1. Temporal stability of the poled (contact poling at 0.9 MV/cm) side-chain polyquinolines at 100 °C in air (normalized r_{33} as a function of baking time).

In summary, we have developed an efficient approach to synthesize side-chain second-order NLO polyquinolines. A series of NLO polyquinolines with thermally and chemically stable chromophores were synthesized by the direct polycondensation of the chromophore-containing bis(ketomethylene) monomers and the bis(*o*-amino ketone) monomers. These side-chain polyquinolines possess excellent solubility, processibility, large E-O coefficients after poling, and good temporal alignment stability at 100 °C. The methodology offers great flexibility in choosing the backbone structures of polyquinolines to fine-tune the physical properties of the polymeric materials for device applications. We are continuing to examine several aspects which may further improve the properties of the side-chain NLO polyquinolines.

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(22) The decomposition temperature (T_d) of chromophores and the glass transition temperature (T_g) of polyquinolines were determined by sealed-pan DSC (20°/min under nitrogen). Thermal stability of polyquinolines were determined by (10°/min under nitrogen).

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