

Study on Preparation and Properties of Side-Chain Polyimide Based Second-Order Nonlinear Optical Materials

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INTRODUCTION

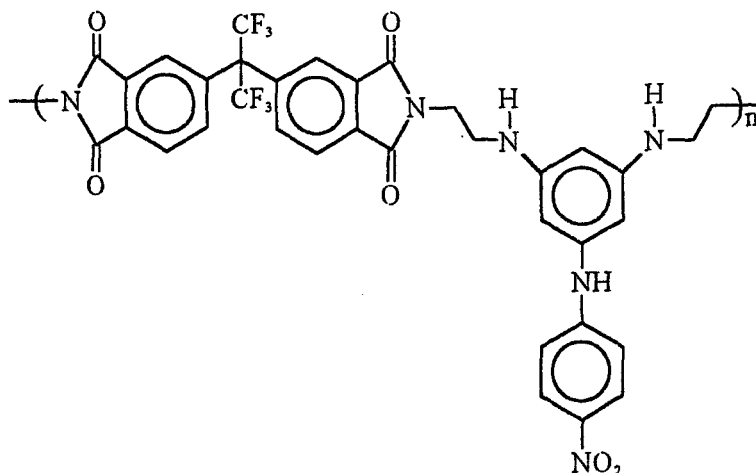
Polyimide based second-order nonlinear optical materials are the subject of intensive study due to their high glass transition temperature, low dielectric constant and compatibility with semiconductive processes¹⁻³. Guest-host NLO materials possess problems including low loading levels of chromophores, plasticization of polyimides by the chromophores and high optical loss¹⁻³ while those having NLO chromophores chemically bonded to the backbones of polyimides have been found to exhibit higher loading levels, higher temperature alignment stability and lower optical loss⁴⁻¹³. Furthermore, fluorination of polyimides has been found to be effective to reduce their optical loss at $1.3 \sim 1.5 \mu\text{m}$ ¹²⁻¹³.

In this paper, two types of side-chain polyimide based second-order nonlinear optical materials were prepared and their properties were evaluated.

EXPERIMENTAL

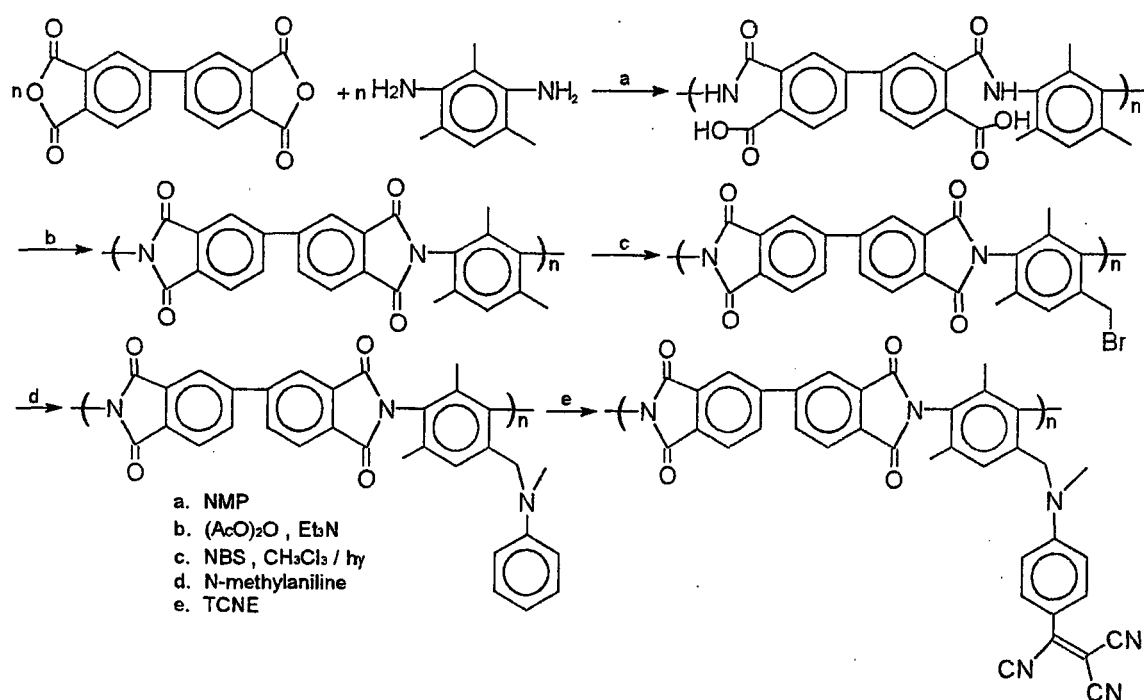
Preparation of side-chain polyimide-based second-order nonlinear optical materials

