Synthesis and Characterization of Main-Chain High-Temperature Nonlinear Optical-Active Polymers. Poly(aryl ether–oxazoles)

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The design and development of new devices for second-harmonic generation and electro-optical applications has spurred much interest in organic nonlinear optical (NLO) materials.[1] In particular, polymer NLO systems have received the most attention, due in part to their ease in processing and their potentially large NLO susceptibilities. The incorporation of the NLO chromophore into a polymeric system can be accomplished in a variety of ways: host–guest, side-chain tethers, main-chain bonding, etc. In these systems, the necessary chromophore orientation is achieved by poling at or near the polymer glass transition temperature, T_g. The magnitude of this induced polar order tends to decrease after removal of the electric field over time, particularly at elevated temperatures. The observed rate of reorientation of NLO chromophore guest molecules in high-temperature thermoplastic hosts has been observed to be slow and is correlated with the T_g of the polymer host.[2] A theoretical high-frequency phase amplitude modulator, integrated into a semiconductor device, could be expected to operate continuously at temperatures in excess of 80 °C and could be exposed to temperatures exceeding 250 °C during fabrication processes. For those reasons, the study of NLO polymer materials must not focus only on chromophore molecules with large quadratic nonlinearities; suitable high-temperature polymer systems as well as thermally stable chromophores must also be identified.

Five-membered heterocyclic azole derivatives containing donor–acceptor groups such as imidazoles, oxazoles, thiazoles, pyrazoles, etc., have been extensively studied and shown to possess, in some cases, significant nonlinearities as well as impressive thermal and oxidative stabilities.[3,4] When used in a host–guest type arrangement, a system containing a substituted triarylimidazole guest molecules in a variety of polyimide hosts resulted in materials with high thermal stabilities and stable poled order at high temperatures.[5] Host–guest systems can exhibit certain drawbacks: (i) phase separation of the host and guest can occur at higher loading levels: (ii) since the guest is a small molecule, it can become lost from the polymer at higher temperatures (e.g., sublimation); (iii) significant plasticization of the host polymer often occurs at moderate guest concentrations, significantly lowering the T_g of the system and adversely effecting the thermal stability of the polar order. All of the above drawbacks can be eliminated or significantly reduced through the incorporation of the NLO chromophore as part of the backbone of the polymer chain.

We now report preliminary results of the synthesis and characterization of new high-temperature thermoplastic materials containing functionalized heterocyclic units, with known NLO polarizability, as a part of the main chain of the polymer backbone. The heterocyclic NLO chromophore chosen for this study was based upon the 2-[4-(phenylsulfonyl)phenyl]-4,5-bis(4-substituted phenyl)oxazole. The chromophore was prepared as the bisphenol and polymerized, via nucleophilic aromatic substitution polymerization with activated aryl difluorides, yielding the corresponding poly(aryl ether–oxazoles). These poly(aryl ether–oxazoles) represent a new class of thermoplastics that are thermally stable and which can be poled. Though other high-T_g NLO-active polymers have been reported, we report the use of a thermally stable chromophore which is incorporated as part of the backbone of a thermally stable thermoplastic, in contrast to other systems in which various chromophores have been attached pendant to the polymer chain.

Experimental Sections. Monomers. The NLO-active bisphenol monomer, 2-[4-(phenylsulfonyl)phenyl]-4,5-bis(4-hydroxyphenyl)oxazole (**1**), was prepared as shown in Scheme 1. While a detailed synthetic description can be found in ref 3, an abbreviated description of the synthesis follows. Anisoin (**A**) is esteified with 4-carboxyphenyl sulfone (**B**) to give the corresponding ketoester (**C**). The heterocycle (**D**) is formed by the reaction with ammonium acetate and the methyl ethers are subsequently cleaved to give the bisphenol **1**.[6] The monomers 4,4-bis(fluorophenyl) sulfone (**2**) and 4,4-difluorobenzophenone (**3**) were commercially available and recrystallized from toluene/ethyl acetate.

