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Synthesis and Second Harmonic Generation Studies of NLO-functionalized Polyimides

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SUMMARY: Several NLO-functionalized polyimides were synthesized through novel synthetic pathways and their NLO properties were characterized. For preventing the disadvantage in poly(amic acid) precursor route, the Mitsunobu reaction and alternative synthetic route for NLO polyimides were chosen. The second-order NLO coefficients ($\chi^{(2)}$) of the synthesized polyimides were between 48pm/V and 122pm/V. The thermal stability of nonlinearity characterized showed that all polyimide films retain their NLO activities at temperatures below 100 °C.

Introduction

Due to the mechanical and cost advantages over inorganic counterpart, organic polymers have been extensively researched as the material for electro-optic switch, frequency doubler and waveguides.1,2) However, the relaxation of NLO activity of polymeric film at high temperature was severe problem for actual application.3,4) For solving such problem, many attempts were introduced including crosslinking after alignment of dipole5,6) and/or rendering polymer backbone rigid.7-9) Among the latter, polyimide derivatives were mostly studied because of their excellent thermal stabilities and high glass transition temperatures (T_g).10,11) Traditional synthetic pathway of polyimides involved the reaction of diamine and dianhydride monomers, resulting the poly(amic acid) precursors which lead to polyimide structure by chemical or thermal treatment.12) This preparation method, however, has restriction in some monomers with NLO chromophores because it requires chemically or thermally harsh condition during imidization process10) or any diamines synthesis.

In this study, we synthesized polyimides via somewhat different pathway. First, for avoiding such harsh conditions we synthesized polyimides directly via Mitsunobu reaction.13) Since Mitsunobu reaction provides relatively mild condition, labile NLO chromophores could be introduced in polyimides more easily. Second, for preventing any hard condition to take place during the synthesis of NLO-phore-bearing diamine monomers, we introduced NLO chromophore into the dianhydride monomers, which enable much wider choice of NLO

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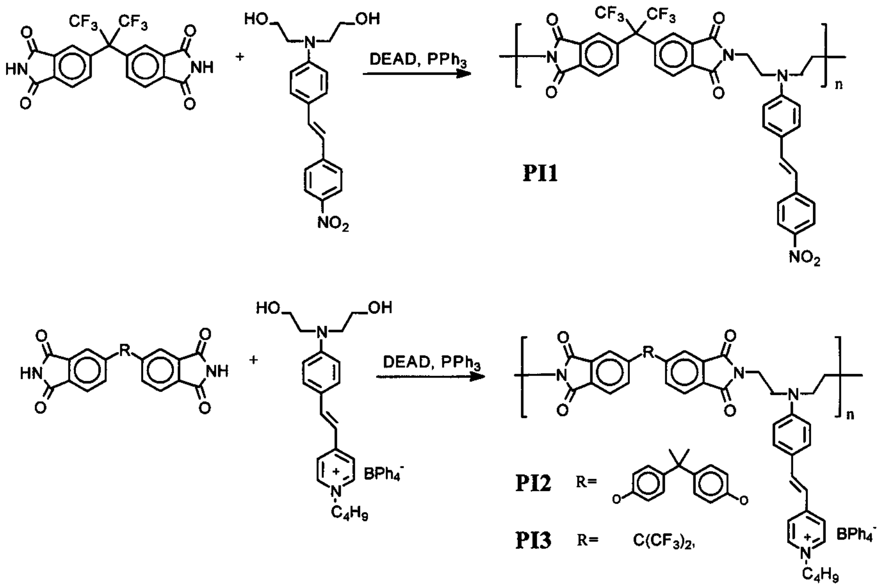
chromophores. In these regards, we report the synthesis and second-harmonic generation properties of the polyimides.