Polyimide based second order nonlinear optical material PINLO-I (Scheme I) was prepared by a solution polycondensation between hexafluoro-isopropylidene bis(3,4-phthalic anhydride) (6FDA) and diamine I in N-methyl-2-pyrrolidone (NMP) at room temperature for 4 hours followed by a chemical imidization reaction with excessive amount of acetic anhydride and triethylamine at room temperature for 16 hours. The obtained polyimide was precipitated from distilled water and dried.



Scheme I PINLO-I

The preparation of polyimide based second order nonlinear optical material (PINLO-II) was described in Scheme II. Polyimide based on biphenyl-3,3',4,4'-tetracarboxylic acid dianhydride (BPDA) and 1,3-diamino-2,4,6-trimethylbenzene was prepared by the same method described above. The brominated polyimide was prepared by a typical bromination reaction between polyimide and NBS in dichloromethane under the irradiation of UV light. The brominated polyimide was then reacted with N-methylaniline to obtain aniline modified polyimide. The highly electro-negative tricyanoethenyl group was introduced by the reaction between the aniline modified polyimide and tetracyanoethylene (1.1 equivalent) (Scheme II).



Scheme II Preparation of PINLO-II

Properties measurement

FT-IR spectra of the polyimide film samples were recorded on a Perkin Elmer Paragon 1000 Infrared Spectrophotometer. Polyimide films were cast from their chloroform solution.

UV-visible spectra of polyimide films were recorded on a Perkin Elmer Lambda 20 UV-Visible Spectrophotometer.

The glass transition temperatures of polyimides were obtained from their DSC spectra. The DSC spectra were recorded on a PE Pyris I DSC under the protection of N₂. The scan rate is 20 °C/min.

The solubility of polyimides were decided by the observation of the solubility of polyimides in various organic solvents at room temperature.

d_{33} s of the materials were measured with a light intensity measurement of the second harmonic generation using a 1.06 μ m YAG pulse laser (bandwidth is 10ns) passing through the polyimide films corona poled at 5kV for several minutes. The intensity of the output 0.53 μ m light was measured with a BOXCAR. d_{33} was calculated by the comparing this intensity to the intensity of the quartz reference.

RESULTS AND DISCUSSION

Infrared Spectra of PINLO I and PINLO-II

Fig. 1 show the IR spectra of PINLO-I and PINLO-II. Absorption bands at $\sim 1778\text{cm}^{-1}$ and $\sim 1720\text{cm}^{-1}$ are the characteristic absorption of the C=O stretching in imide groups while absorption bands at $\sim 1340\text{cm}^{-1}$ are the characteristic absorption of the C-N stretching in imide groups. The characteristic absorption band of tricyano ethenyl group is also observed at 2216.5cm^{-1} in PINLO-II.

