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A Novel Class of Nonlinear Optical Side-Chain Polymer: Polyquinolines with Large Second-Order Nonlinearity and Thermal Stability

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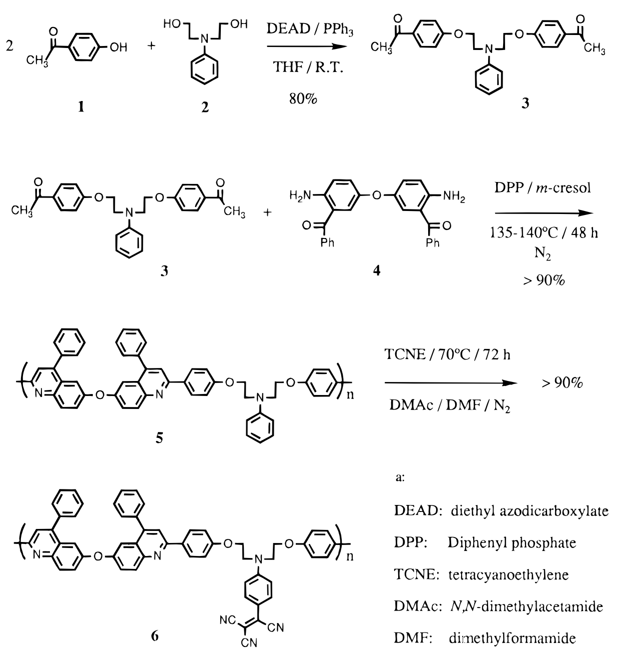
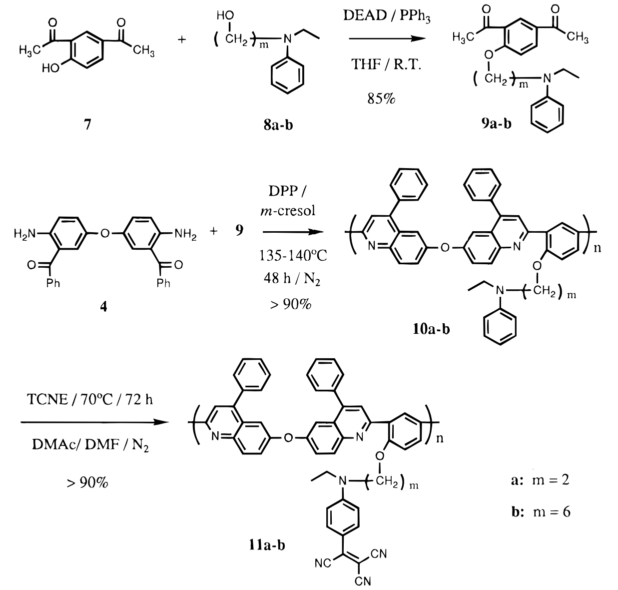
Recent scientific reports[1] have shown great improvements and promising results in the development of high-speed light modulators and switches based on the second-order nonlinear optical (NLO) polymers. The challenges to achieving useful NLO polymeric material systems for practical devices are still based on resolving of the following key issues: the electrooptical (E−O) coefficients of the systems must be large enough to accommodate the operating voltage of the devices; they must retain a significant fraction of their initial values at continuous operating temperatures of approximately 80 °C and during short exposure to temperatures >250 °C; the material systems must possess good mechanical properties for multilayer processing; and low optical attenuation.[2−4] To date, polyimides were considered to be the most attractive host candidates for the development of high-temperature NLO polymers.[2−5] In particular, the NLO side-chain or cross-linked polyimides were considered to be the most promising systems among different NLO polyimides.[6−10] Although the results reported for these NLO polyimides are quite encourging, there are some deficiencies, such as a highly reactive environment during the imidization process, which severely limits the selection of usable chromophores. Recently, we have reported achieving very high electrooptical coefficient (r_{33} = 45 pm/V at 1.3 μm) and long-term temporal stability of E−O signal at 80 °C for more than 2500 h in a guest/host polyquinoline system.[11] This guest/host polyquinoline polymer provides very promising results; however, there is a strong need to further improve their mechanical properties (for multilayer integration) and thermal stability in order to accommodate the processing requirements of E−O devices. Herein, we report a novel class of high-temperature NLO side-chain polyquinolines. Our approach to these NLO side-chain polyquinolines includes the synthesis of chromophore precursor-containing bis(ketomethylene) monomers and bis(*o*-amino ketone) monomers, the polycondensation of the two monomers, and posttricyanovinylation of the polyquinolines to activate the side-chain NLO chromophores (Schemes 1 and 2). The wide variety of monomers and the relatively mild conditions of the quinoline-forming reaction to generate high molecular weight polymers allows the synthesis of a large series of NLO polyquinolines with different polymer backbones (such as aliphatic embed-

Scheme 1. Synthesis of Aliphatic Imbedded NLO Side-Chain Polyquinolines[a]



[a] DEAD: diethyl azodicarboxylate
DPP: Diphenyl phosphate
TCNE: tetracyanoethylene
DMAc: *N*,*N*-dimethylacetamide
DMF: dimethylformamide

Scheme 2. Synthesis of Aromatic NLO Side-Chain Polyquinolines



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ded as shown in Scheme 1 and aromatic polyquinoline as shown in Scheme 2) and different chromophores to fine-tune the physical properties of the polymers. Preliminary results of the electrooptical coefficients, thermal stability, temporal stability of the poling-induced dipole moments of the polymer films, and other physical properties are also reported in this paper.

