

Synthesis and Properties of a Second-Order, Nonlinear-Optical, Addition-Type Polyimide with High Thermal and Temporal Stability

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ABSTRACT: A highly thermally and temporally stable, second-order, nonlinear-optical polyimide with an X-type chromophore (2-[4-[4,5-di(4-nitrophenyl)imidazolyl]phenyl]-4,5-di(4-aminophenyl)imidazole) was synthesized by the Michael addition reaction. The structure of the prepolymer was characterized with Fourier transform infrared (FTIR). Its thermal stability and curing behavior were studied with differential scanning calorimetry, thermogravimetric analysis, and FTIR. After the curing, the glass-transition temperature of the polyimide greatly increased. The FTIR results suggested that addition and/or crosslinking reactions were carried out during the thermal curing of the prepolymer. A

poling polyimide film was achieved, and the thermal and temporal stability of the poling-induced orientation were evaluated with a multistep corona-poling technique at an elevated temperature and with *in situ* second harmonic generation (SHG) measurements. The temporal orientation of the poled polyimide film was over 1000 h at 150°C; it retained 85% of the initial second-order, nonlinear-optical coefficient. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3758–3762, 2008

Key words: NLO; polyimides; thermal properties

INTRODUCTION

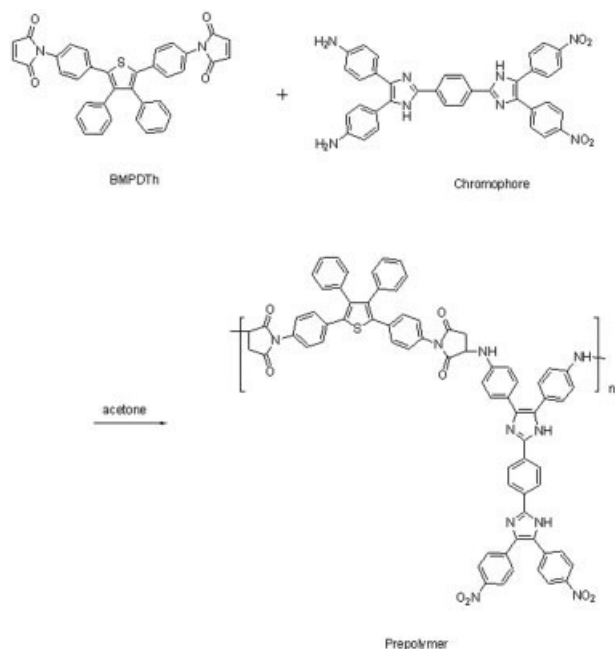
Second-order, nonlinear-optical (NLO) polymers have been an interesting topic of research in recent years because of their potential applications in photonics, especially in electrooptic modulators and frequency doublers.^{1–3} However, most polymers used as NLO materials suffer from the decay of field-induced, second-order nonlinearity arising from the relaxation of the induced noncentrosymmetric alignment of chromophore molecules to the original configuration, which greatly limits their applications in devices. To overcome this problem, significant effort has been devoted to stabilizing the poling-induced alignment, and considerable progress has been achieved with poled polymers with high glass-transition temperatures (T_g 's).^{4–7} Efficient NLO polymers have been designed and synthesized by the covalent linking of the NLO chromophore to their backbone as a side chain or structural unit of the main chain. The high performance of chromophore-functionalized polyimides is strong evidence for this strategy.^{8,9}

For materials with polyimides, the high T_g values of fully imidized polyimides are desirable for stable, poling-induced, second-order optical nonlinearity, but their unsatisfactory processibility makes it more difficult to get quality poled films. If a prepolymer with poly(amic acid) were used for film casting, then the water molecules released during subsequent imidization could increase the conductivity of the film, thereby decreasing the poling efficiency.¹⁰ Employing addition-type polyimides is a good solution for the shortcomings arising in condensation-type systems.^{5,11,12}