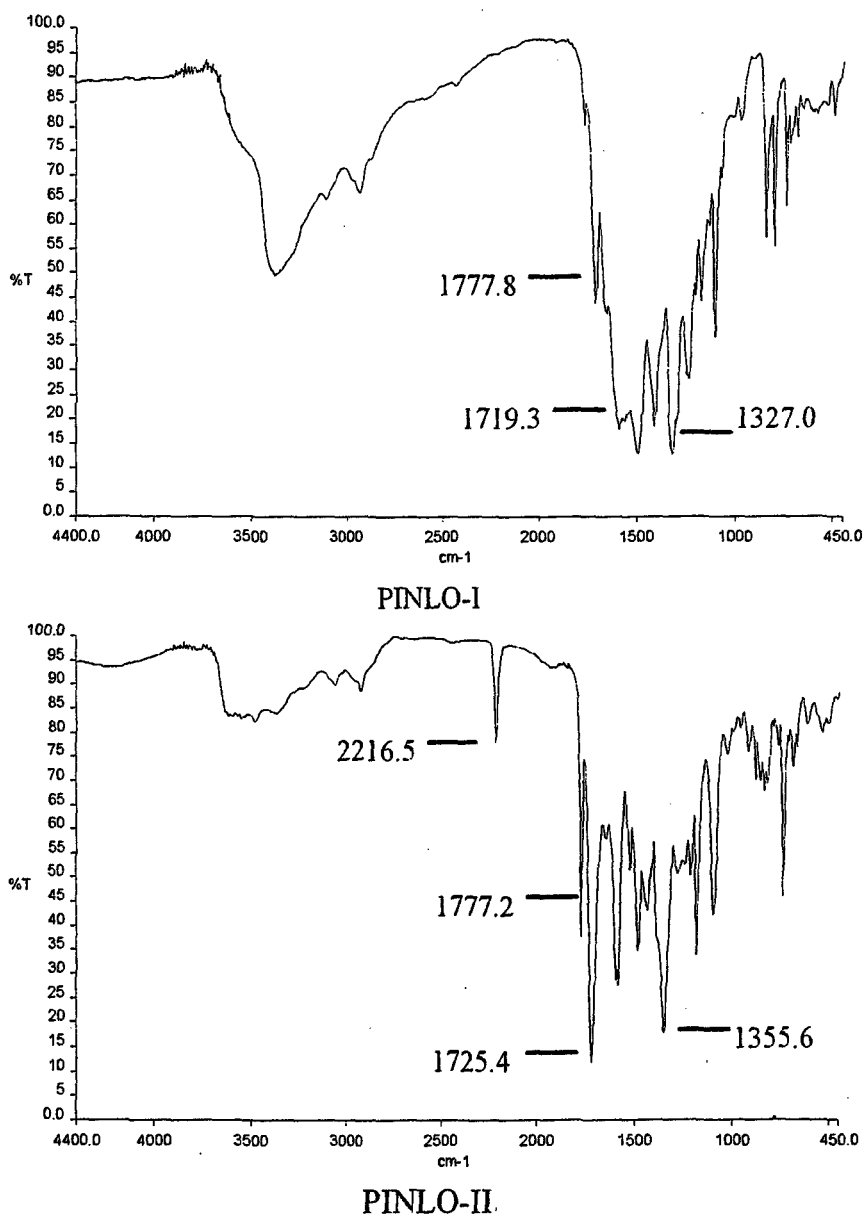


Fig.1 Infrared Spectra of PINLO-I and PINLO-II

UV-vis Spectra of PINLO-I and PINLO-II films

UV-visible spectra of PINLO-I and PINLO-II are shown in Fig. 2. PINLO-I exhibits an absorption band peaking at about 360nm. PINLO-II shows two absorption at about 400nm and 530nm, respectively. A should at about 340nm is also observed.