Result and discussion

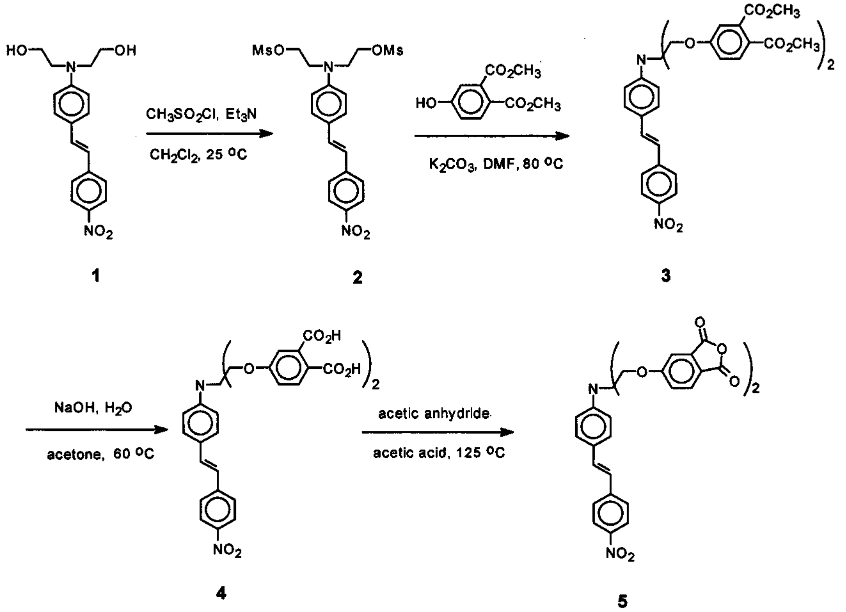
The Synthesis of Polyimide

For avoiding chemically and thermally harsh process, we introduced two synthetic methods involving the preparation of polyimides. One is the direct synthesis via Mitsunobu reaction (Scheme 1) and the other is related to the synthesis of chromophore-containing dianhydride monomers. (Scheme 2,3)

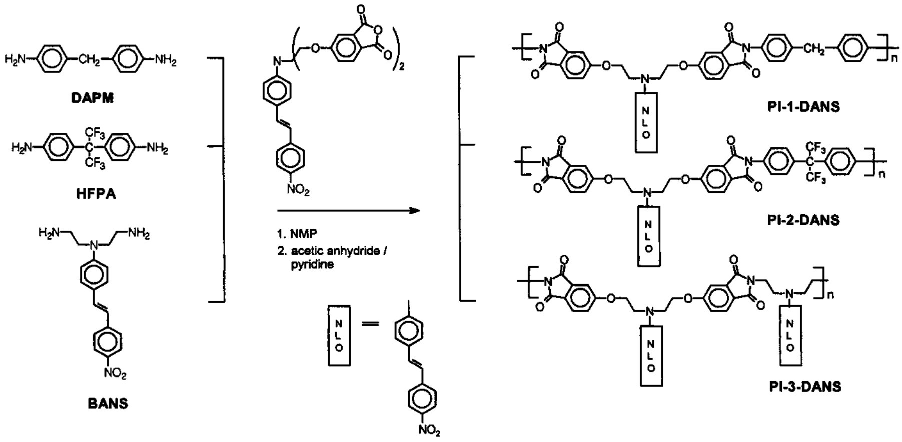


Scheme 1. Synthesis of polyimide via Mitsunobu reaction

The first synthetic procedures for polymers are shown in Scheme 1. The diimide and dihydroxy monomers were synthesized as reported earlier.[14,15] The polymerization reaction was executed by Mitsunobu reaction using diethyl azodicarboxylate (DEAD) and triphenylphosphine in anhydrous tetrahydrofuran (THF) solvent to give soluble polyimides directly. By performing direct polymerization under the mild Mitsunobu condition, the harsh imidization process of the poly(amic acid) can be avoided and the synthesis of chromophore-containing diamine monomers is also unnecessary. Therefore, the chromophore which has a large first-order hyperpolarizability could be incorporated in the polyimide backbone without decomposition of the chromophore molecules. We chose hemicyanine dye as the NLO component since it has extraordinarily high β value compared with other NLO chromophores,[16)] but is relatively labile toward chemical or thermal harshness.[17)]



Scheme 2. Synthetic route for the NLO chromophore-containing dianhydride monomer.



Scheme 3. Synthetic route for the polyimides.

