

# High $T_g$ Second-Order Nonlinear Optical Poly(urethane-imide)s Prepared from Disperse Red 19, Pyromellitic Dianhydride, and Toluene Diisocyanate

YU SUI, JIONG-XIN LU, JIE YIN, DONG WANG, ZI-KANG ZHU, ZONG-GUANG WANG

Research Institute of Polymer Materials, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 15 March 2001; accepted 29 May 2001

**ABSTRACT:** A series of poly(urethane-imide)s with high glass transition temperatures were easily prepared from a commercial nonlinear optical (NLO) chromophore (Disperse Red 19), pyromellitic dianhydride (PMDA), and 2,4-toluene diisocyanate (TDI). The resulting polymers possessed good solubility and high glass transition temperatures (231–272°C) and thermal decomposition temperatures. They exhibited excellent film-forming properties and good-quality films were easily obtained by spin coating. These polymers also possessed a high coefficient of optical nonlinearity with good temporal stability of the dipole orientation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 944–949, 2002

**Key words:** poly(urethane-imide); high  $T_g$ ; second-order nonlinear optics; preparation; characterization

## INTRODUCTION

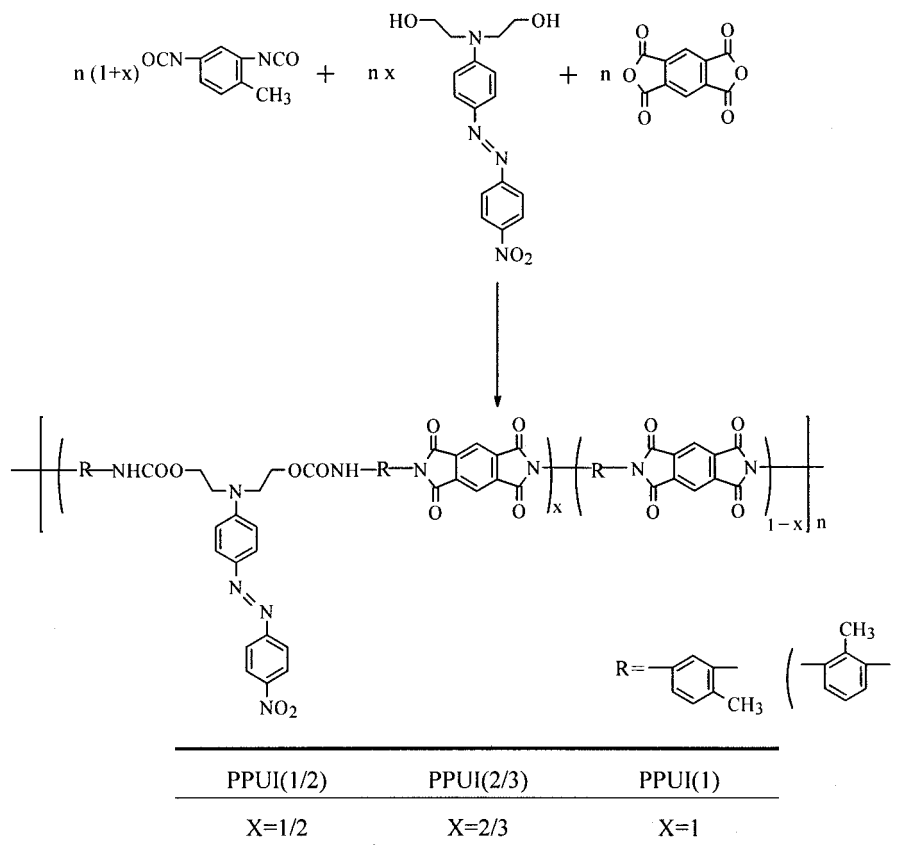
Second-order nonlinear optical (NLO) polymers offer great promise for use in electrooptic modulators, optical interconnects, and other devices due to their large linear electrooptic coefficients, low dielectric constants, flexibility in fabrication, and processing techniques that are compatible with integrated circuit technology.<sup>1–5</sup> One of the major problems limiting the practical application of these NLO polymers is their relatively low temporal stability of dipole orientation.<sup>4</sup> This is the reason why much attention has been paid to use of polyimide (PI), which has a very high glass transition temperature ( $T_g$ ), as the base material and to have NLO chromophores chemically

