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THERMALLY STABLE 2ND-ORDER NLO POLYAMIDEIMIDES BASED ON FUNCTIONALIZED STILBENE DERIVATIVES

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Abstract The polyamideimides having NLO-active chromophores were synthesized by the condensation polymerization of DANS-diamine with trimellitic acid chloride. The polymer was characterized by IR, NMR, UV, DSC, and TGA. The polymer was highly soluble in nonpolar aprotic solvents such as DMF, DMAc, NMP, etc. The polyme was easily spin-coated on a silicon wafer, indium-tinoxide (ITO) coated glass, quartz discs, and NaCl substrates, forming the good quality of thin films. The electro-optic coefficent of r_{33} at the wavelength of 1.3 μm for polymer thin films poled around the glass transition temperature of 142 °C measured by simple reflection method was 5.4 pm/V.

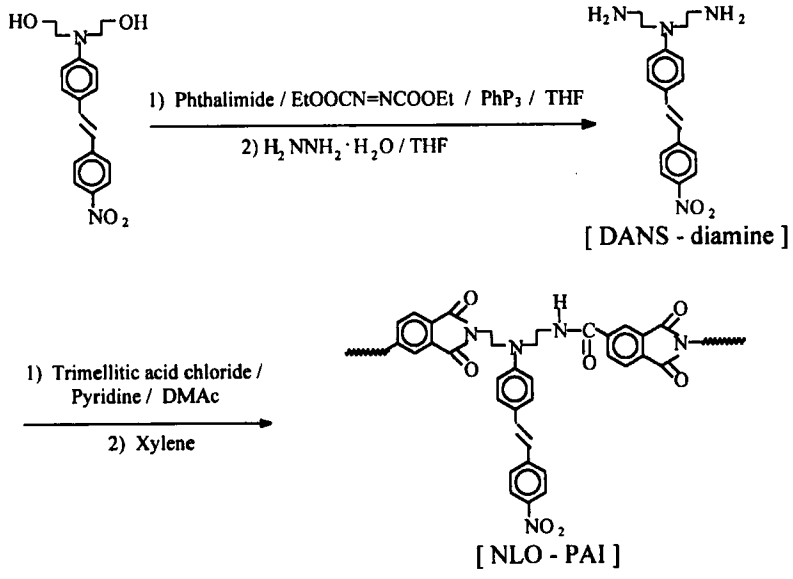
INTRODUCTION

Recently, poled NLO polymeric materials must retain thermal stability and EO thermal stability at both manufacturing and end-use environments, which require long-term stability up to 125 °C and short excursions to the temerature of 300 °C or higher for practical applications[1-4]. Our main material efforts have been focussed on improving the EO thermal stability of NLO polymers, associate with high glass transition[2]. We have synthesized polyamideimides containing NLO chromophores, since polyamideimides lead to the improvement of their processability and solubility. We should note that these NLO side chain polyimide-based materials have serveral advantages, including higher temperature alignment stability, better mechanical properties, and lower optical propagation loss over other polyimides[5].

In this paper, the polyamideimides having NLO-active chromophores were synthesized by the condensation polymerization of DANS-diamine with trimellitic acid chloride in a condensation manner, as shown in SCHEME 1. The polymer was dissolved in nonpolar aprotic solvents such as DMF, DMAc, NMP, etc. Thin films were prepared by spin-coating a solution onto a silicon wafer, indium-tinoxide (ITO) coated glass, quartz discs, and NaCl substrates. The electro-optic coefficent of r_{33} at

the wavelength of 1.3 μm for polymer thin films poled at the function of the electric field was measured by simple reflection method[6].

SCHEME 1



EXPERIMENT

DANS-diol and DANS-diamine were prepared by the previous reports[5,7].

Polymerization

The polymerization was carried out under dry nitrogen atmosphere with a concentration of 15 % monomers by weight in DMAc. A stoichiometric amount of trimellitic acid chloride (1.53mmol) was added to a solution of DANS-diamine (1.53 mmol) and pyridine (1.5 mL) in DAMc (10mL) at 0 °C. The solution was then warmed to room temperature and magenetically stirred overnight under nitrogen atmosphere, forming a polyamic acid solution. The viscosity of the solution increased greatly during polymerization. Dry xylene (5mL) was added to the polyamic acid solution and the polyamic acid solution was heated thermally to be cyclized at 160 °C for 4 hrs with the generation of water which was removed by a Dean-Starke. The resulting solution was prepicitated into an agitated solution of methanol (400 mL) and 2N HCl (8 mL), yielding a dark red poly(amide-imide) bearing a DANS chromophore. The polymer was redissolved in DMAc (40mL) and further purified by reprecipitating with an agitated solution of methanol (400mL) and 2N HCl (8 mL).