Polymer Synthesis. An in-depth discussion of poly(aryl ether) syntheses can be found elsewhere.[7] The synthesis of the poly(aryl ether–oxazole) **4a** derived from **1** and **2** is given here (Scheme 2). A 50-mL three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean–Stark trap, and a condenser was charged with 4.076 g (8.6 mmol) of **1** and 2.186 g (8.6 mmol) of **2**. The monomers were carefully washed into the flask with 20 mL of a 1:1 *N*-methyl-2-pyrrolidinone/*N*-cyclohexyl-2-pyrrolidinone (NMP/CHP) mixture.[8] An excess of K_2CO_3 (5.8 g, 41.9 mmol) and approximately 10 mL of toluene were added. The reaction mixture was heated to 145 °C, at which point the toluene began to reflux. Collected toluene was removed from the Dean–Stark trap, and more toluene was added periodically and then subsequently collected and drained from the trap. The reaction mixture was maintained at this temperature for 4–6 h to ensure complete dehydration of the system. The temperature was increased to 175 °C, and the mixture was allowed to react for approximately 20 h. Completion or near completion was qualitatively estimated by the point where the reaction mixture viscosity increased dramatically. The polymer solution was precipitated by being poured into 500 mL of a MeOH/water (1:1) solution followed by vigorous stirring prior to filtering. The precipitated polymer, **4a**, was washed several times with methanol. The polymer was reprecipitated from CH_2Cl_2 and vacuum dried to a constant weight, 5.11 g. Polymer **4b**, derived from **1** and **3**, was similarly prepared.

Electric Field Poling of Main-Chain Nonlinear Optical Polymers. Thin films (1–4 μm) of the polymers were prepared by spin-coating the polymers from the appropriate solvent, in this case cyclohexanone, on to a transparent conducting substrate (ITO-coated quartz). The polymers were heated to above T_g for several hours to remove all solvent before electric field poling was attempted. The top surface of the polymer film was charged to a positive voltage using a corona discharge from a thin tungsten wire, creating a high electric field (3×10^6 V/cm) across the polymer film. Each polymer was heated while the poling voltage was applied. Poling was monitored by means of second-harmonic light generated at 523.5 nm using a pulsed 1047-nm Nd:YLF laser as the fundamental light source. Both polymers, **4a** and **4b**, were poled at temperature approximately 25 °C below their respective

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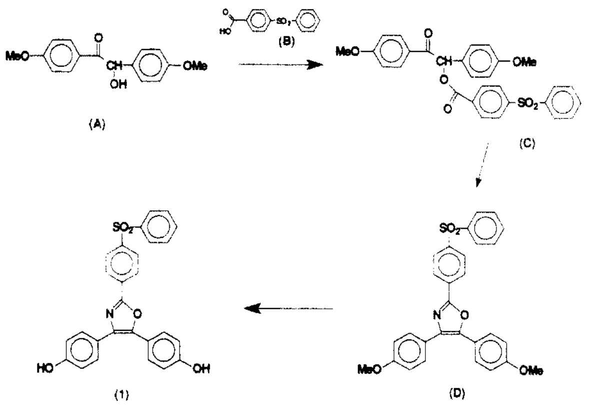
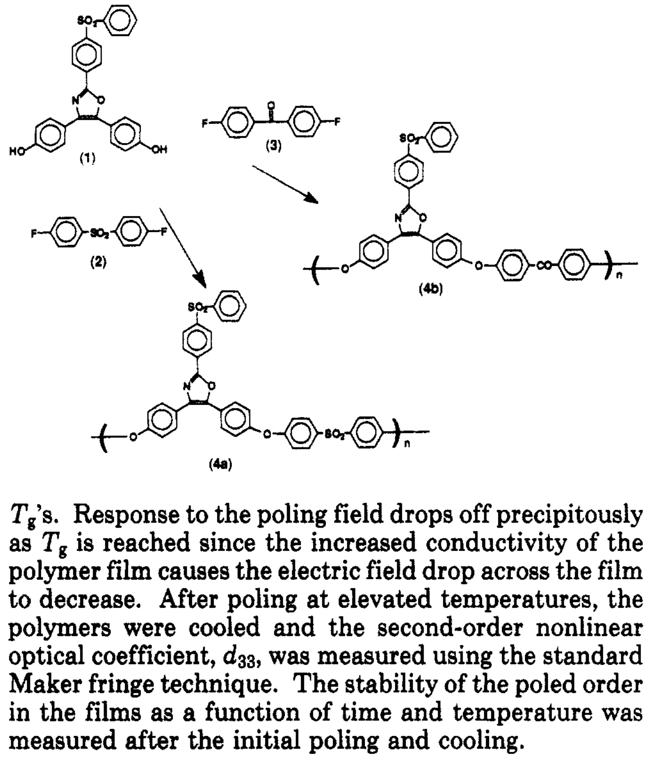
Scheme 1



Scheme 2



T_g's. Response to the poling field drops off precipitously as T_g is reached since the increased conductivity of the polymer film causes the electric field drop across the film to decrease. After poling at elevated temperatures, the polymers were cooled and the second-order nonlinear optical coefficient, d_{33}, was measured using the standard Maker fringe technique. The stability of the poled order in the films as a function of time and temperature was measured after the initial poling and cooling.

