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Facile Synthesis of New Polyimides Containing Hemicyanine Dye as a Nonlinear Optical Chromophore

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New polyimide derivatives containing hemicyanine dye were synthesized by mild Mitsunobu pathway. High $\chi^{(2)}$ value of 100pm/V was obtained, which was higher value than those of other NLO-functionalized polyimides.

Keywords: NLO, polyimide; nonlinear optics; electrooptic device

INTRODUCTION

Poor temporal stability of the induced polar ordering of nonlinear optical (NLO) chromophores at high temperatures is a major restraint in developing polymeric NLO devices[1]. Functionalized polymers with NLO chromophore covalently attached to the polymer backbone have been a typical approach, but other systems such as thermal or photo-crosslinkable network polymers, main chain polymers and guest-host systems with polyimides have been reported for the thermally stable NLO activity. Crosslinking the polymer matrix increases the glass transition temperature (T_g). However, some problems such as thermal degradation of the chromophore associated with extended thermal crosslinking and photostability of typical chromophores during photo-crosslinking processes occurred. So polyimide systems with high T_g were extensively

considered due to their advantages such as higher temperature stability, lower optical loss and better mechanical properties[2]. The methods that were reported for the synthesis of NLO functionalized polyimide include the polymerization of polyamic acid precursor and imidization for cyclic imide structure.[2,3] These methods include a difficult procedure for the synthesis of the chromophore-containing diamine monomers. Furthermore, the fact that few chromophores can survive under the relatively harsh chemical conditions of the monomer synthesis and the imidization of the polymer severely limits the application of the methodologies. We have devised a facile approach for the synthesis of NLO-functionalized polyimides.[4] This is the direct preparation of polyimide from diimide monomer and dihydroxy monomer through the Mistunobu condensation. By the introduction of the chromophores at the polymerization stage through the very mild Mitsunobu reaction, the harsh imidization process of the polyamic acid can be avoided and the synthesis of chromophore-containing diamine monomers is also unnecessary.

The hemicyanine dye has extraordinarily high β value compared with other NLO chromophores. We have reported several polymer systems containing this moiety[5]. However, the difficulty to synthesize the chromophore-containing diamine monomer and the instability toward high temperature have prevented the introduction of hemicyanine moiety to polyimide system. In this study, we discuss about the synthesis of two polyimides containing hemicyanine moiety and the preliminary results of second-order NLO properties of the polymeric materials.

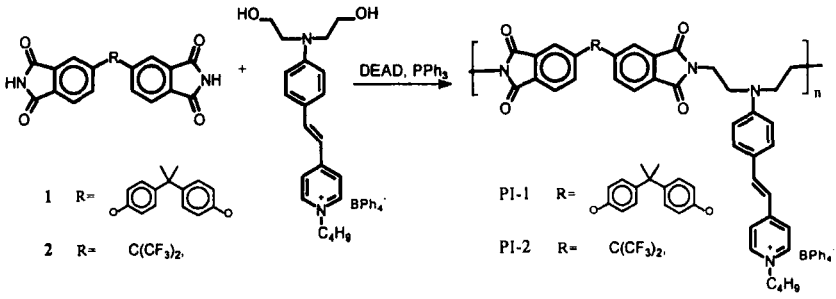

FIGURE 1 Synthetic pathway for PI-1 and PI-2.

RESULTS AND DISCUSSION

The structures of the monomers and the synthetic procedures for the polymers are shown in Fig. 1. There are two diimide compounds from two popular sources. For better solubility of the final polyimide, 2,2'-bis[4-(2,3-dicarboxyphenoxy) phenyl]propane dianhydride(BEA) which is well known as the monomer for ULTEM(General Electric) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride(HDPA) were used. The synthesis of **1** was reported in the previous paper[4] and the synthetic step of compound **2** is one-pot imidization of HDPA using urea as nitrogen source. The peak at 11.3 ppm of ^{1}H-NMR spectra of both monomers was originated from the imide protons. The dihydroxy monomer containing hemicyanine dye was synthesized according to our previous method.[5] The polymerization between the diimide monomers and dihydroxy monomers was carried out using diethyl azodicarboxylate(DEAD) and triphenylphosphine in anhydrous tetrahydrofuran(THF). The Soxhlet extraction using methanol was done for two days to purify the two polymers, PI-1 and PI-2. After the polymerization, the peak at 11.3 ppm completely disappeared in the ^{1}H-NMR spectra of final polymers. In the UV-visible spectra, both polymers exhibited similar absorption peaks around 450-600nm, which were characteristic absorption of the hemicyanine dye. It was also observed the peak at 1720cm^{-1} corresponding to stretching band of carbonyl group of imide moiety in FT-IR spectra. Other properties of the polymers are listed in Table 1.

Among the two polyimides, the PI-2 was selected for measurement of NLO property because of its higher T_g. PI-2 was dissolved in cyclohexanone and cast onto indium-tin oxide (ITO) coated glass to form thin films of 1-3μm. We performed the poling step at slightly higher temperature than T_g(175°C) holding electric field under nitrogen flow. The second-order nonlinearity of the polymer sample was measured with second harmonic generation (SHG) method at 1064nm, as fundamental wavelength. The preliminary $\chi^{(2)}$ value of this polymer (PI-2) with a quartz crystal as the reference, was found to be 100pm/V, which was stable at room temperature for several days.

TABLE 1. The Properties of PI-1 and PI-2

Polymer	M_w	PDI(M_w/M_n)	T_g(°C)
PI-1	4,409	1.48	145
PI-2	5,182	1.92	175

CONCLUSION

We have successfully prepared two polyimides which contain the hemicyanine dyes through the direct condensation of dihydroxy monomer and diimide monomer. Mild Mitsunobu reaction enabled the incorporation of hemicyanine dye in the polyimide backbone. These polymers showed high nonlinearity ($\chi^{(2)}$) of 100pm/V and good temporal stability.

Acknowledgments

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References

[1.] P. N. Prasad and D. J. Williams, *Introduction of Nonlinear Optical Effect in Molecules and Polymers* (Wiley, New York, 1991).
[2.] D. M. Burland, R. D. Miller, and C. A. Walsh, *Chem. Rev.*, **94**, 31(1994).
[3.] T. A. Chen, A. K-Y. Jen, Y. Cai, *J. Am. Chem. Soc.*, **117**, 7295 (1995).
[4.] K. S. Lee, K. J. Moon, H. Y. Woo, and H. K. Shim, *Advanced Material*, in press.
[5.] K. J. Moon, H. K. Shim, K. S. Lee, J. Zieba, and P. N. Prasad, *Macromolecules*, **29(3)**, 861 (1996).