Polyquinolines, which were first developed by Stille[12] *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 (0.10−0.15%), low optical loss, low shrinkage, very high T_g (250−400 °C), excellent processibility, and compatibility with plasma or reactive ion etching. Their mechanical properties, electrical properties, linear optical, and third-order nonlinear optical properties were well established by Stille[12] and recently by Jenekhe[13] and co-workers. A polyquinoline composition (PQ-100) was recently commercialized by Maxdem Inc. To our knowledge, no studies related to NLO side-chain polyquinolines have been reported prior to this work.

The chromophore precursor-containing bis(ketomethylene) monomers **3**, **9a**, and **9b** were prepared as shown in Schemes 1 and 2. The related starting compound 2,4-diacetylphenol (**7**) and bis(*o*-amino ketone) **4** were synthesized according to the literature methods.[14,15] The precursor polyquinolines, **5**, **10a**, and **10b**, were synthesized via polymerizations of the ketomethylene and the amino ketone monomers in diphenyl phosphate/*m*-cresol at 135−140 °C for 48 h under nitrogen with a yield of >90%.[16] The NLO side-chain polyquinolines **6**, **11a**, and **11b** were prepared by the posttricyanovinylation of the precursor polyquinolines with tetracyanoethylene (TCNE) in DMAc/DMF at 70 °C for 72 h with a yield of >90%.[17] To unambiguously verify the polymer structures shown in Schemes 1 and 2, the polyquinolines were characterized by NMR spectroscopy. Surprisingly, excellent proton resonances and splittings and their correct integration signals can be observed in the ^{1}H NMR (pyridine-d_6) spectra for all the protons in the polymer repeat units (see Figure 1a for polyquinoline **5**, for example). The posttricyanovinylation of the precursor polyquinolines was monitored by proton NMR spectroscopy. The completion of the tricyanovinylation was also verified by spectroscopy. For example, the three sets of chemical shifts at 6.9 (triplet), 7.0 (doublet), and 7.3 ppm (triplet) were attributed to the protons 10, 8, and 9 of precursor polyquinoline **5** (Figure 1a). The resonance peak for the proton 10 disappeared after the proton was replaced by the tricyanovinyl group, and the protons 8 and 9 were downshifted to 7.1 (doublet) and 8.2 ppm (doublet) after the tricyanovinylation (see Figure 1b for side-chain polyquinoline **6**). The NLO side-chain polyquinolines can also be prepared through a post-Mitsunobu condensation between hydroxyl-polyquinolines and hydroxyl chromophores with different functional groups such as tricyanovinyl, nitro, and dicyanivinyl, etc.[18]

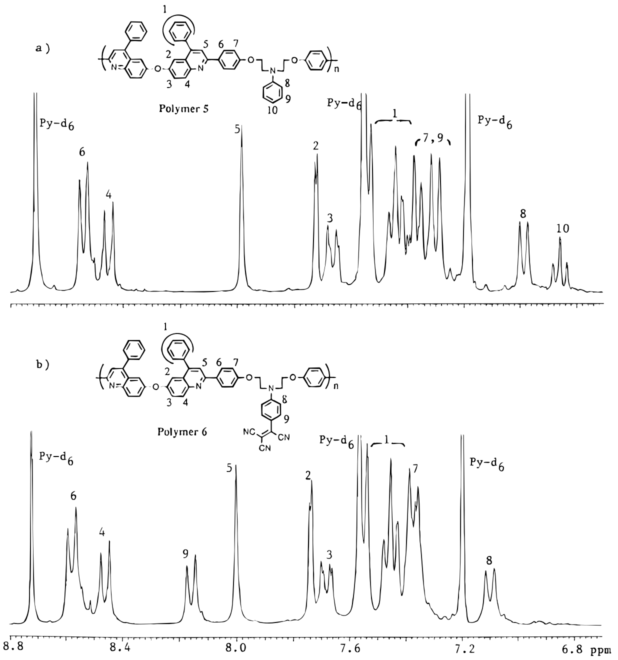

Figure 1. Aromatic region of ^{1}H NMR (pyridine-d_6) spectra opf the precursor polyquinoline 5 and the side-chain polyquinoline 6.

