

Synthesis and third-order nonlinear optical property of poly(urethane-imide)

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Received September 12, 2008

The poly(urethane-imide) (PUI) which uses isophorone diisocyanate, dispersed red 19 (DR-19), and pyromellitic dianhydride is synthesized. The PUI is characterized by Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The results of DSC and TGA indicate that the PUI exhibits high thermal stability up to its glass-transition temperature of 209 °C and 5% heat weight loss temperature of 296 °C. The fluorescence spectra of PUI and DR-19 are measured, showing that the fluorescence effect of PUI is very similar to that of DR-19 except for the light decrease of fluorescence intensity, which indicates that the fluorescence effect of PUI is generated by the azobenzene groups in its macromolecular chains. The maximum molar absorption coefficient, absorption wavelength, and chromophores density are measured and used to calculate the third-order nonlinear optical coefficient $\chi^{(3)}$ to be 3.96×10^{-13} esu. The nonlinear refractive index coefficient and molecular hyperpolarizability of PUI are also obtained. PUI is proved to have an excellent optical performance.

OCIS codes: 190.4400, 160.4330, 220.4840, 310.6860.

doi: 10.3788/COL20090706.0527.

In recent years, the study of nonlinear optical (NLO) polymer materials has been developed much faster because of their good processing property, diversity, and the wide future of application in the high-speed and high-frequency electro-optical devices^[1-6]. The NLO polymers based on polyurethane are all along one of the important research fields because of the excellent optical quality, dielectric property, and good heat-stability. Moreover, the activity of diisocyanate monomer could supply several approaches for the design of NLO polymers. Diazo organic compound is a kind of substance with big π electron highly conjugated structure in its molecule. Because the energy gap between its ground state and excited state is small, when connected with electron contributing or withdrawing groups, its electron is easy to shift, which is helpful to endow it an outstanding NLO property.

The isocyanate groups ($-NCO$) terminated polyurethane containing an azo NLO chromophore in the side-chain was synthesized based on isophorone diisocyanate (IPDI) with two active isocyanate groups and dispersed red 19 (DR-19) with two isolated hydroxyl groups, and then the polyurethane terminated with $-NCO$ groups was used to synthesize the poly(urethane-imide) (PUI) with pyromellitic dianhydride (PMDA). The synthetic route for PUI is shown in Fig. 1.

The Fourier transform infrared (FT-IR) spectrum of the prepared PUI thin film was obtained on a KBr pellet using Nicolet AVATAR 360 spectrometer, as shown in Fig. 2. The characteristic absorption bands of the urethane group are observed at ~ 3410 cm^{-1} ($N-H$), 1730 cm^{-1} ($C=O$), and 1780 , 1718 , 1501 cm^{-1} of the symmetry coupling vibration of the carbonyl, anti-symmetric coupling vibration of the carbonyl in imide ring, and anti-symmetric stretch vibration of $-N=N-$ bond, respectively. And the absorption bands at 1512 and 1340 cm^{-1} are assigned to the symmetric and anti-symmetric stretch

vibrations of nitro-group in the side-chain of NLO chromophore. The 1245-cm^{-1} band is attributed to the ether ($C-O-C$) band of DR-19. The absence of the absorption band at 2270 cm^{-1} corresponding to the characteristic absorption of isocyanate group indicates that all the monomers are consumed out.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NET-ZSCH STA449C. The programmed heating range was from room temperature to 700 °C, at a heating rate of 10 °C/min under nitrogen atmosphere. The results are shown in Fig. 3. The DSC curve shows that the glass transition temperature T_g of PUI is 209 °C, which is much higher than that of the corresponding side-chain NLO polyurethanes of about 137 °C^[7]. The TGA curve shows that the initial decomposition temperature of PUI

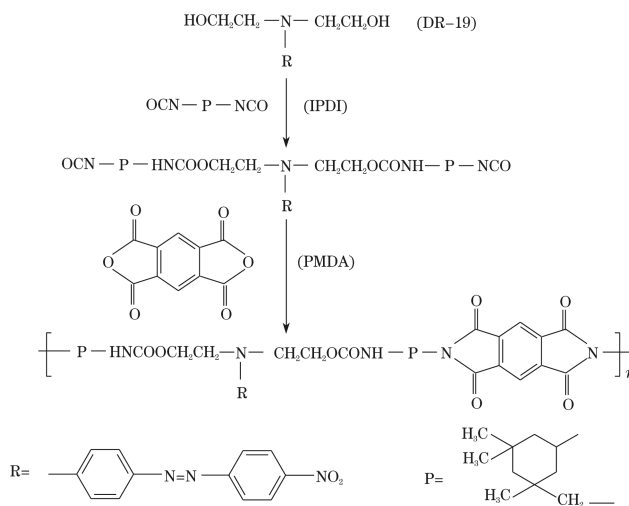


Fig. 1. Synthesis of PUI.