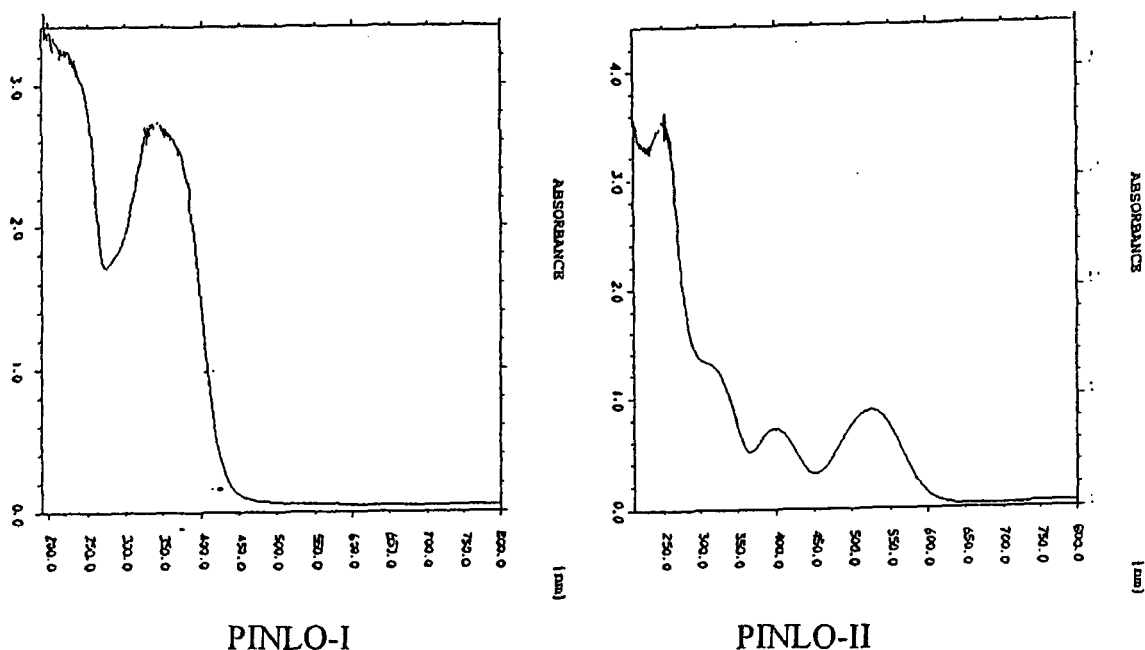


Fig. 2 UV-visible spectra of PINLO-I and PINLO-II

Solubility of PINLO-I and PINLO-II

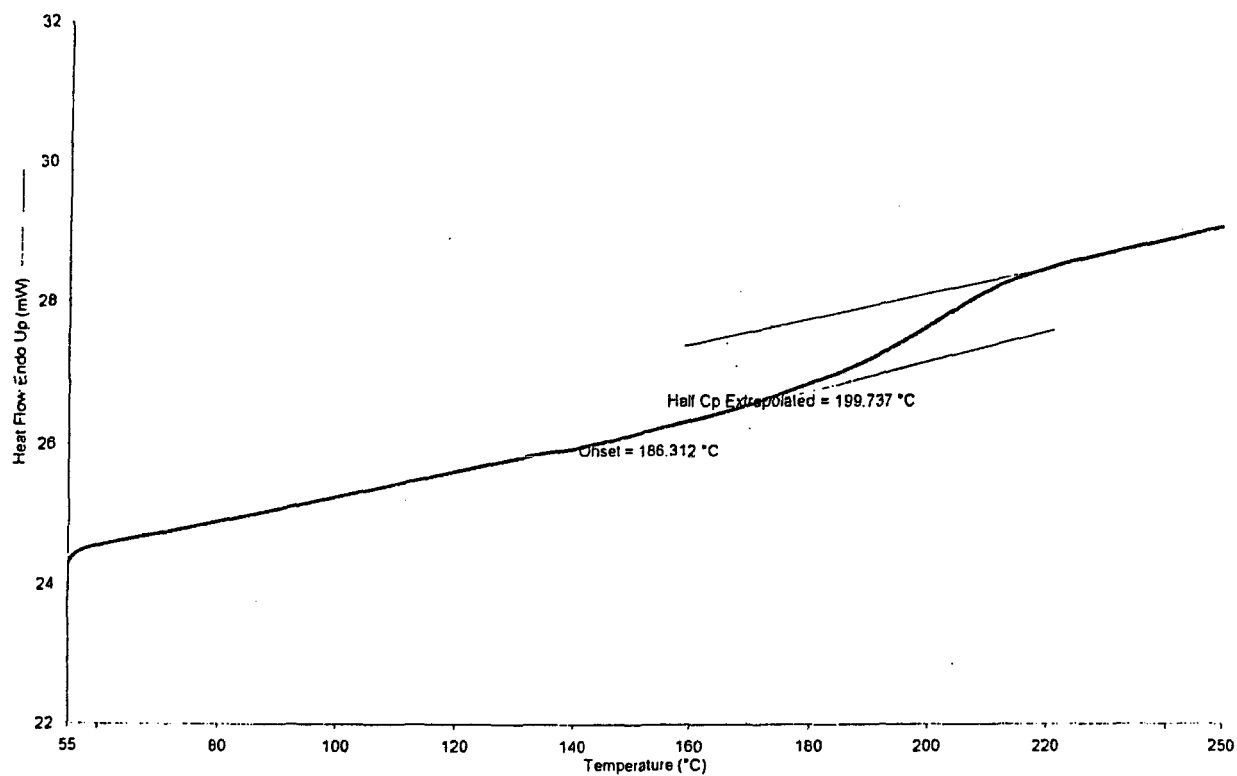
It is observed that PINLO-I is soluble not only in aprotic organic solvents such as NMP, DMAc, DMF, *m*-cresol, but also in common low boiling point solvents, THF and chloroform. The high solubility of PINLO-I is caused by existence of 6FDA moiety and the incorporation of the bulky nonlinear optical chromophores. PINLO-II, however, can only be dissolved in NMP and can not be dissolved even in DMAc and DMF. The mainchain of this polyimide is of high rigidity. The introduction of the three methyl substitutes, which reduce the intermolecular packing and the intermolecular interaction to some extent, leads to its solubility in NMP.

