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Electro-optic Fluorinated Polyimides with Benzoxazole-based Chromophores

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Second-order nonlinear optical polyimides were successfully synthesized by Mitsunobu reaction of polyhydroxyimides with hydroxylated benzoxazole chromophores. These resultant fluorinated polyimides were fairly soluble in pyridine, cyclohexanone, and therefore could be easily spin casted for electro-optic thin films. The polyimides had glass transition temperatures of 175~195 °C, and the electro-optic coefficients were in the range of 8.5~12.3 pm/V at 1.3 μm and showed long-term temporal stability

Keywords: nonlinear optical polyimides; Mitsunobu reaction; benzoxazole chromophores; electro-optic coefficients

INTRODUCTION

Polymeric second-order nonlinear optical (NLO) materials might be a promising candidate for low cost devices and their mass productions due to their excellent processability compared to general lithium niobate crystals for electro-optic modulators. One of the most critical problems in polymeric systems is the gradual decay of NLO activity during prolonged period. Recently, the problems could be considerably overcome by using several polyimides, which had high glass transition temperatures and decomposition temperatures.^[1-5] The reported NLO polyimides were prepared by the following representative three methods; 1) directly from diamines and

dianhydrides with NLO chromophore, 2) by post-tricyanovinylolation of polyimides having N-phenyl pendant, and 3) by Mitsunobu reaction of polyhydroxyimide with hydroxyalkyl-terminated NLO chromophores. Especially the third method was very useful because versatile NLO chromophores could be easily introduced to polyimides.

Recently, we have proposed novel benzoxazole-based NLO chromophores for the improvement of thermal stability compared to conventional stilbene-type chromophores.^[6] In this study, we synthesized soluble polyhydroxyimides with trifluoromethyl groups, and incorporated two benzoxazole chromophores into the polyhydroxyimides by Mitsunobu reaction, respectively. Their synthesis, thermal properties, and electro-optic properties were investigated.

RESULTS AND DISCUSSION

Polymer Synthesis

Polyhydroxyimide (P1) was synthesized by conventional two-step procedure starting from 6FDAP and 6FDA through ring opening polyaddition and subsequent thermal cyclohydration. The detail synthetic procedure of NLO polyimides will be reported in an other literature. The inherent viscosity of P1 was 0.24 dL/g at a concentration of 0.5 g/dL at 30 °C in NMP. The NLO active polyimides were synthesized by Mitsunobu reaction of P1 with benzoxazole chromophores (Bz and BzTh), respectively. The structures and their properties of polyimides are drawn in Fig. 1, and Table I, respectively. The Mitsunobu condensation could be monitored by ¹H-NMR spectroscopy. The ¹H-NMR spectrum of P1 shows an aromatic hydroxy peak at 10.4 ppm (Fig. 2 (a)). The hydroxy peak was almost disappeared after the post-Mitsunobu reaction between polyhydroxyimide and hydroxylated chromophore as shown in Fig. 2 (b).

Due to high content of trifluoromethyl groups, two NLO polyimides were highly soluble in tetrahydrofuran, cyclohexanone, pyridine, dimethylformamide. The optically transparent films were obtained by pyridine solution. The glass transition temperatures (*T_g*) of P2 and P3 were

195 and 175 °C, respectively. After the introduction of side-chain chromophores, the T_g 's of both polyimides decreased due to long side chains. The polyimides began to decompose above 250 °C, which is responsible for thermally weak aliphatic side-chain.

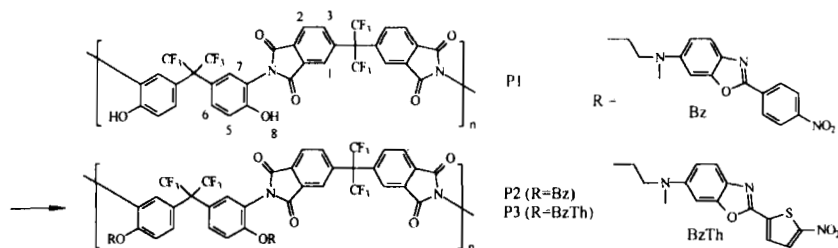


FIGURE 1. Synthesis of NLO polyimides

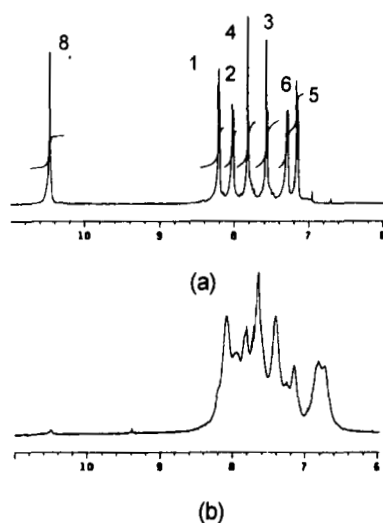


FIGURE 2. ¹H-NMR spectra of P1 (a) and P2 (b).

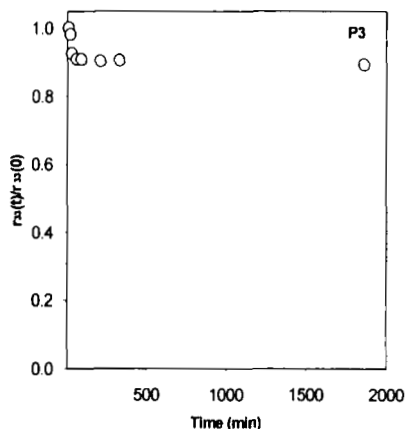


FIGURE 3. Temporal stability of r_{33} of polyimide, P3.

Polyimides were dissolved in pyridine at 10 wt % concentration, and filtered through a 0.2 μ m syringe filter. Thin films (about 1 μ m) were spin-casted onto a glass pre-coated with indium tin oxide by using above polymer

solutions. Contact electrode poling was conducted between the two electrodes at near T_g and cooled under the existence of external field (poling field: 1.5 MV/cm). The electro-optic coefficient (r_{33}) was measured by the well known simple reflection method. Polyimide, P3 exhibited a r_{33} value of 12.3 pm/V at 1.3 μm . The r_{33} value retained >90 % of original value at 100 $^{\circ}\text{C}$ for 2000 min, which indicates the excellent temporal stability of r_{33} as shown in Fig. 3.

TABLE I Physical properties of polyimides

Co	$\eta_{\text{inh}}^{\text{a)}$ (dL/g)	$T_g^{\text{b)}$ ($^{\circ}\text{C}$)	$\lambda_{\text{max}}^{\text{c)}$ (nm)	solubility ^{d)}				$r_{33}^{\text{e)}$ (pm/V)
				THF	CY	Py	DMF	
P1	0.24	280	-	++	+	++	++	-
P2	0.33	195	427	++	++	++	++	8.5
P3	0.24	175	472	++	++	++	++	12.3

a) determined at a concentration of 0.5 g/dL at 30 $^{\circ}\text{C}$ in NMP.

b) glass transition temperature measured by DSC at a heating rate of 20 $^{\circ}\text{C}/\text{min}$.

c) maximum absorption in the film.

d) ++: soluble, +: soluble on heating, -: insoluble.

e) at a wavelength of 1.3 μm .

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