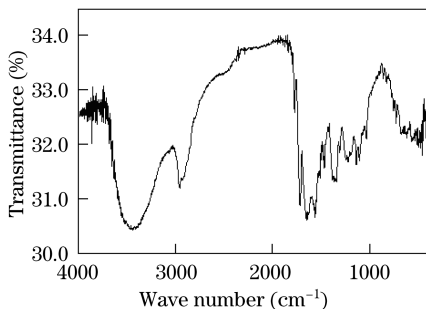


Fig. 2. FT-IR spectrum of PUI.

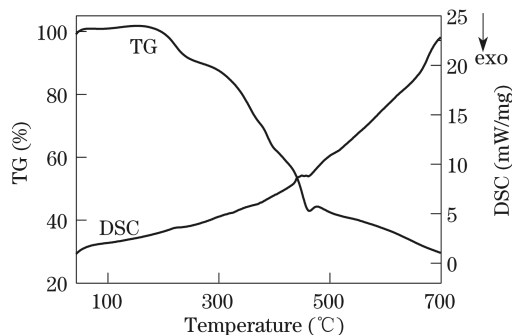


Fig. 3. TGA and DSC curves of PUI.

is at 180 °C, and the 5% heat weight loss temperature of PUI is at 296 °C. These results indicate the obtained polymer PUI possesses excellent thermal stability.

The photoluminescence measurement was performed on a VARIAN Cary Eclipse spectrofluorophotometer. The fluorescence spectra of DR-19 and PUI at the excitation wavelength of 300 nm are shown in Fig. 4. It is shown that their fluorescence peaks have similar fluorescence effects, which indicates that the fluorescence effect of PUI is generated from the azobenzene groups in its macromolecular chains. But at the same concentration, the fluorescence intensity of PUI is lower than that of DR-19. In the molecular chain of PUI, there are different lengths of un-conjugated chains (which come from the $-\text{O}(\text{CH}_2)_2\text{N}-$ in DR-19 and $-\text{NCH}_2\text{CH}_2\text{CCH}_2\text{N}-$ in IPDI) and definite lengths of conjugated chains, forming the un-luminiferous and luminiferous chains of polymer PUI. At the same time, there exist both pyromellitic dianhydride of small size and strong stiffness and carbonyl with electron donor groups and electron acceptor in PUI, which form the intramolecular or intermolecular exciplex through the transfer of the electric charges under excitation. So the fluorescence intensity of PUI decreases with the self-quenching of the macromolecules in ground state and excited state when transferring among the molecules^[8,9]. The structure of the exciplex is shown in Fig. 5.

The ultraviolet-visible (UV-vis) spectrum of the PUI solution was measured by Shimadzu UV-240 spectrophotometer. The experimental UV-vis absorption data show that the absorption peak of DR-19 in dimethylformamide (DMF) is 500 nm, while the absorption peak of PUI in DMF is 454 nm. So the absorption peak has a blue shift after polymerization. The two hydroxyl groups in DR-19 form ester bond after poly-condensation. The

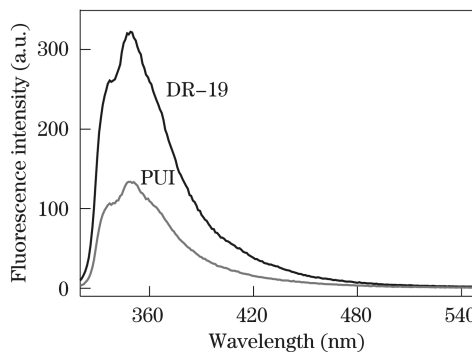


Fig. 4. Fluorescence spectra of DR-19 and PUI.

