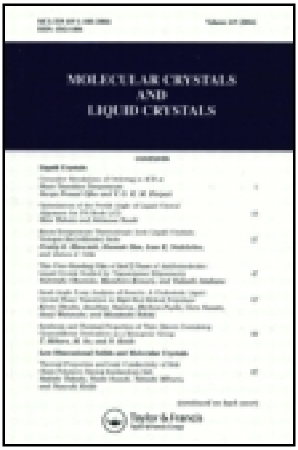

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# An Alternate Synthetic Route for the Soluble Nonlinear Optical Polyimides

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Version of record first published: 04 Oct 2006

To cite this article: Han Young Woo, Ki-Jeong Moon, Hong-Ku Shim, Kwang-Sup Lee, Mi-Yun Jeong & Tong-Kun Lim (1998): An Alternate Synthetic Route for the Soluble Nonlinear Optical Polyimides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 316:1, 39-42

To link to this article: http://dx.doi.org/10.1080/10587259808044455

*Mol. Cryst. Liq. Cryst.*, 1998, Vol. 316, pp. 39–42
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# An Alternate Synthetic Route for the Soluble Nonlinear Optical Polyimides

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Two functionalized second-order nonlinear optical polyimides were synthesized by the polycondensation reaction between chromophore-containing dianhydride and diamine monomer. The molecular weights of the final polymers were determined to be $M_n$=10000-11800. No melting was detected and they showed relatively low glass transition temperature at 160.7 °C and 180.7 °C due to ether linkage in the polymer backbone. In the case of PI2-DANS, high optical quality films were prepared by spin casting. The second harmonic generation coefficients, $d_{33}$ and $d_{31}$ of PI2-DANS were measured to be 24 and 4.8 pm/V respectively. They exhibited no decay until *ca.* 100 °C.

Keywords: nonlinear optics (NLO); polyimides; second harmonic generation

## INTRODUCTION

Recently, much attention has been focused on processible NLO thermoplastic polymers with high glass transition temperatures.[1] Among these thermostable polymers, functionalized aromatic polyimides have attracted much attention due to high temperature alignment stability, good mechanical property, low optical loss, *etc.* Several synthetic routes for NLO-functionalized polyimides have been reported.[2]-[4] A common synthetic route for NLO polyimide is the condensation polymerization of dianhydride with diamine compound containing a NLO chromophore through a poly(amic acid) prepolymer.[2] But this method includes a tedious procedure for the synthesis of the chromophore-containing diamine monomers. The fact that few chromophores can survive relatively harsh chemical conditions of the monomer synthesis limits the kind of chromophores that can incorporate in the polyimide backbone. To avoid troublesome synthesis of the chromophore-containing diamine compounds, we incorporated a NLO active chromophore into the dianhydride unit instead of the diamine unit. This method permits the versatility in selection of the chromophores which are incorporated into the polyimide backbone. Also, to improve solubility of the polyimide system, we introduced ether linkage into the polymer main chain.