The synthetic routes for the chromophore-containing dianhydride monomer and resulting polyimides are presented in Scheme 2 and 3. We incorporated 4-bis(hydroxyethyl)amino-4'-nitrostilbene (compound **1**), which is representative for second-order nonlinear optical material, into the polyimide backbone. It was synthesized according to the method described in the previous literature.$^{18)}$ This simple synthetic route may be applied to many kinds of NLO chromophores which have dihydroxy functional groups. The difficulty in the synthesis of chromophore-containing diamine compounds has limited the type of chromophores which may be incorporated into the polyimide backbone. However, thorough this simple methodology, a wider variety of chromophores can be incorporated into the polyimide backbone without the synthesis of NLO-diamine compounds. To vary the physicochemical and optical properties such as solubility, glass transition, second-order optical nonlinearity, *etc.*, three types of diamine compounds were used to synthesize final polymers. Both of PI1- and PI2-DANS are different with PI3-DANS in the chromophore contents in the polymer backbone. Until now, in most NLO polymers synthesized previously, only one monomer partner contains a NLO chromophore because of solubility, synthetic difficulty, optical quality, *etc.*, of final polymers. There have been very few reports where the functionalities are introduced into both comonomers.$^{19)}$ However, in the PI3-DANS case, both the monomer partners have NLO chromophores. This induces double chromophore density different from those of PI1-, PI2-DANS cases, from which much higher NLO activity can be anticipated. In addition, due to presence of alkyl space tether groups and ether linkages it is very flexible to give good processibility also.

The Physiochemical and Optical Properties of Synthesized Polyimides

The molecular weights of the polyimides synthesized through Mitsunobu reaction(Tab. 1), determined by gel permeation chromatography (GPC) with a polystyrene standard, ranged in 8,200 ~ 14,400 for weight averaged molecular weight (M_w). The PI2 and PI3 showed lower molecular weight than that of PI1. The bulkiness and ionic character of tetraphenylborate anion should have retarded the Mitsunobu reaction to give shorter polymer chain. The weight averaged molecular weights of three polymers synthesized from NLO-functionalized dianhydride monomer, determined by GPC with a polystyrene standard, were 15,900 (M_w/M_n=1.59) for PI1-DANS, 38,300 (M_w/M_n=2.28) for PI2-DANS, and 25,300 (M_w/M_n=2.13) for PI3-DANS, respectively.

These polymers were readily soluble in THF, cyclohexanone, *etc.* From cyclohexanone solutions of PI1, PI2 and PI3, good optical quality thin films could be prepared onto glass substrate by spin coating. The polymer structures were characterized by UV-visible absorption and FT-IR spectroscopy. The FT-IR transmittance spectra of the polymers showed structural similarity concerning with the formation of imide group in all cases. The peaks at 1772 and 1719 cm^{-1} are ascribed to the carbonyl groups in the imide linkages. These results are well consistent with the proposed structures, indicating that the NLO chromophore survived the imidization process. In the UV absorption spectra, the polyimides containing DANS as NLO chromophore (PI1, PI1-DANS, PI2-DANS, PI3-DANS) showed absorption maximum around 430 nm corresponding to that of dialkylaminonitrostilbene (DANS) moiety. The PI2 and PI3 also showed similar characteristics of hemicyanine dye that gave maximum absorption at 467 nm. No detectable change of UV absorption in PI2 and PI3 indicated that the chain polarity of polymer backbones of PI2 and PI3 was not significantly different from each other.

Tab. 1. The Properties of polyimides synthesized via Mitsunobu reaction

Polymer	M_w(PDI)	T_g(°C)	T_d(°C) [a]	α [b] (μm^{-1})	$\chi^{(2)}_{33}$ (pm/V)	λ_{max} (nm)	$\chi^{(2)}_{33}(0)$ [c] (pm/V)
PI1	14,400(1.87)	198	332	0.33	82	432	26
PI2	10,800(1.48)	135	226	0.81	-	467	-
PI3	8,200(1.89)	175	227	0.82	122	467	24

[a] temperature of 95% weight retention.
[b] absorption constant
[c] $\chi^{(2)}_{33}(0)$ is calculated with two-level model

Tab. 2. The Properties of of polyimides from NLO-functionalized dianhydride monomer

Polymer	M_w (PDI)	T_g (°C)	T_d (°C)	α (μm^{-1})	$\chi^{(2)}_{33}$ (pm/V)	λ_{max} (nm)	$\chi^{(2)}_{33}(0)$ (pm/V)
PI1-DANS	15,900 (1.59)	161	318	0.49	74	439	20
PI2-DANS	38,300 (2.28)	181	315	0.33	48	431	14
PI3-DANS	25,300 (2.13)	168	305	0.57	72	438	20

Thermal properties of the polyimides were examined by TGA and DSC measurements. In the TGA thermograms of polyimides, the thermal stabilities of those polymers were observed.