To date, the majority of the high- T_g polymers studied for poled polymer films have one-dimensional, dipolar chromophores. They are usually accompanied by a bathochromic shift of the maximum absorption peak as well as a decrease in the thermal stability.¹³ To improve this, two-dimensional, octupolar chromophores, defined as multidimensional chromophores, have been theoretically and experimentally investigated recently.^{14–16} Because of their off-diagonal tension component in comparison with one-dimensional chromophores, multidimensional chromophores can enhance the thermal stability.¹⁷ In this article, the synthesis of an addition-type polyimide functionalized with an X-type chromophore is presented. Its properties, such as thermal curing, poling action, and nonlinearity, are discussed too.

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Scheme 1 Preparation of the prepolymer.

EXPERIMENTAL

Materials

2,5-Bis(4-Aminophenyl)-3,4-diphenylthiophene bismaleimide (TBMI)⁵ and 2-[4-[4,5-di(4-nitrophenyl)imidazolyl]phenyl]-4,5-di(4-aminophenyl)imidazole (DNPIPDAPI)¹⁸ were synthesized by our group. *N,N*-Dimethylformamide (DMF) was purified by distillation over CaH₂ before utilization. Other reagents and solvents were purified by the standard methods before use.

Preparation of the polyimide prepolymer and its film

The Michael addition polymerization of TBMI and the X-type chromophore (DNPIPDAPI) was performed as shown in Scheme 1. DNPIPDAPI was stirred with TBMI in an equal molar ratio under N₂ with acetone as the solvent at 100°C for 8 h to prepare the low-molecular-weight prepolymer. The resulting solution was filtered through a 0.45- μm syringe polytetrafluoroethylene filter. Direct spin coating onto an indium tin oxide coated glass slide gave quality films with a thickness of 0.6–1.5 μm . The films were then dried *in vacuo* at 60°C overnight to remove the residual solvent.

Measurements

Ultraviolet–visible (UV–vis) spectra were measured with a Hitachi u3010 spectrometer, The Fourier transform infrared (FTIR) spectra were recorded with a

PerkinElmer model 7 spectrophotometer (Waltham, MA); differential scanning calorimetry (DSC) was conducted on a Mettler–Toledo DSC 822e (Columbus, OH) at a heating rate of 20°C/min, and thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA-7 thermogravimetric analyzer at a heating rate of 5°C/min.

The second-order, NLO coefficient (d_{33}) of the film was measured by *in situ* SGH measurements with an Nd:YAG laser at 1064 nm, whose laser pulse width was 10 ns with a repetition of 10 Hz.¹⁹ The multistep corona-poling technique at an elevated temperature was used to make the prepolymer film poled, and it was cured in a close temperature-controllable oven in the range of 25–250°C. The poling temperature could be controlled and recorded by the computer continuously. The corona poling was carried out with three tungsten needle electrodes under a voltage of 6–7 kV. The distance between the film surface and needles was 1 cm.

RESULTS AND DISCUSSION

Synthesis and characterization of the polyimide prepolymer

The X-type chromophore (DNPIPDAPI) and bismaleimide monomer (TBMI) in this work were synthesized by our group. The polyimide prepolymer was prepared with an equal molar ratio of TBMI to DNPIPDAPI by the Michael addition reaction in acetone, as shown in Scheme 1. According to ref. 20, the reaction of bismaleimide with a diamine chromophore in acetone proceeds so quickly that prolonging the reaction time has no influence on the molecular structure and molecular weight of the formed prepolymer; this can help the formed polymer with excellent film-forming quality and solubility. Because of the unsatisfactory solubility of DNPIPDAPI in acetone, a little DMF was added to dissolve the monomers. The formed prepolymer exhibited good film-forming quality and solubility in the solvent.

