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Thermally Stable Nonlinear Optical Polyimides: Synthesis and Electro-optic Properties

Alex K-Y. Jen,*[a] Kevin J. Drost,[a] Yongming Cai,[a] V. Pushkara Rao[a] and Larry R. Dalton[b]

[a] *EniChem America Inc., Research and Development Center, 2000 Cornwall Road, Monmouth Junction, New Jersey 08852, USA*

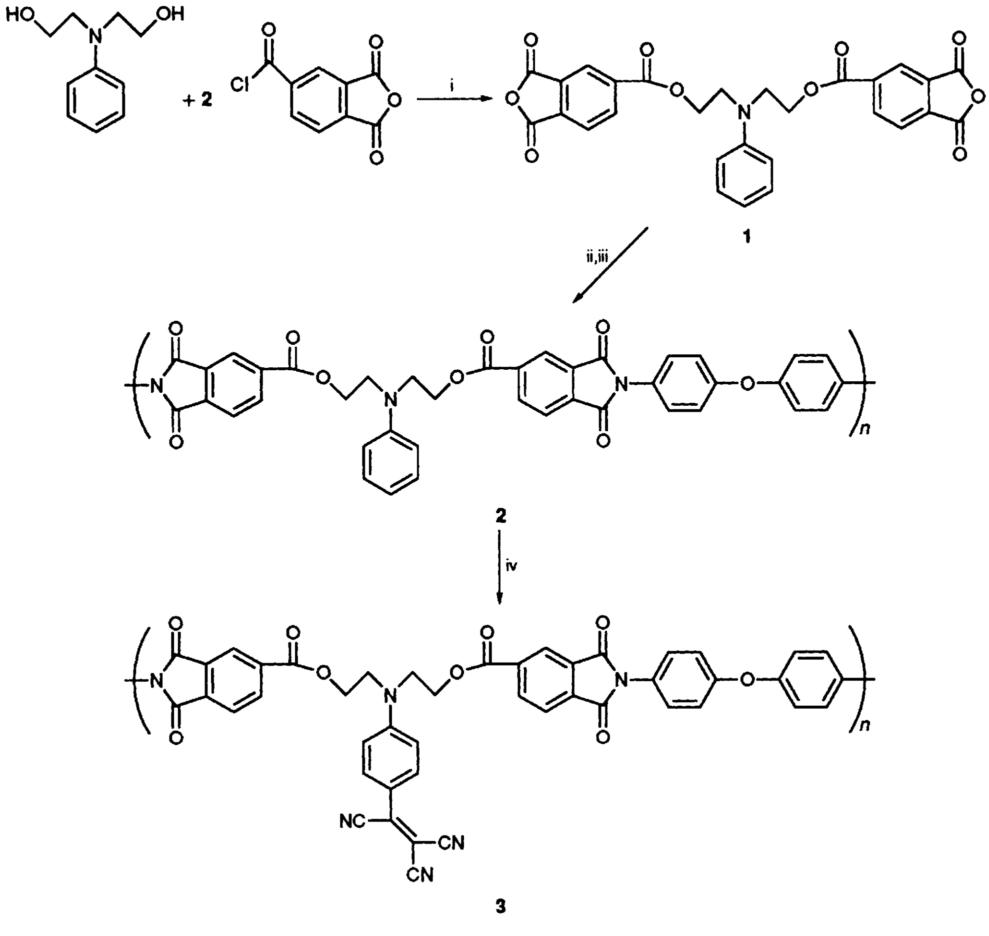
[b] *Department of Chemistry, University of Southern California, Los Angeles, California, 90089, USA*

A facile synthetic method has been developed to incorporate efficient nonlinear optical chromophores as side-chains into high temperature polyimides resulting in high electro-optic activity and long-term thermal stability at 90 °C for over one month.

Organic polymeric electro-optic (E-O) materials offer great promise for the fabrication of integrated optical devices.[1] Among the many advantages, large electro-optic coefficients and ease of processing are major attractive features. For these polymers to be used in electronic devices they must meet many requirements, most notably, thermal stability in manufacturing, assembly and end-use. To date, many studies[2–10] have been performed to optimize one or several required properties by (*i*) the design and synthesis of more efficient nonlinear optical (NLO) chromophores, (*ii*) the incorporation of efficient NLO chromophores into thermally stable and processible polymers, and (*iii*) improving the alignment stability of poled NLO polymer films.

Polyimides are found to be attractive candidates for polymeric (E-O) materials particularly because of their low dielectric constants, high glass-transition temperatures (T_g) and compatibility with semiconductor processes. Recently, several classes of NLO chromophore doped high temperature polyimides have been examined[11,12] to achieve long-term thermal stability of E-O coefficients. Although the results reported with these guest/host type NLO materials are quite encouraging, several deficiencies do exist, such as a highly reactive environment during the imidization process, low chromophore loading level and plasticization effects.[13] Many known chromophores which possess high inherent thermal stability are unstable in the polyamic acid/polyimide curing process. This may be attributed to the sensitivity of the chromophores to (*i*) the very acidic environment of the medium, (*ii*) the processing solvents, and/or (*iii*) the byproducts formed at high curing temperatures (200–300 °C). To overcome these deficiencies, we have focused on covalent incorporation of NLO chromophores into polyimides.