The precursor polyquinolines **5** and **10** and the side-chain polyquinolines **6** and **11** were all soluble in polar solvents, such as cyclopentanone, cyclohexanone, *N*,*N*-dimethylacetamide, *m*-cresol, *N*-methylpyrrolidinone, pyridine, and tetrahydrofuran (THF). The precursor polymers **5** and **10** were soluble in chloroform, while the side-chain polymers **6** and **11** were only slightly soluble in chloroform. Due to the solubility in THF, the molecular weights of both precursor and side-chain polymers can be estimated by gel permeation chromatography (GPC).[19] Polyquinoline **5**, for example, has a weight average molecular weight M_w = 41 000 with a polydispersity index of 1.90. Polyquinoline **6** has a higher M_w of 46 000 and a smaller polydispersity of 1.68 due to the posttricyanovinylation and the further purification. The UV−vis spectra of thin films of the side-chain polyquinolines exhibited a strong absorption pattern (λ_{max} of 519 nm for polymer **6** and of 530 nm for polymer **11**) due to the $\pi-\pi^*$ charge-transfer band

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(16) The precursor polyquinolines (**5**, **10a**, and **10b**) were prepared by the polymerization of 1:1 equivalent of the corresponding bis-(ketomethylene) and bis(*o*-amino ketone) monomers 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 polymers were precipitated into a large amount, agitating solution of MeOH containing 10% (V/V) of triethylamine. The polymers were purified by Soxhlet extraction with MeOH (10% triethylamine) for 24 h, redissolved in $CHCl_3$, and reprecipitated into the MeOH solution (10% triethylamine). The collected polymers were dried under vacuum at 100 °C for 24 h. The structures and the purities of the polymers were verified by ^{1}H NMR spectroscopy and by satisfying elemental analysis.

(17) The posttricyanovinylations were carried out with 1:5 equiv of the polymer unit vs TCNE in the solution of DMAc/DMF, 3/1 (V/V) at 70 °C under N_2 for 72 h. The resulting side-chain polyquinolines (**6**, **11a**, and **11b**) were precipited into the solution of MeOH and triethylamine and purified by Soxhlet extraction with acetone for 24 h. The polymers were dried under vacuum at 50 °C for 24 h. The structures and the purities were verified by ^{1}H NMR and elemental analysis.

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(19) 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).

of the NLO chromophore of the *p*-(diethylamino)tricyanovinylbenzene. All the resulting side-chain polyquinolines have a high T_g and good thermal stability. Both polymers **6** (chromophore loading level of 27 wt %) and **11b** (loading level of 29 wt %) have a T_g of 175 °C, while polymer **11a** has a T_g of 200 °C by differential scanning calorimetry (DSC) analysis. They all have a thermal stability of <3% weight loss up to 300 °C by thermogravimetric analysis (TGA).

Optical-quality thin films (~1.2 μm) of the polyquinolines **6** and **11** were prepared by spin-coating of the polymer solutions in cyclopentanone (15% m/m solution, filtered through a 0.2 μm syringe filter) onto an indium tin oxide (ITO) glass substrate. The films were kept in a vacuum oven at 120 °C overnight to ensure the removal of the residual solvent. Dipole alignments in the NLO side-chain polyquinolines can be achieved, and the second-order nonlinearity can be induced by either contact poling or corona poling. The E−O coefficient (r_{33}) was measured with an experimental setup similar to that decribed by Teng[20] et al. Polyquinoline **11b**, for example, exihibited a preliminary r_{33} value of 29 pm/V measured at 0.63 μm and 16 pm/V at 0.83 μm with a poling field of 1.0 MV/cm. Polyquinoline **6** exihibited an r_{33} value of 21 pm/V at 0.63 μm, and 9 pm/V at 0.83 μm. The r_{33} value of polymer **6** retained >95% of the original value at 100 °C for 500 h, and the r_{33} value of polymer **11b** retained ~80% of the original value at 80 °C for more than 500 h (Figure 2). Polyquinoline **6** has a dielectric constant of 3.89 and polyquinoline**11b**, 3.74 calculated from the capacitance of the films measured using an HP 4192A impedance analyzer.

In conclusion, we have developed a synthetic methodology for a novel class of second-order NLO side-chain polyquinolines which demonstrates excellent temporal stability of the poling-induced dipole moments of the polymer films at elevated temperatures. This class of side-chain polyquinolines has great flexibility both in backbone structures and in side-chain chromophores for fine-tuning the properties of the polymeric materials. The material system is a potential alternative or a superior substitute for existing systems of polyimide. The synthesis of higher T_g side-chain polyquinolines and the optimization of their E−O coefficient and thermal alignment stability are presently in progress.

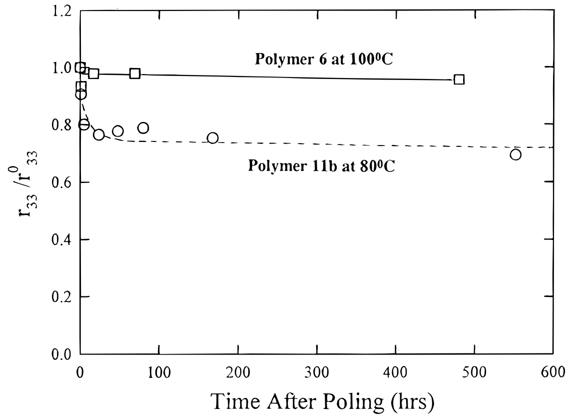

Figure 2. Temporal stability of the poled side-chain polyquinoline 6 at 100 °C, 11b at 80 °C. (Normalized r_{33} as a function of baking time).

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