The FTIR spectra of the prepolymer and monomers are shown in Figure 1. According to the assignment of bands in ref. 21, the band at $\sim 3100\text{ cm}^{-1}$ is associated with $\nu_{\text{C-H}}$, and the band at $\sim 1150\text{ cm}^{-1}$ is associated with $\nu_{\text{C-N-C}}$ of the maleimide ring. Other identified bands of the maleimide ring at ~ 830 and 690 cm^{-1} were found, too. On the other hand, the band at 1180 cm^{-1} in the spectrum of the prepolymer should be due to the formation of the succinimide ring in the polyaddition reaction. The ratio of the band intensities at 1150 and 1180 cm^{-1} was used to monitor the polyaddition reaction process.

The UV–vis absorption spectra of the prepolymer and monomers are shown in Figure 2. The absorption of the longer wavelength was the same as that of the

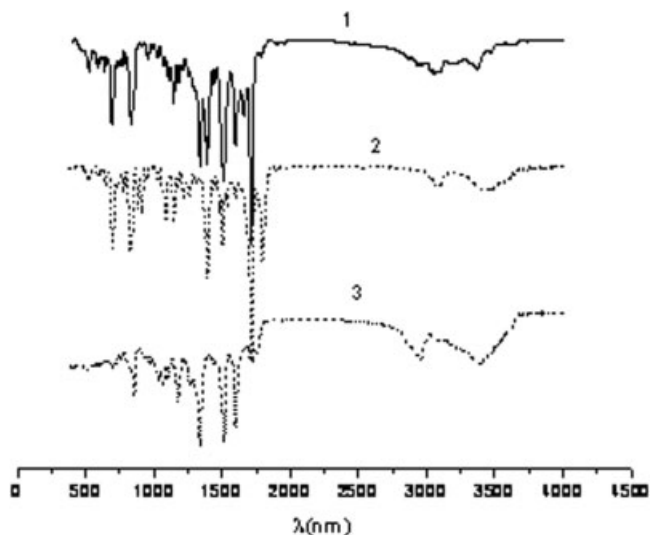


Figure 1 FTIR spectra of the prepolymer and monomers: (1) the FTIR spectra of prepolymer of TBMI with DNPIP-DAPI, (2) FTIR spectra of TBMI, and (3) FTIR spectra of DNPIP DAPI.

chromophore, so the prepolymer did not affect the chromophores much; this may be good for improving the propagation loss of the materials.

T_g was recorded by DSC, as shown in Figure 3(1). T_g of the prepolymer was very low (70°C), and in the range of the $100\text{--}180^\circ\text{C}$, there was a heat-releasing peak with partial heat of reaction developed during an isothermal DSC experiment (ΔH) = 18.7 J/g ; this showed that the reaction could be carried out further in this temperature range via heating. The thermal stability of the prepolymer was evaluated with TGA (Fig. 4). The weight losses of the prepolymer started the 380°C with the 2% weight loss. There was no small molecule released before 350°C , and this could benefit the polymer film's poling behavior.

Curing behavior

The prepolymer was cured by a treatment at 200°C for 2 h. After the curing, the peak at 1180 cm^{-1} in Figure

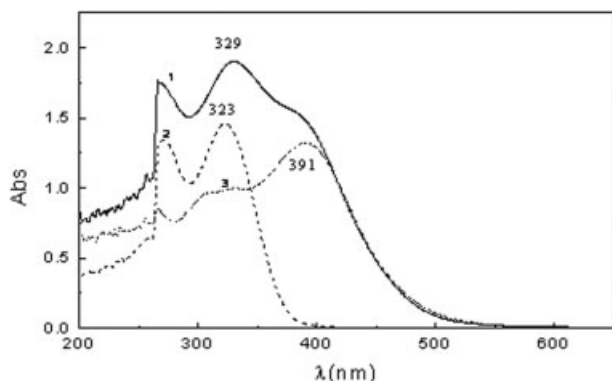


Figure 2 UV-vis spectra of the prepolymer and monomer (with DMF as the solvent): (1) the prepolymer, (2) TBMI, and (3) DNPIP DAPI.