bonded to the backbone of PI.<sup>6–21</sup> The most common synthetic route for these NLO PIs is condensation polymerization of dianhydrides with diamines containing an NLO chromophore via a poly(amic acid) (PAA) prepolymer followed by a high-temperature imidization or a chemical imidization process.<sup>7–14</sup> This method, however, often involves a tedious synthesis and purification of the chromophore-containing diamine (or dianhydride) monomers. Sometimes, the fact that few chromophores can survive the relatively harsh chemical conditions of the monomer synthesis and the imidization of the PAAs and the difficulty in the synthesis of the NLO chromophore-containing diamine (or dianhydride) compounds greatly limit the type of chromophores that may be incorporated into the PI backbone. For this article, we prepared a series of poly(urethane-imide)s (PUIs) directly from Disperse Red 19 (DR-19), pyromellitic dianhydride (PMDA), and toluene diisocyanate (TDI) via an isocyanato (NCO)-terminated

Correspondence to: J. Yin (imsun@mail.sjtu.edu.cn).

Contract grant sponsors: Ministry of Education of China; Shanghai Science and Technology Commission.

*Journal of Applied Polymer Science*, Vol. 85, 944–949 (2002)  
© 2002 Wiley Periodicals, Inc.



**Scheme 1** Synthesis of PPUI( $x$ ).

polyurethane prepolymer. By using this method to prepare NLO PI, the troublesome synthesis of NLO diamine (or NLO dianhydride) and the harsh imidization process could be avoided. The synthesized PUIs [PPUI( $x$ ) series] exhibit high  $T_g$ 's, which are at the same level as those side-chain aromatic NLO PIs<sup>6-8,11-16</sup> and much higher than polyurethanes,<sup>22</sup> polyetherimides,<sup>18</sup> and polyesterimides<sup>9,19</sup> based on DR-19. They also possess high coefficients of optical nonlinearity, good processibility, and film-forming properties.

## EXPERIMENTAL

### Materials

DR-19 was purchased from the Aldrich Chemical Co. and purified by recrystallization in ethanol prior to the reaction. PMDA was purchased from the Shanghai Tar Chemical Co. (Shanghai, China) and dried at 160°C for 2 h before use. TDI was purchased from the Shanghai Reagent Co. (Shanghai, China) and purified by distillation be-

fore use. *N,N*-Dimethylacetamide (DMAc) was purchased from the Shanghai No. 1 Reagent Co. (Shanghai, China) and purified by distillation over CaH prior to the reaction. Common solvents for solubility measurement such as acetone, chloroform, tetrahydrofuran (THF), *N,N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 1,4-butyrolactone were used without purification.

### Preparation of PPUI( $x$ )

The polymerization procedure exemplifies the synthesis of PPUI( $x$ ) (see Scheme 1): TDI, 0.976 g (5.604 mmol), was dissolved in 12 mL anhydrous DMAc. To this solution was added slowly 0.907 g (2.747 mmol) of DR-19, and the resulting reaction mixture was stirred at 40 and 75°C, each for 1 h and at 90°C for 4 h. After cooling in an ice bath, 0.599 g (2.747 mmol) PMDA was added to the mixture. After further reaction at 40 and 90°C, each for 2 h, the mixture was refluxed overnight. The resultant product PPUI(1) was precipitated into the mixture of methanol and water (100/100

mL) and further purified by repeated dissolution in DMAc and precipitation into the mixture of methanol and water.