Our earlier results demonstrated enhancement of second-order NLO properties through the functionalization of a tricyanovinyl electron-accepting group on a series of electron-rich thiophene derivatives[14] and side-chain acrylate polymers.[15] Here, we present the facile synthesis of covalently bonding an efficient NLO chromophore, *N*,*N*-diethylamino-4-tricyanovinylbenzene on polyimides using a two-stage process. By functionalization of the acceptor at the last stage, the harsh environment during the imidization process is avoided. The synthetic procedures are shown in Scheme 1. The



Scheme 1 *Reagents and conditions*: *i*, pyridine, CH_2Cl_2, 0 → 25 °C; *ii*, 4,4′-oxydianiline, NMP, N_2, 0 → 25 °C; *iii*, 1,2-dichlorobenzene, N_2, heat, 180 °C; *iv*, TCNE, DMF, N_2, heat, 70 °C

dianhydride **1** was obtained in 85% yield by treating *N*-phenylethanolamine (1 equiv.) with trimellitic anhydride chloride (2 equiv.) in dichloromethane–pyridine at 0 °C. The dianhydride was then reacted with 4,4′-oxydianiline (1 equiv.) in NMP at 0 °C (N_2) to give a viscous solution. The concentration of this reaction mixture was adjusted to obtain a solution with 15% by mass solid content. After overnight reaction, 1,2-dichlorobenzene (same amount as original NMP) was added to the solution as cosolvent to remove the water formed during the imidization process. The solution was refluxed for 3 h to ensure the ring cyclization of the imide linkage. Then, the hot solution was added dropwise to methanol to precipitate the polyimide **2**. The post tricyanovinylation of polyimide **2** was carried out by dissolving **2** and tetracyanoethylene (TCNE) (1.1 equiv.) in DMF and heating at 70 °C (N_2) for 24 h. The resulting red solution was added dropwide to an agitated methanol solution to obtain the red polyimide **3** (90% yield).

Polyimide **2** has a lower T_g (158 °C) and good solubility in common organic solvents. After tricyanovinylation, the resulting polyimide **3** has a much higher T_g (189 °C) and is only soluble in polar solvents such as Me_2SO, DMF and cyclohexanone. This large change in T_g has been observed in our previous study on the side-chain polyacrylate systems and may be attributed to the influence of the highly dipolar nature of the NLO chromophores on the polymer main chain motions. The T_g of these side-chain polyimides can easily be fine tuned by reacting **1** with more rigid diamines such as 2,2′-bis(trifluoromethyl)benzidine to obtain a higher T_g (200 °C) polymer. This approach provides almost unlimited variations of monomer for fine tuning the structural and electrical properties of the desired E-O polymers. The structures of **2** and **3** were confirmed by conventional spectroscopic techniques (IR, UV, ^{1}H NMR) and elemental analysis. The imidization and tricyanovinylation processes were monitored by using FTIR and ^{1}H NMR. New sharp IR peaks at 1775, 721 and 2240 cm^{-1} are the characteristic bands of the imide group and CN on the tricyanovinyl group. The disappearance of the chemical shift (δ 6.62) of the proton *para* to the amino functional group on the benzene ring was used to monitor the progress of the tricyanovinylation.

Thin films (1–3 μm) of **3** were spun-coated onto an indium tin oxide (ITO) substrate by using a 15% by mass solution of the resin in cyclohexanone. The films were kept in a vacuum oven at 120 °C for more than a week to ensure the removal of residual solvent. A thin layer of gold was vacuum evaporated on the polyimide films to serve as the top electrode for poling. The samples were poled at 190 °C for 20 min with an applied DC electric field of 0.6 MV cm^{-1}, cooled to room temp. and the poling field subsequently removed. The E-O activity of the poled polymer film was measured at a λ of 0.83 μm with an experimental setup similar to that described by Teng and Meng.[16] For a polyimide containing 32% m/m of NLO chromophore *N,N*-diethylamino-4-tricyanovinylbenzene ($\beta\mu$ = 650 × 10^{-48} esu measured at 1.9 μm), we obtained an r_{33} value of 16 pm V^{-1}. The thermal stability of the poled side-chain polyimide was demonstrated by heating the poled sample in a oven at 90 °C for over 1000 h. The E-O activity of the sample shows negligible change during this period of time (Fig. 1).

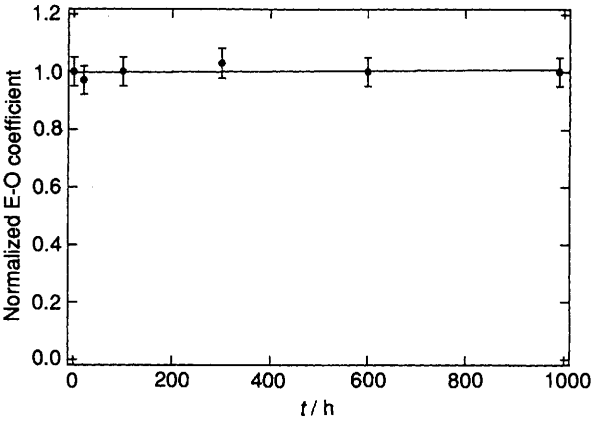


Fig. 1 Temporal stability of side-chain polyimide **3** at 90 °C in air. Normalized r_{33} as a function of baking time.

Through the covalent bonding of the NLO chromophore on the polyimide backbone, we have demonstrated the advantages of achieving a higher loading level of chromophores, larger E-O activity and better thermal stability.

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