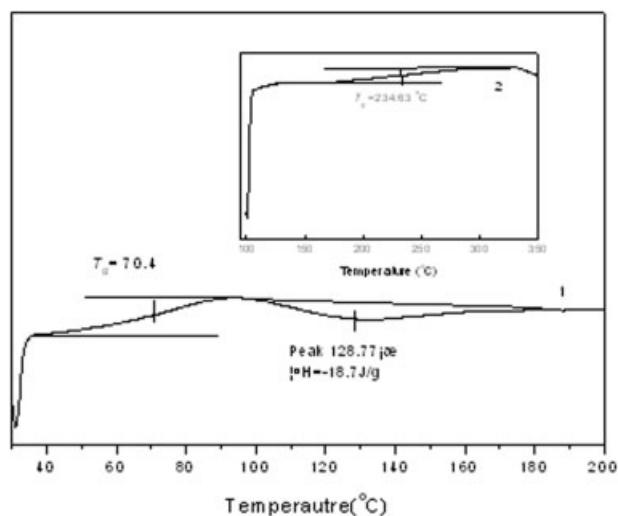


Figure 3 DSC traces of the polyimide (1) before and (2) after curing at 200°C .

5, associated with the succinimide ring, became larger, whereas the bands at 1150 cm^{-1} , associated with the maleimide rings, weakened and almost disappeared. This meant that most of the double bonds of the maleimide ring were reacted with the NH — group during the thermal curing process of the prepolymer. The band at 1640 cm^{-1} suggested that a crosslinking reaction (Scheme 2) was carried out.²²

T_g of the polymer [Fig. 3(2)] after it was cured increased to 234°C from 70°C (before the curing). This also suggests that an addition or crosslinking reaction was carried out during the thermal curing.

Poling behavior

As discussed previously, to achieve optimum poling efficiency, the NLO polyimide was synthesized in two steps: first, the synthesis of the prepolymer solution

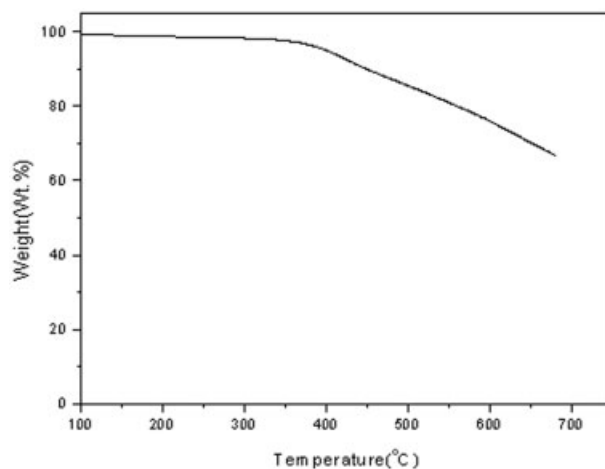


Figure 4 TGA trace of the prepolymer.