Glass transition temperatures of PINLO-I and PINLO-II

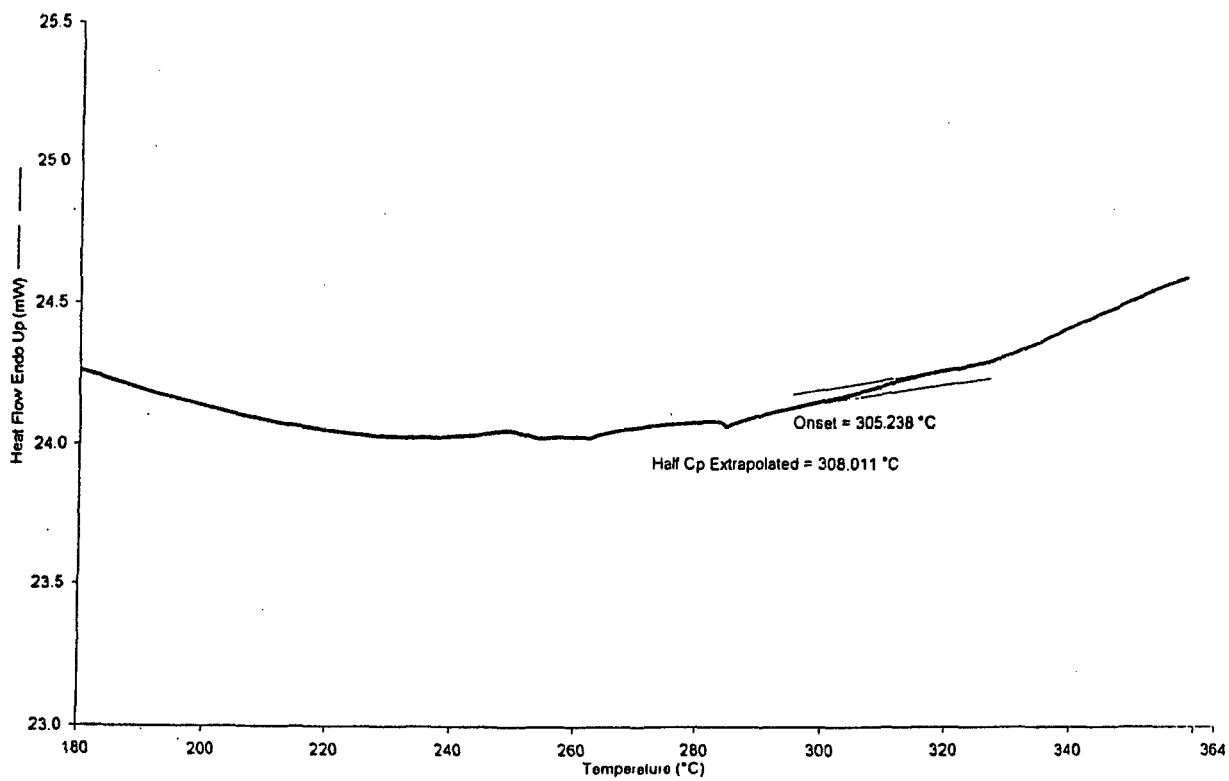
Fig. 3 are the DSC spectra of PINLO-I and PINLO-II. The T_gs of 199.7 °C and 308.0 °C, respectively, are obtained. Both materials possess quite high T_g. Because 6FDA moiety possesses lower rigidity than BPDA moiety and existence of the two flexible -CH₂-CH₂- groups in the backbone of PINLO-I, PINLO-I exhibits a lower T_g than PINLO-II.

d₃₃ results

d₃₃ of PINLO-I and PINLO-II is observed to be 69pm/V and 15pm/V.



PINLO-I



PINLO-II

Fig. 3 DSC spectra of PINLO-I and PINLO-II

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