RESULTS AND DISCUSSION

The polyamideimides having NLO-active chromophores were synthesized by the condensation polymerization of DANS-diamine with trimellitic acid chloride in a condensation manner. The ring-closure reaction of polyamic acid solution was achieved by heating thermally up to 160 °C for 4 hrs in the presence of xylene, generating water which was azeotropically removed by a Dean-Starke. The polymer was dissolved in nonpolar aprotic solvents such as DMF, DMAc, NMP, etc. The solutions in all cases were filtered using either 0.45 or 0.25 μm teflon membrane filter. Thin films were prepared by spin-coating the solution on a silicon wafer for refractive index measurement, quartz discs for UV/vis study, and NaCl substrates for IR study. The polymer was characterized by FT-IR, NMR, UV, DSC, and TGA. A FT-IR spectrum of the resulting polymer show the characteristic carbonyl bands of an imide group and an amide group at 1794 cm^{-1} and 1736 cm^{-1}, and 1665 cm^{-1}, respectively. The ^1H NMR spectra of the DANS-diamine and polyamideimides having NLO-active chromophores show the broad multiplet peaks of both aromatic groups and vinyl group appeared around 6.7 ~ 8.4 ppm, indicating the formation of DANS-diamine and NLO-PAI (see FIGURE 1).

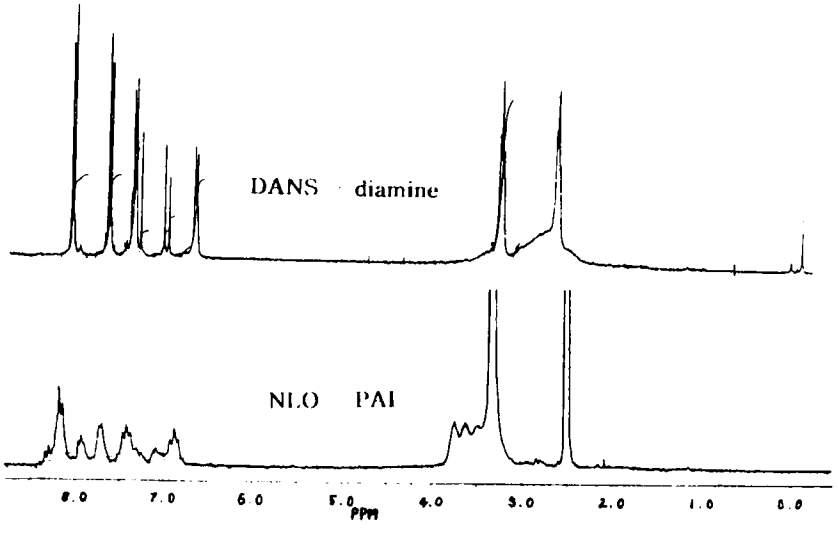


FIGURE 1. ^1H NMR spectra of the DANS-diamine and NLO-PAI.

The UV-vis spectra of thin film based on polyamideimides having NLO-active chromophores exhibited a strong absorption band with λmax of 451 nm, due to π–π* electronic transition of the DANS chromophore. The polyamideimides having NLO-

active chromophores has a Tg of 142 °C, analyzed by differential scanning calorimetry (DSC) and the polyamideimides having NLO-active chromophores was thermally stable up to 203 °C, obtained from the thermogravimetrical analysis.

TABLE 1. Polymerization results, physical and optical property of NLO-PAI.

Sanple	Yield (%)	η_{inh}[a] (dL/g)	T_g[b] (℃)	T_{ID}[c] (℃)	n[d] (1.3 μm)	λ_{max}	V_P[e] (1.3 μm)	r_{33}, pm/V[f] (1.3 μm)	Optical Property
NLO-PAI	72	0.14	142	203	1.660	451	123	5.4	Good

[a] Inherent viscosity ; [b] Glass transition temperature ; [c] Initial decomposition temperature ; [d] Index of refraction determined from the prism coupling experiment ; [e] Electric field during poling ; [f] Electro-optic coefficient

The electro-optic coefficent of r_{33} at the wavelength of 1.3 μm for polymer thin films poled at the function of the electric field was measured by simple reflection method[6]. The polymer was dissolved in DMAc. This solution was filtered using either 0.45 or 0.25 μm teflon membrane filter and thin films with 1 ~ 2 μm thickness were prepared by spin-coating the solution on indiumtinoxide (ITO) coated glass. Table 1 summarizes the optical property of NLO-PAI film measured at 1.3 μm wavelength. In the present study, the poled films poled by the electrode contact poling method have the maximum r_{33} value of 5.4 pm/V for the DANS--containing PAI. All of the r_{33} values remained unchanged at room temperature within 20 days and the 80 % of the initial r_{33} value was remained after heating at 80 °C for 20 hrs.

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