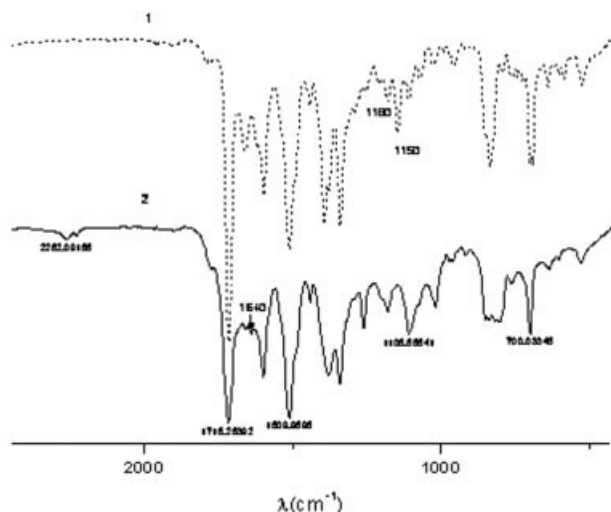


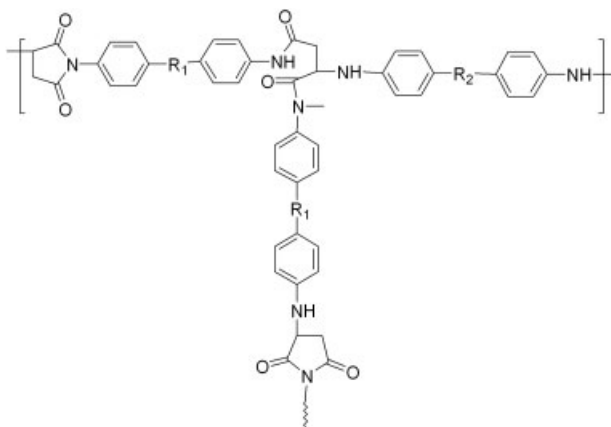
Figure 5 FTIR spectra of the polyimide (1) before and (2) after curing at 200°C.

and formation of the prepolymer films, which could help in obtaining films of good quality, and second, the making of the polymer films poled/thermally cured *in situ* to obtain crosslinked NLO polymer films with high T_g . A multistep corona-poling technique at an elevated temperature and *in situ* SHG measurements were used in this process. d_{33} for the film samples was calculated with eq. (1):²³

$$\frac{d_{33,s}}{d_{11,q}} = \frac{\chi_s^{(2)}}{\chi_q^{(2)}} = \sqrt{\frac{I_s l_{c,q}}{I_q l_s}} F \quad (1)$$

where $d_{11,q}$ is d_{11} of quartz crystal (i.e., 0.45 pm/v); I_s and I_q are the SHG intensities of the sample and quartz, respectively; $l_{c,q}$ is the coherence length of quartz; l_s is the thickness of the sample; and F is a correction factor (equal to ca. 1.2 when $l_s \ll l_{c,q}$).

From the poling dynamic behavior (Fig. 6), the SHG signal of the polymer film appeared at about 100°C, a



Scheme 2

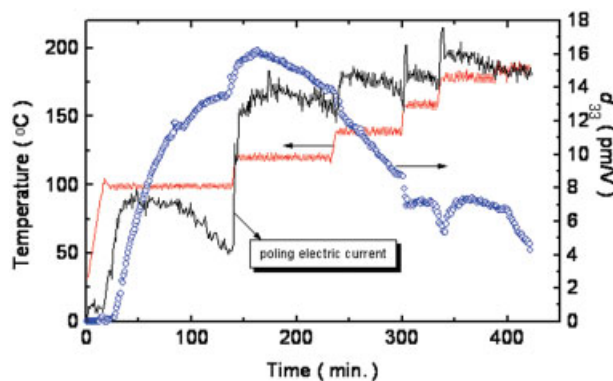


Figure 6 Poling dynamics of the polymer film (poling voltage = 6–8 kV). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

little higher than T_g of the prepolymer. With the temperature kept unchanged at 100°C over 120 min, the orientation induced by poling became near saturation. This may have been because T_g of the prepolymer increased over 100°C with the thermal curing of the prepolymer. At this moment, the poling electric current decreased, and the SHG signal did not increase obviously. With the poling temperature raised, the signal of the SHG signal increased again. At 120°C for 30 min, the SHG intensity achieved a maximum (16.4 pm/V); extending the time at this temperature or even elevating the temperature could not increase the SHG intensity further. That means that the optimal orientation was achieved. However, curing at a higher temperature (e.g., 180°C) for a longer time was useful for complete solidness, which was necessary to improve the orientation stability. Then, a highly thermally stable poled polymer was obtained, although the onset poling temperature was far lower than T_g of the final polyimides (234°C).

