Design and Synthesis of Thermally Stable Side-chain Polyimides for Second-order Nonlinear Optical Applications

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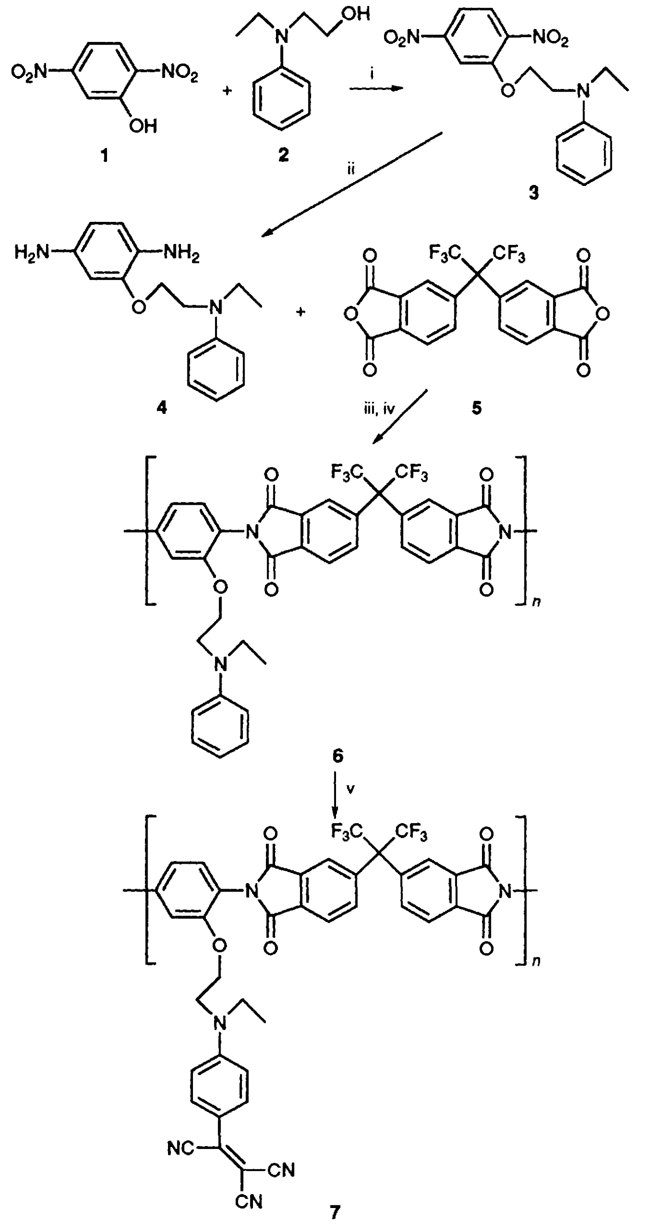
Novel Mitsunobu and tricyanovinylation reactions have been employed to incorporate efficient nonlinear optical chromophores as side-chains into aromatic polyimides resulting in high electro-optic activity and long-term alignment stability at 100 °C for more than 500 h.

Organic nonlinear optical (NLO) polymers have recently attracted considerable interest due to their potential applications in electro-optic (E-O) devices.[1,2] Among the many advantages, large E-O coefficients (*r*), ease of multilayer processing and low cost are major attractive features. However, there are major challenges in the development of efficient E-O polymers which include alignment (a condition for macroscopic non-centrosymmetry) stability of poled polymers at the processing and operating temperatures of electronic devices. In order to be useful in projected E-O devices, the poled polymers must retain a significant fraction of their initial E-O coefficient at continuous operating temperatures of approx. 80 °C and during short exposures to temperatures >250 °C. These practical considerations have led scientists to investigate new E-O polymer systems with high temperature stability.

Polyimides are commonly employed for electronic packaging uses because of their low dielectric constant, high glass transition temperature (T_g) and compatibility with semiconductor processes.[3] Recently, several classes of NLO chromophores doped or covalently attached to polyimides have been examined[4–8] to improve the long-term thermal stability of poled E-O signals. Although the results reported with the guest–host E-O polymers are quite encouraging, several deficiencies exist. For example, the low chromophore loading level and plasticization effects significantly lower the performance of the E-O polymers. In addition, a highly reactive environment during the imidization process severely limits the selection of usable chromopores. Dalton,[9] Yu[10] and our earlier paper[11] have demonstrated the superior electro-optic properties and thermal stability of covalently attached aliphatic polyimides. In the former two examples, the relatively weak nitro group was used in both disperse red 19 and *p*-*N*,*N*′-diethylaminonitrostilbene (DANS) chromophores as the electron-acceptor. In the synthesis of our early NLO polyimide, we have employed a two stage process to incorporate the *N*,*N*′-diethylamino-4-tricyanovinylbenzene chromophore into the polyimide. By functionalization of the tricyanovinyl acceptor at the last stage, the harsh environment during the imidization process of the polyamic acids is avoided. Although these aliphatic polyimides provide fairly promising results, 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. Aromatic polyimides possess much higher thermal stability (higher glass transition temperatures) and provide almost unlimited variations of monomers for fine tuning the structural and electrical properties.[12] However, so far there are no aromatic NLO polyimides reported in the literature. This is partially due to the difficulty involved in functionalizing the very reactive aromatic diamine and dianhydride monomers. In this paper, we present the facile synthesis of covalently bonding an efficient NLO chromophore, *N*,*N*-diethylamino-4-tricyanovinylbenzene on aromatic polyimides using the Mitsunobu reaction and post tricyanovinylation.