## RESULTS AND DISCUSSION

The synthetic routes of the chromophore-containing dianhydride monomer and the final polyimide systems are presented in Fig. 1. We incorporated 4-bis(hydroxyethyl)amino-4'-nitrostilbene (compound **1**), which is famous for the second-order nonlinear optical material, into the polyimide backbone and it was synthesized according to the method described in the previous literature.[5] Compound **1** was mesylated and followed by successive $S_N2$ alkylation with 4-hydroxyphthalic acid dimethyl ester in N,N'-dimethylformamide solvent. Hydrolysis catalyzed by NaOH in $H_2O$/Acetone cosolvent gives tetraacid **4** which is precipitated by adding the reaction solution dropwise to the aqueous HCl solution. Dehydration of compound **4** afforded the dianhydride monomer **5** containing NLO chromophore. By this simple method, more various chromophores can be incorporated into the polyimide backbone. Two types of polyimides were condensed in N-methylpyrrolidinone solvent and followed by chemical imidization with acetic anhydride and pyridine. The polymers were purified by a Soxhlet extraction for 2 days using methanol as a solvent. The polymers are very soluble in aprotic polar solvents such as DMF, NMP, THF, *etc*. The $^1$H NMR spectra of two polymers show a signal broadening due to polymerization, but the chemical shifts are well consistent with the proposed polymer structures. The UV/vis absorption spectra of the polymers indicated the absorption maxima at around 430 nm owing to the π-π* transition of the stilbene chromophore. From TGA and DSC thermograms of the polymers, it is noticed that the initial decay of the systems starts at *ca.* 280 °C that is ascribed to the decomposition of stilbene moiety and that the breakdown of the polymer main chain happens at around 455 °C. The DSC curves show a glass transition area starting at 160.7 °C in PI1-DANS and 180.7 °C in PI2-DANS. The CF$_3$- unit in the polymer backbone increased the chain rigidity and improved solubility noticeably. These physicochemical properties are summarized in Table 1.

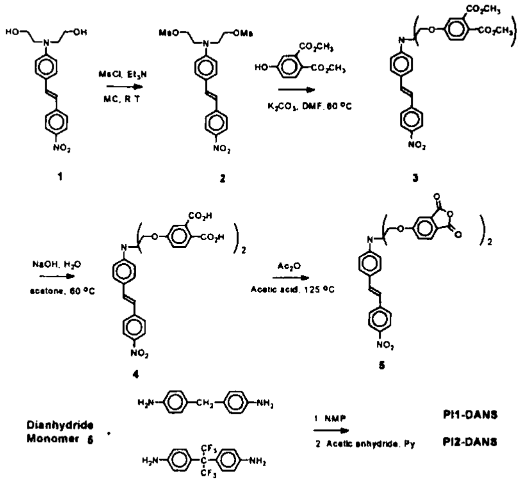

FIGURE 1 . The synthetic scheme of the monomer and polymers.

The nonlinear optical characteristics were studied by second harmonic generation (SHG) method with the PI2-DANS films. In the case of PI2-DANS rather than PI1-DANS, a higher optical quality film was prepared by spin casting from 10 wt. % cyclohexanone solution. The poling voltage dependence of the SHG signal shows that dipole aligning happens above

TABLE 1. The physicochemical properties of the resulting polyimides

| | $M_n$ (PDI) | $T_g$ (°C) | 1st $T_d$ (°C) | $\lambda_{max}$ (UV/vis) nm |
|---|---|---|---|---|
| PI1-DANS | 10,000 (1.59) | 160.7 | 272.32 | 437.6 |
| PI2-DANS | 11,800 (2.13) | 180.7 | 280.80 | 430.5 |

2.6 KV at room temperature. It is anticipated that no SHG signal is detected at room temperature due to the orientational inability of the dipoles in the hard polymer matrix. This aligning is attributed to somewhat easy rotation of the chromophores due to free volume between the polymer chains. However, the SHG signal disappeared in 10 minutes after electric field was removed. After the film was poled at around $T_g$ of 180 °C under the electric field of 3.6 KV for 2 h, relaxation of the signal was measured immediately for 1 hour in the absence of electric field, which shows a typical temporal decay of the poling induced nonlinearity and stabilization of the intensity at about 70 % of the initial maximum value. It informs that the stable conformation of the polymer chains was accomplished above the temperature of glass transition to lock the dipole alignment. The second harmonic generation coefficients, $d_{33}$ and $d_{31}$ were determined to be 24 and 4.8 pm/V at 1064 nm, respectively. In calculating of the SHG coefficients, we have made correction on the absorption of the film at 532 nm. The study of the real time NLO stability of the poled polymer films as a function of temperature indicated that the initial NLO value was maintained until *ca.* 100 °C.

## Acknowledgments

This work was financially supported by the Korea Science and Engineering Foundation (KOSEF).

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