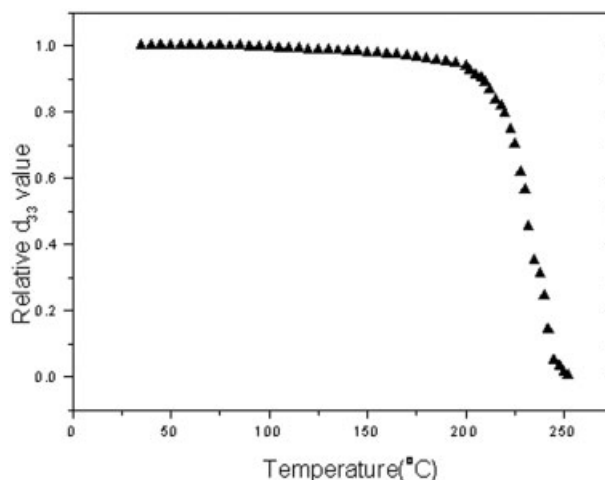


Figure 7 Dependence of the orientation stability of the polyimide materials on the temperature (heating rate = 5°C/min).

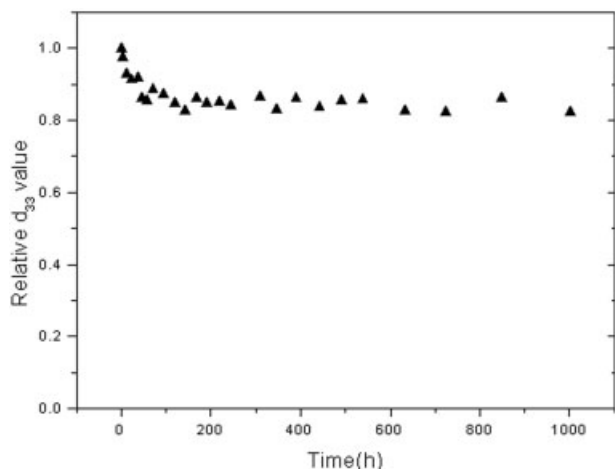


Figure 8 Dependence of the orientation stability of the polyimide material on the time at 150°C (heating rate = 5°C/min).

Dependence of the orientation stability on the temperature and time

The dependence of the poling-induced orientation stability on the temperature was measured with depoling experiments in which the decay of the SHG intensity was monitored as a function of the temperature. It provided information on the maximum device processing temperature that the films could withstand and allowed a quick evaluation of the temporal and thermal stability of the poling films. Figure 7 shows the relationship of d_{33} and the temperature for the polyimide at a heating rate of 5°C/min. The result showed that the orientation order was without any decay at temperatures below 170°C. At a higher temperature, relaxation was gradually obvious. When the temperature was higher than 213°C, the relaxation of the orientation order became more rapid. The half-decay temperature of the samples was as high as 225°C. Dalton et al.²³ pointed out that materials would have long-term stability at temperatures approximately 30°C below the temperature at which the NLO activity started to decrease. The dependence on the time, measured by the decay of the SGH intensity with the time (Fig. 8), offered strong evidence for this point, and this shows that the poled polymer film possessed good temporal stability at 150°C, retaining 85% of the initial SHG signal over 1000 h.

CONCLUSIONS

An addition-type, second-order, NLO polyimide with an X-type chromophore and bismaleimide as monomers was synthesized by the Michael addition reac-

tion. The structure of the prepolymer was characterized with FTIR. Its thermal stability and curing behavior were studied with DSC, TGA, and FTIR. The results of FTIR and DSC suggested that addition and/or crosslinking reactions were carried out during the thermal curing of the prepolymer. The poling polyimide film was achieved at a lower temperature than T_g of the final polyimide by a multistep corona-poling technique at an elevated temperature. The decay of its orientation order was over 170°C, and its half-decay temperature was as high as 225°C. The temporal orientation of the poled polyimide film with DNIPDAP was over 1000 h at 150°C; 85% of the initial d_{33} value was retained.

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