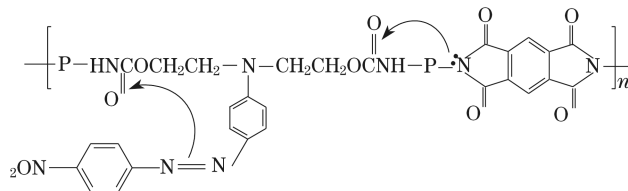


Fig. 5. Structure of the exciplex.

electron cloud in azobenzene groups of DR-19 shift to the ester bond because of the electron acceptance of $\text{C}=\text{O}$, which decreases the electron cloud density in azobenzene groups, so the absorption band of azobenzene groups would shift to the short wavelength region with the high energy demand of the electron transfer. Because the absorption of PUI is from the azobenzene groups in its side-chain, the UV-vis data verify the graft reaction of azobenzene monomer with polymer.

The NLO theory has pointed out that the materials with the central non-symmetric structures possess the second order nonlinear polarization coefficient, even if the arrangement of the molecular orientation is totally random and the molecule is isotropy, the third NLO coefficient $\chi^{(3)}$ of the material is not equal to zero. The polymer with delocalized π electron has high third-order NLO coefficient and fast response speed, so it is possible to be used in the integrated optics, logic optical path, and optical computing. It has been indicated that there is direct relationship among the NLO coefficient $\chi^{(3)}(-3\omega, \omega, -\omega, \omega)$, maximum absorption wavelength (λ_{max}), and maximum mole absorbance coefficient (ε_{max}) of the conjugated polymer^[10]. The third-order NLO coefficient is defined by

$$\chi^{(3)} = \frac{\varepsilon_{\text{max}}}{\lambda_{\text{max}}^6}. \quad (1)$$

According to UV-vis spectrum, λ_{max} is 484 nm. Different contents of PUI in DMF were prepared and the absorbance was determined at 454 nm, respectively. The working curve was obtained and ε_{max} was 5100 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. $\chi^{(3)}$ of PUI was 3.96×10^{-13} esu. From the result, we can find that PUI has a high third-order NLO coefficient. Because the azo bonds connecting with phenyl possess large π electron conjugated structure, it would increase the conjugated degree of the PUI backbone chain and enhance its third-order NLO coefficient

when introduced to the backbone of the polymer as side-chain. In addition, the push-pull structure of the exciplex shown in Fig. 5 increases the conjugated length of the diazo bonds in side-chain, and thus increases the electron shift of the whole conjugated system and the third-order NLO coefficient of PUI polymer. Compared with the theoretical calculation value of 4.20×10^{16} molecule/cm³, the chromophore density of PUI measured by the method of working curves is 3.31×10^{16} molecule/cm³. This indicates that the polymerization is according with the stoichiometric ratio.

The nonlinear refractive index coefficient can be obtained from the third-order NLO coefficient by^[11]

$$n_1 = \frac{12\pi\chi^{(3)}}{n_{\text{sample}}}, \quad (2)$$

where n_{sample} is the refractive index of PUI (1.426). According to Eq. (2), the nonlinear refractive index coefficient of PUI is 7.34×10^{-12} esu.

The molecular hyperpolarizability of sample γ can be calculated from

$$\gamma = \frac{\chi^{(3)}}{T^4 N_0}, \quad (3)$$

where N_0 is the number of molecules per milliliter (3.31×10^{16} molecule/mL), T is the local field revision factor and can be expressed by

$$T = \frac{n_{\text{sample}}^2 + 2}{3}. \quad (4)$$

According to Eqs. (3) and (4), T and γ are 1.344492 and 3.67×10^{-30} esu, respectively. The results indicate that PUI has a high third-order nonlinear polarizability.

In conclusion, we synthesized a novel PUI containing azo NLO chromophore in the side-chain. The glass-transition temperature (T_g) and 5% heat weight loss temperature indicated that the material possessed excellent thermal stability. Measurement result of the chromophore density of PUI showed that the polymerization

was according with the stoichiometric ratio. The PUI has high third-order nonlinear coefficient and polarizability. These results show that PUI polymer is a promising material for NLO applications.

This work was supported by the Natural Science Foundation of Jiangsu Province (No. BK2008247), the China Postdoctoral Science Foundation (No. 20070420973), the Jiangsu Planned Projects for Postdoctoral Research Funds (NO. 0602037B), the Jiangsu Provincial Key Laboratory for Science and Technology of Photon Manufacturing, and the Natural Science Foundation of Jiangsu Educational Department (No. 08KJB150004).

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