Since the polyimide chain maintained its stability over 500°C,[20)] the weight losses should solely result from the chromophore decomposition. We defined the T_d as the temperature of 95% weight retention. In Tab.1, the T_d of PI1 was 332 °C, that is similar result with NLO-functionalized polyimide prepared by other methods. The T_d's of PI2 and PI3, however, were around 226°C showing relatively unstable thermal properties. The instability of PI2 and PI3 is attributed to the hemicyanine moiety with bulky tetraphenylborate anion.[15)] In the comparison of PI1 with PI3, the PI1 showed higher T_g than PI3, which can be thought of as the effect of chromophore difference. The bulkier hemicyanine dye should lower the crystallinity to yield the glass transition at lower temperature. Especially low T_g of PI2 is thought to be due to more flexible units (bisphenol A unit). In the case of PI1-, PI2-, PI3-DANS, it is noticed that the initial decay of the system takes place in *ca.* 305-318 °C range, which is ascribable for the decomposition of the stilbene moiety in the NLO-phore, and the breakdown of the polymer main chain occurred at around 455 °C. The DSC curves showed the glass transition area starting at 161 °C for PI1-DANS, 181 °C for PI2-DANS, and 168 °C for PI3-DANS. These are relatively low temperatures compared to those of common rigid polyimdes and are attributed to a flexibility of polymer backbone containing ether linkages and alkyl tether groups. In the PI2-DANS case, the CF_3- unit in the polymer backbone increased the chain rigidity due to the polarity of trifluoromethyl group and thus resulted in high T_g.

The Sample Preparation and Measurement of Second-order NLO Properties

The second-order NLO process requires that the material must be noncentrosymmetric. For the amorphous polyimide films, the centrosymmetry can be broken by corona-discharge poling when the film is heated up to the T_g so that the molecular dipole can be oriented.[5,21)] The PI1 and PI3 were dissolved in cyclohexanone and cast onto indium-tin oxide (ITO) surfaces to form thin films of 1-3μm. As the decomposition temperatures of polyimides were higher than T_g of those polymers, we performed the poling step at slightly higher temperature than T_g of each polymer in electric field under nitrogen flow. Tungsten wire of 20μm thickness was used to generate the corona charge. The second-order nonlinearity ($\chi^{(2)}{}_{33}$)of the polymer samples (PI1, PI3) was measured with second harmonic generation (SHG) method at 1064nm, as reference wavelength. The $\chi^{(2)}{}_{33}$ values of PI1 and PI3 measured by the angular dependence method using a quartz crystal as the reference[22,23)] were found to be 82 and 122pm/V, respectively. The PI3 which contains the hemicyanine dye showed larger $\chi^{(2)}{}_{33}$ value compared with that of PI1 containing DANS moiety. However, the resonance effect on

SHG measurement should not be ignored in real device applications. We calculated nonresonant values by two-level model.[24)] The calculated $\chi^{(2)}_{33}$ (0) value of PI1 became similar to that of PI3. Although hemicyanine dye has larger β value than that of DANS to increase $\chi^{(2)}$ values, its bulkiness should have lowered chromophore density in the polymer films to lower $\chi^{(2)}_{33}(0)$ values.[4] In the case of PI1-, PI2-, PI3-DANS, the results of second harmonic generation measurements performed at a wavelength of 1064 nm, revealed large $\chi^{(2)}_{33}$ values, 74 pm/V for PI1-DANS and 72 pm/V for PI3-DANS. (Fig. 1). It was found that the disperseless $\chi^{(2)}_{33}$ value of PI1-DANS was *ca.* 20 pm/V and *ca.* 14 pm/V for PI2-DANS and *ca.* 20 pm/V for PI3-DANS respectively. The relatively low value of PI3-DANS in comparison to others, irrelevant of the double chromophore density, may result from the ineffective poling due to the matrix rigidity.