### Characterization

The FTIR spectra of PPUI(*x*) were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer. A Perkin–Elmer Lambda 20 UV-vis spectrophotometer was used to record the UV-vis spectra of PPUI(*x*) films (cast from their 5 wt % DMAc solutions on quartz substrates). The inherent viscosity of PPUI(*x*) was measured with an Ubbelohde viscometer using NMP as the solvent at a concentration of 0.5 g/dL at 30°C. The solubility of PPUI(*x*) was determined by observing the solubility of the solid polymers in various solvents at room temperature. The  $T_g$ 's of the PPUI(*x*) were determined by differential scanning calorimetry (DSC). The DSC curves were recorded on a Perkin–Elmer Pyris I DSC under N<sub>2</sub> with a scan rate of 20°C/min. The thermal stability of PPUI(*x*) was characterized by thermogravimetric analysis (TGA). The TGA curves were recorded on a Perkin–Elmer TGA7 under N<sub>2</sub>, with a scan rate of 20°C/min.

Thin films with a thickness of about 1 μm were obtained by spin-coating 0.5-μ microfiltered PPUI(*x*) solutions in DMAc onto cleaned glass substrates. The spin-coated films were dried under a vacuum at about 120°C for 2 days before corona poling at a temperature approximately 10°C above the  $T_g$ . The samples were poled for 30 min, which gave the best results in terms of second-harmonic efficiency. The second-harmonic coefficient  $d_{33}$  was measured using the Maker-fringe method. The light source was a Q-switched Nd<sup>3+</sup>:YAG laser delivering 7-ns pulses at 1064 nm with a 5–10-Hz repetition rate. A quartz crystal was used as a reference ( $d_{11} = 0.46$  pm/V).<sup>23</sup>

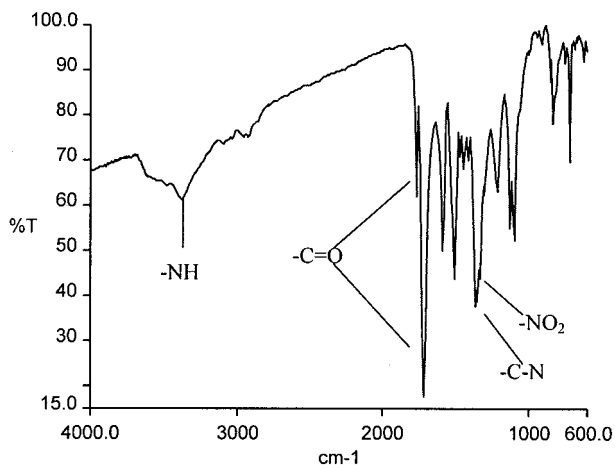
**Table I** Physical Properties of PPUI(*x*)

Polymer	PPUI(1/2)	PPUI(2/3)	PPUI(1)
$\eta_{inh}$ (dL/g) <sup>a</sup>	—	0.26	0.25
$T_g$ (°C) <sup>b</sup>	272	242	231
$T_{d1}$ (°C) <sup>c</sup>	308	328	299
$T_{d2}$ (°C) <sup>c</sup>	470	561	520

<sup>a</sup> Measured at 30°C using NMP as the solvent at a concentration of 0.5 g/dL.

<sup>b</sup> Obtained from DSC curves; scan rate: 20°C/min, under nitrogen.

<sup>c</sup> Obtained from TGA curves; scan rate: 20°C/min, under nitrogen.



**Figure 1** FTIR spectrum of PPUI(2/3).

## RESULTS AND DISCUSSION

### Synthesis and Characterization of PPUI(*x*)

The synthetic procedure is shown in Scheme 1. The reaction was performed in a two-step process. Initially, the NCO-terminated polyurethane prepolymer was synthesized using an excess of diisocyanate (TDI) and DR-19. Then, the condensation polymerization reaction between a dianhydride (PMDA) and the NCO-terminated polyurethane prepolymer was executed in an anhydrous DMAc solvent. The inherent viscosity of PPUI(*x*) was about 0.25 dL/g (Table I). This simple synthetic route is generally applicable and it may be applied to many kinds of NLO chromophore-containing diols. Using this method to prepare NLO PI, the troublesome synthesis of NLO-diamine (or NLO-dianhydride) and the harsh imidization process could be avoided.