Results and Discussion. The synthesis of the desired polymers **4a** and **4b** was achieved via nucleophilic aromatic substitution polymerization of the NLO chromophore bisphenol monomer **1** with the activated aryl fluorides **2** and **3**. Polymer **4a** had an observed T_g of 242 °C and an intrinsic viscosity of 0.46 dL/g, while polymer **4b** had an observed T_g of 145 °C and an intrinsic viscosity of 0.64 dL/g. The polymers could be solution processed (DMPU, NMP, cyclohexanone) into clear, strong, fingernail creasable films.

These polymers contain the NLO chromophore, the functionalized oxazole ring, in the backbone of a high-temperature polymer system. Poling of this chromophore can be imagined to take place orthogonal to the polymer backbone, thereby not requiring the alignment of the whole polymer molecule but rather reorientation along the polymer chain. Model compounds of **1** have been prepared and measured by EFSH in order to determine the value of the microscopic hyperpolarizability.[4] The magnitude of these values would be expected to limit the observed values of d_{33} of polymers incorporating the chromophore molecule. The methyl ether compound, **D**, has a measured d_{33} of 17.1 (10^{-30} esu) at 1064 nm. The values of d_{33} for the polymers **4a** and **4b** were small, only 1 pm/V at 1047 nm. These low d_{33} values are due to the low d_{33} of the chromophore itself, not due to a lack of poling of the polymer. The polymers were successfully poled, and the stability of the poled order was monitored as a function of time and temperature. The decay of poled order of **4a** as a function of temperature is shown in Figure 1. As expected, the magnitude of the decay is more pronounced as temperatures approach the T_g of the polymer. Similar behavior was observed for polymer **4b**, with lower temperature stability observed due to the lower T_g of that polymer. The decay of poled order was found to be highly nonexponential, leveling off at a percentage of the original d_{33} value after the initial decay. The samples show that these polymers can retain nearly 75% of their initial poled order at 100 °C for extended periods of time.

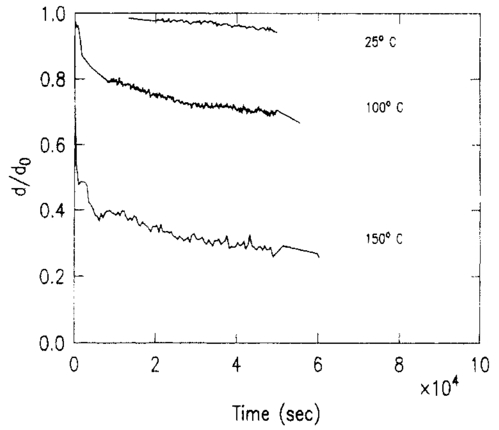


Figure 1. Decay of poled order of poly(aryl ether–oxazole) **4a** as a function of temperature.

Summary. New high-temperature poly(aryl ether–oxazoles) have been synthesized, thereby incorporating an NLO chromorphore (the functionalized oxazole ring) into the main chain of the polymer backbone. Our methodology has allowed for the incorporation of a thermally stable chromophore into the backbone of a high T_g thermoplastic. We have demonstrated that these main-chain high-temperature NLO-active polymers can give materials that have a good stability of poled order at higher temperatures. Work continues on the development of polymers with higher d_{33} values for actual device applications including the creation of NLO monomers that have higher values of d_{33} than the oxazole monomer used in this study.

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References and Notes

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(6) **1** isolated as yellow crystals: mp 277–278 °C; ^{1}H NMR (DMSO-d_6) δ 8.25 (d, 2H), 8.12 (d, 2H), 7.99 (d, 2H), 7.69 (m, 3H), 7.46 (t, 4H), 6.83 (t 4H). Anal. Calcd for $C_{27}H_{19}NO_5S$: C, 69.07; H, 4.08; N, 2.98. Found: C, 69.87; H, 4.48; N, 2.86.

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(8) Alternatively, *N,N*-dimethylpropyleneurea (DMPU) was used as the polymerization solvent. Care was taken to remove all traces of DMPU from the polymer films prior to poling measurements.