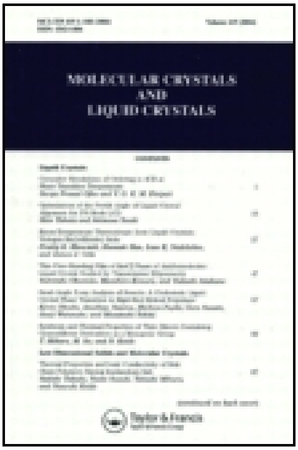

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Electro-optic Polyimide with Tricyanovinyl Group as an Electron Acceptor

K. H. Park [a] , M. G. Kwak [a] , J. T. Lim [a] , Y. S. Lee [a] , C. J. Lee [a] & N. Kim [a]

[a] Division of Polymer Research, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, 130-650, Korea

Version of record first published: 04 Oct 2006

To cite this article: K. H. Park, M. G. Kwak, J. T. Lim, Y. S. Lee, C. J. Lee & N. Kim (1998): Electro-optic Polyimide with Tricyanovinyl Group as an Electron Acceptor, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 316:1, 57-60

To link to this article: http://dx.doi.org/10.1080/10587259808044459

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 57–60
Reprints available directly from the publisher
Photocopying permitted by license only

Electro-optic Polyimide with Tricyanovinyl Group as an Electron Acceptor

K. H. PARK, M. G. KWAK, J. T. LIM, Y. S. LEE, C. J. LEE, and N. KIM
Division of Polymer Research, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

New second-order nonlinear optical polyimide was synthesized by post-tricyanovinylation of N-phenyl containing polyimide. The tricyanovinylation in *para*-position of aniline was well identified by ^{1}H-NMR spectroscopy. The polyimide had a high glass transition temperature of 218 ℃, and showed an excellent thermal stability. The electro-optic coefficient (r_{33}) and nonlinear optical coefficient (d_{33}) was 38 pm/V (at 0.63 μm) measured by simple reflection method and 84 pm/V (at 1.06 μm), respectively.

Keywords: nonlinear optical polyimide, tricyanovinylation, electro-optic coefficient

INTRODUCTION

Second-order nonlinear optical (NLO) polymers can be important substitute materials for expensive inorganic crystals like lithium niobate currently used an electro-optic modulator. One of the advantages of polymeric system for electro-optic waveguide materials is better processability; a large film could be easily prepared by spin casting, and the waveguide could be easily manufactured by a photobleaching or a lithographic method. However, the fatal problem of polymeric system is the tendency of gradual decay of NLO activity. To overcome this temporal dipolar relaxation, polyimides as a polymer backbone might be effective constituent structure due to their high glass transition temperature as well as high thermal decomposition temperature.[1-4] Among the synthesis of NLO polyimides, the simplest one would be the post-tricyanovinylation of polyimides having N-phenyl pendant.[5]

In this study, we newly synthesized a diamine with N-phenyl pendant and a polyimide therefrom, followed by tricyanovinylation. The synthesis, thermal properties, and NLO properties of these polyimides were investigated.

EXPERIMENTAL

Synthesis, Characterization and Measurement

The details of synthesis of diamine and polyimide will be reported in an other literature. Characterizations, film processing, poling, electro-optic, and SHG measurement were reported in our recent literature in detail.[6]

RESULTS AND DISCUSSION

Synthesis of polyimides

The synthetic routes of NLO polyimide were drawn in Fig. 1.

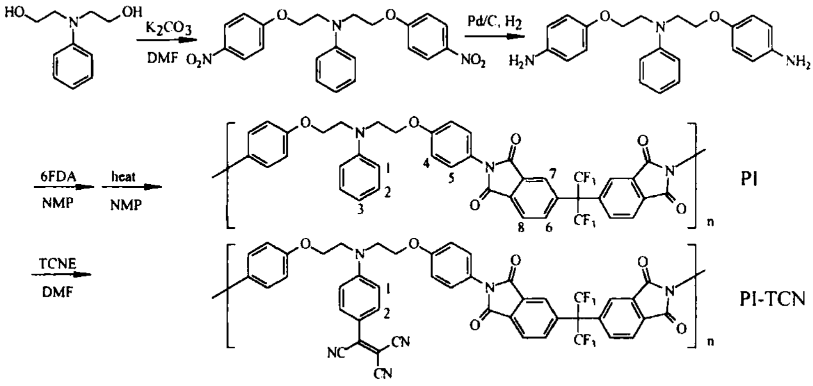

FIGURE 1. Synthesis of diamine and polyimide

Diamine 1 was easily synthesized with high yield by a condensation of N-phenyldiethanolamine with 4-nitrofluorobenzene, followed by catalytic reduction. Polyimide was synthesized by polycondensation of diamine with 6FDA, followed by chemical imidization using an acetic anhydride and a pyridine. The post tricyanovinylation of polyimide was generally carried out by reacting PI with tetracyanoethylene (1.1 equiv.) in DMF at 80 ℃ for 12 h. The degree of substitution of tricyanovinyl group in N-phenyl pendant was almost quantitative, which was determined by ^{1}H-NMR spectroscopy. After tricyanovinylation, the proton at *para*-position (6.6 ppm) in N-phenyl was completely disappeared and the peaks of aromatic protons were shifted because of strong electron-acceptors as shown in Fig. 2.