The chemical structure of the obtained PPUI(*x*) was characterized with FTIR and UV-vis spectroscopy. The representative FTIR spectrum of PPUI(2/3) is shown in Figure 1. The clear appearance of ~1780- and ~1725-cm<sup>-1</sup> bands, characteristic of C=O stretching in imide rings, and the ~1375-cm<sup>-1</sup> band, characteristic of C—N stretching in imide rings, indicated the existence of the imide groups. The characteristic absorption of the N—H stretching in the urethane linkage was observed at 3380 cm<sup>-1</sup>. The characteristic absorption peaks of the nitro groups at ~1515 and ~1340 cm<sup>-1</sup> also indicated the existence of the NLO chromophores. No absorption at ~2270 cm<sup>-1</sup>, characteristic of the isocyanato group, was visible. The representative UV-vis spectrum of

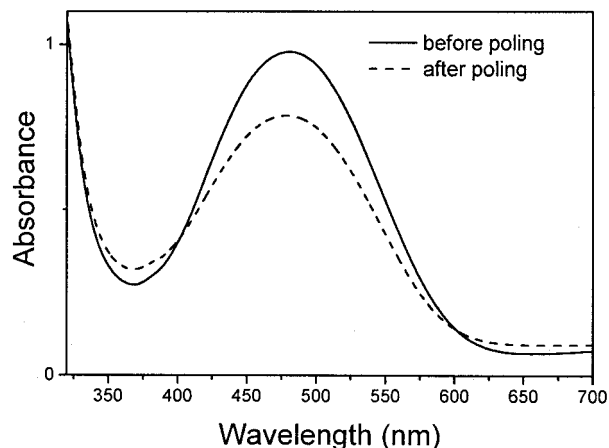


Figure 2 UV-vis spectrum of PPUI(1) film.

the PPUI(1) film is shown in Figure 2. The characteristic absorption of the NLO chromophore (DR-19) was observed in the UV-vis spectrum of the polymer film at 482 nm (Fig. 2). This result suggests that the chromophore was not affected by the polymerization process.

#### Solubility of PPUI(x)

The solubility of the obtained polymers in various solvents is listed in Table II. The PPUI(x) were soluble or partially soluble in strong polar organic solvents such as 1,4-butyrolactone, DMAc, NMP, DMF, and DMSO and some low boiling point solvents such as THF, chloroform, and acetone. As the NLO chromophore content was increased, the solubility of PPUI(x) also increased. PPUI(1) showed the best solubility and can even be completely dissolved in THF. This might result from

Table II Solubility of PPUI(x) in Various Solvents at 25°C

Solvent	PPUI(1/2)	PPUI(2/3)	PPUI(1)
NMP	+–	+	+
DMAc	+–	+	+
DMF	+–	+	+
DMSO	+–	+	+
1,4-Butyrolactone	+	+	+
THF	+–	+–	+
Acetone	+–	+–	+–
CHCl <sub>3</sub>	–	+–	+–
Toluene	–	–	–
Cyclohexane	–	–	–

+: soluble; +–: partially soluble; –: insoluble.