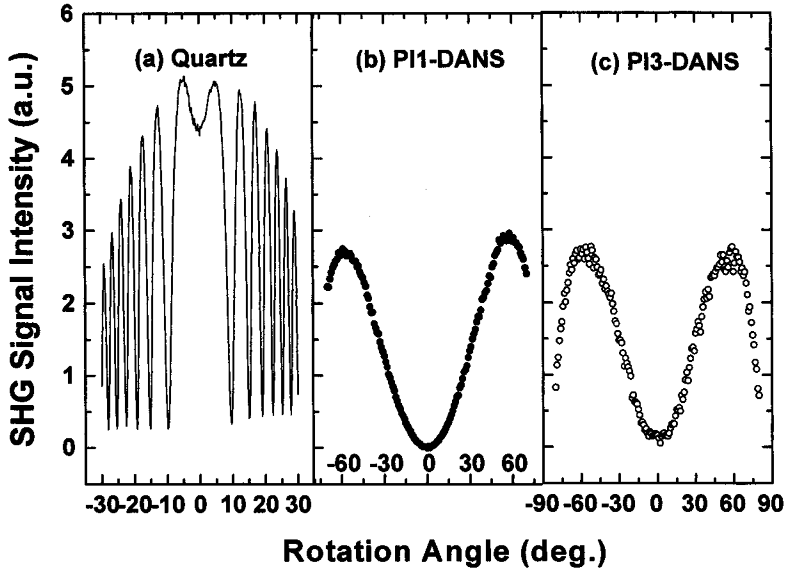


Fig.1: Maker-fringe pattern of (a) quartz crystal, (b) PI1-DANS and (c) PI3-DANS

As the thermal relaxation of dipole orientation is related to the free volume that is concerned to the glass transition temperature, the thermal stability of the NLO properties of the poled polymers can be predicted from the T_g of each polymer. At room temperature, all polyimides were significantly stable and there is no decay in the intensity of SHG signal. All polymers sustained their nonlinearity at 100°C in air for several hundred hours. Because the observation of temporal stability is a time-consuming experiment, we performed the temperature-dependent SHG measurement. Fig. 2 shows the dynamic thermal stabilities of PI1 and PI3. The PI1 and PI3 maintained 90% of original nonlinearity at temperatures below 150°C. The SHG signal of both polyimides was quite stable until the temperature reached 150°C. As the temperature reached the glass transition temperature of the polymers, fast relaxation of NLO activity was observed. The PI3 showed sudden relaxation around 170°C corresponding to the T_g of PI3. In the case of PI1, it showed similar relaxation profile with that of PI3, although it has higher T_g (198°C). We thought that the bulkiness of NLO chromophore should affect the thermal stability of NLO activity. DANS chromophore of PI1 is less bulky than the hemicyanine dye containing tetraphenylborate anion. Bulkier tetraphenylborate ion should prevent the aligned dipoles (hemicyanine chromophore) from reorienting to random direction.[14] So PI1 and PI3 showed similar thermal stability, even though PI3 has lower T_g.

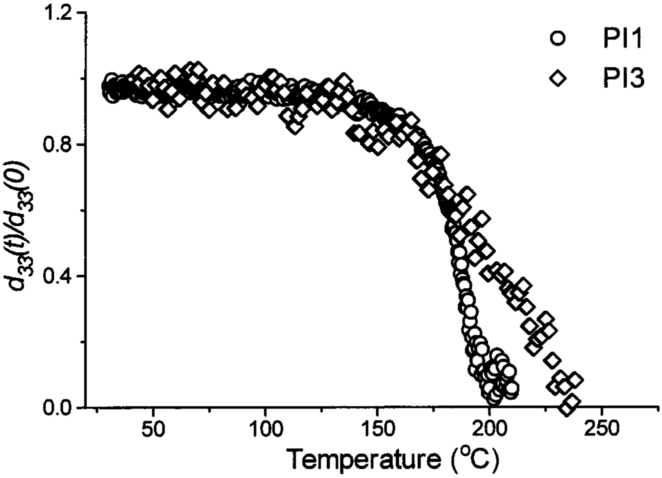


Fig. 2: Dynamic thermal stability of NLO activity of PI1 and PI3 (temperature rate: 10°C/min, in air).

Conclusion

We successfully synthesized the NLO-functionalized polyimides containing DANS and the hemicyanine dye. Mild Mitsunobu reaction condition enables the incorporation of chemically labile hemicyanine dye into polyimide backbone. These polymers showed high nonlinearity and good temporal stability. The Mitsunobu reaction is a versatile way to the synthesis of polyimide which contains the NLO chromophore of high β value. We also prepared three kind of polyimides through a new alternative synthetic route in which NLO chromophore was incorporated into the dianhydride monomer. They showed high second-order optical nonlinearity and good thermal stabilities of the aligned dipoles. The measured $\chi^{(2)}{}_{33}$ values ranged between 48 and 122 pm/V. The proposed synthetic route may be applied to various NLO chromophores and due to the versatility of the reaction scheme, many new materials can be expected.

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