General and nonlinear optical properties of polyimides

The properties of polyimides were summarized in Table I. The precursor polyimide, PI, had a glass transition temperature (T_g) of about 170 ℃. The T_g of polyimide (PI-TCN) after tricyanovinylation was increased up to 218 ℃, showing the introduction of extended rigid tricyanovinyl unit. Moreover, the thermal stability determined by thermogravimetry (TG) was remarkably enhanced. The initial decomposition temperature of PI-TCN was about 340 ℃ as shown in Fig. 3, which indicated an excellent thermal stability.

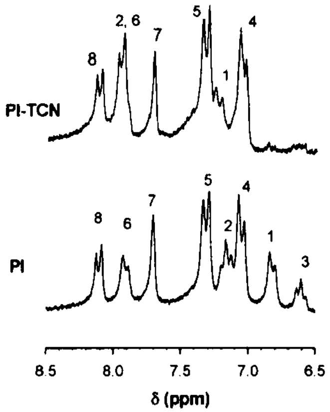

FIGURE 2. ^{1}H-NMR spectra of PI and PI-TCN.

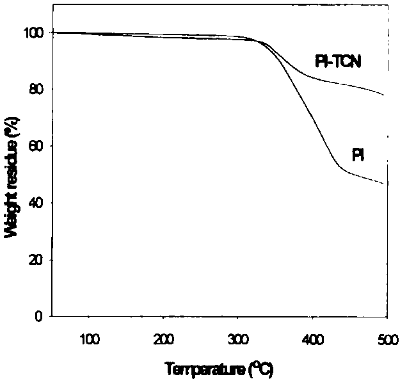

FIGURE 3. TG curves of PI and PI-TCN.

The PI-TCN was soluble in organic solvents such as cyclohexanone and 1,1,2,2-tetrachloroethane, therefore could be spin-casted onto an indium tinoxide (ITO) coated substrate to give an optically transparent polymer film.

Gold was evaporated as a top electrode on the thin film of PI-TCN casted onto the ITO substrate as a bottom electrode, and poled at 210 ℃. At a poling field of 1.5 MV/cm, the electro-optic coefficient, (r_{33}) was as high as 38 pm/V at a wavelength of 0.63 μm measured by simple reflection method. The temporal stability of r_{33} was measured at 100 ℃, which is evaluated by the curve of $r_{33}(t)/r_{33}(0)$ *vs.* time. This poled PI-TCN showed an excellent temporal stability at 100 ℃ for long term period, that was in good agreement with general NLO polyimide systems.

TABLE 1. Properties of polyimides

	η_{inh} a) (dL/g)	T_g b) (℃)	T_d c) (℃)	λ_{max} d) (nm)	r_{33} e) (pm/V)	d_{33} f)
PI	0.35	170	340	-	-	-
NPI	0.51	218	345	509	38	84

a) determined at a concentration of 0.5 g/dL at 30 ℃ in NMP.
b) measured by DSC at a heating rate of 20 ℃/min.
c) measured by TGA at a heating rate of 10 ℃/min under nitrogen.
d) maximum absorption in the film.
e) at a wavelength of 0.63 μm., f) by Maker-fringe method.

References

[1.] Z. Peng and L. Yu, *Macromolecules*, **27**, 2638 (1994).
[2.] D. Yu, A. Gharavi, and L. Yu, *Macromolecules*, **28**, 784 (1995).
[3.] T. Verbiest, D.M. Burland, M.C. Jurich, V.Y. Lee, R.D. Miller, W. Volksen, *Science*, **268**, 1604 (1995).
[4.] D. Yu, A. Gharavi, and L. Yu, *J. Am. Chem. Soc.*, **117**, 11680 (1995).
[5.] A. K.-Y. Jen, V. P. Rao, K. J. Drost, Y. Cai, R. M. Mininni, J. T. Kenny, E. S. Binkley, and L. R. Dalton, *Proc. SPIE*, **2285**, 49 (1994).
[6.] D. H. Choi, S. Song, T. S. Lee, S. Y. Park, and N. Kim, *J. Appl. Polym. Sci.*, **59**, 9 (1996).