The synthetic procedures are shown in Scheme 1. Compound **3** was obtained in 92% yield by condensing 2,5-dinitrophenol **1** with 2-(*N*-ethylanilino)ethanol **2** under conditions described by Mitsunobu *et al.*[13] The dinitro compound **3** was then reduced by hydrogenation in DMF with catalytic amount of Pd/C to give diamine **4** as a viscous liquid in 80% yield.† The diamine **4** was then reacted with 2,2′-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) **5** (1 equiv.) in NMP at 0 °C (N_2). 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



Scheme 1 *Reagents and conditions*: i, PPh_3, DEAD, THF; ii, Pd/C, [H]; iii, NMP, 0–25 °C; iv, dichlorobenzene, 180 °C, 3 h; v, TCNE, DMF, 70 °C

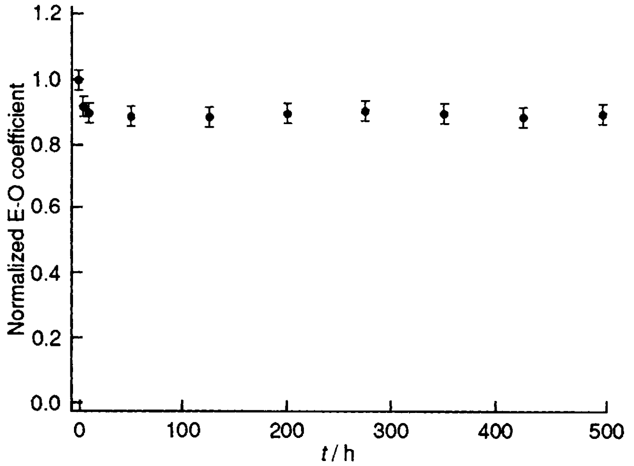


Fig. 1 Stability of the poled side-chain polyimide **7** at 100 °C in air. Normalized r_{33} as a function of baking time.

solution as a cosolvent to remove the water formed during the imidization process. The solution was heated under reflux 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 **6**. The post tricyanovinylation of polyimide **6** was carried out by dissolving **6** and tetracyanoethylene (TCNE) (1.1 equiv.) in DMF and heating at 70 °C (N_2) for 24 h. The resulting red solution was added dropwise to an agitated methanol solution to obtain the red polyimide **7** (92% yield).

The structures of **6** and **7** were confirmed by conventional spectroscopic techniques (IR, UV and ^{1}H NMR) and elemental analysis. The tricyanovinylation and imidization processes were monitored by using ^{1}H NMR and FTIR. The disappearance of the chemical shift (δ 6.41) of the proton *para* to the amino functional group on the benzene ring **6** was used to monitor the progress of the tricyanovinylation. New IR peaks at 1780, 730 and 2240 cm^{-1} are the characteristic bands of the imide group and CN on the tricyanovinyl group. The UV–VIS spectrum of a thin film of **7** exhibited a strong absorption pattern (λ_{max} = 520 nm) due to the π–π* charge transfer band of the NLO chromophore.

The polyimide **7** is very soluble in polar solvents such as cyclohexanone, dimethyl sulfoxide and dimethylacetamide. The T_g (224 °C) of this aromatic polyimide which contains 32% m/m of NLO chromophore *N,N*-diethylamino-4-tricyanovinylbenzene is 35 °C higher than the aliphatic polyimide reported earlier[11] with the same chromophore loading level. This may be attributed to the polymer chain motion being hindered by the more rigid aromatic structure of this polyimide. Thermal stability of the polyimide **7** was determined by using two heating methods. From the TGA studies, the polyimide **7** was thermally stable up to 310 °C under nitrogen atmosphere. Since the studies were based on the dynamic heating at a relatively fast rate (20 °C min^{-1}), some ambiguity may arise in determining the inherent thermal stability of the polymer. For this reason, we have heated a thin film sample of the polymer on a hot stage isothermally at 250 and 275 °C for 30 min, respectively. The π–π* charge transfer absorption band of the chromophore was used to monitor the decomposition temperature. Less than 5% change in the intensity of the absorption due to the chromophore was observed at 275 °C indicating the high thermal stability of this NLO polymer. Thin films (1–2 μm) of **7** were spin-coated onto an indium tin oxide (ITO) glass substrate by using a 17% m/m solution (filtered through 0.2 μm syringe filter) of the resin in dimethylacetamide. The films were kept in a vacuum oven at 120 °C for more than a week and briefly heated in a hot stage at 215 °C (N_2) for 15 min to ensure the removal of the 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 215 °C for 5 min with an applied DC electric field of 0.5 MV cm^{-1}, cooled to room temperature and the poling field was subsequently removed. The E-O activity of the poled polymer film was measured at a wavelength of 0.83 mm with an experimental setup similar to that described by Teng and Meng.[14] We obtained an r_{33} value of 15 pm V^{-1}. The thermal stability of the poled side-chain polyimide was demonstrated by heating the poled sample in an oven at 100 °C for over 500 h. The E-O activity of the sample shows an initial drop to 90% of its original value within 10 h then remains unchanged during this period of time (Fig. 1).

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Footnote

† The diamine was purified through a silica gel column by using ethylacetate and dichloromethane (1 : 1) as eluent. The diamine is very sensitive to light and oxygen before it reacted with dianhydride.

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