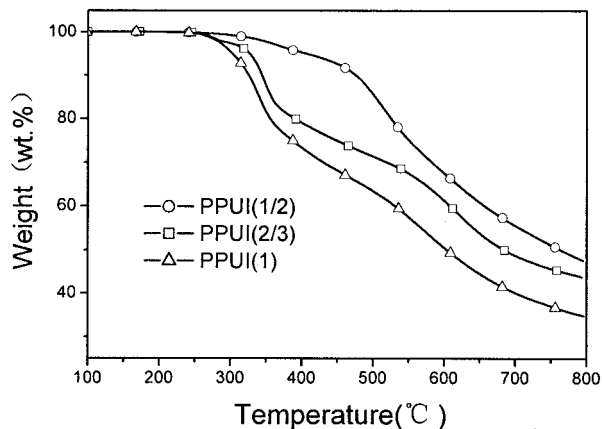


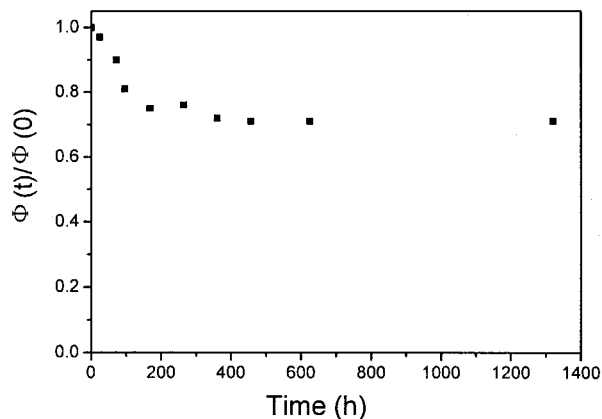
Figure 3 TGA curves of PPUI(x).

the fact that, as the NLO chromophore content was increased, the amounts of both the flexible urethane linkages and the side-chain azo chromophore in the polymer backbone increased, leading to looser chain packing and larger free volume.

#### Thermal Properties of PPUI(x)

The thermal properties of PPUI(x) are listed in Table I. DSC analysis showed  $T_g$  values in the range between 231 and 272°C for the obtained polymers. These  $T_g$ 's are in the same region as those of side-chain aromatic NLO PIs<sup>6–8,11–16</sup> and much higher than those of polyurethanes,<sup>22</sup> polyetherimides,<sup>18</sup> and polyesterimides<sup>9,19</sup> based on DR-19. The high  $T_g$ 's of PPUI(x) clearly resulted from the high rigidity of the PMDA moiety and the “two bonding site” linkage of the NLO groups. The  $T_g$ 's of the polymers can be adjusted by choosing dianhydrides with different rigidity or by changing the chromophore loading level.

Apart from high  $T_g$ , PPUI(x) also require high thermal stability because the polymer films have to be poled around the glass transition temperatures to generate an optical nonlinearity. The thermal decomposition temperatures are listed in Table I. It is observed that PPUI(x) possessed high thermal stability. The initial thermal decomposition temperatures ( $T_{d1}$ ) of PPUI(x) are more than 40°C higher than are the corresponding  $T_g$ 's and this high thermal stability would ensure high-temperature electric poling of the polymers. Figure 3 shows the TGA curves of PPUI(x). Two weight loss stages can be observed in the TGA curves. The first, at 260–350°C, was from the decomposition of the urethane linkages and the



**Figure 4** Temporal behavior of the order parameter ratio  $\phi(t)/\phi(0)$  of the poled PPUI(1) film at 150°C.

NLO chromophore, and the second, at a higher temperature, was from the decomposition of the imide linkages.

#### NLO Properties of PPUI(x)

PPUI(1) was spin-coated onto cleaned glass substrates from its DMAc solution, yielding high-quality films. The samples were dried at 80°C for 3 h and 120°C in a vacuum for 2 days to remove the residual solvent. The films obtained were about 1  $\mu\text{m}$  in thickness. Noncentrosymmetry in the polymer films was induced by the corona discharge poling method at 240°C with a poling voltage of 3 kV and a poling current of about 2  $\mu\text{A}$ . The distance between the sample surface and the needle diode was about 1 cm. The poling temperature was slightly higher than the  $T_g$  of the polymer, which would lead to a high dipole orientation according to the literature.<sup>4</sup> Another sample which experienced the same heating history, but without corona poling, was used as a reference. The UV-vis spectrum and IR spectrum of this reference sample did not change after heating at 240°C, which might demonstrate that no significant decomposition of the polymer occurred during the corona poling. After the corona poling, the dipole moments of the NLO chromophore were aligned and the UV-vis spectrum of the polymer film exhibited a blue shift and a decrease in absorption due to birefringence (Fig. 2).<sup>7,8</sup> The order parameter can be calculated from this change in the absorbance by  $\phi = 1 - A_1/A_0$ , where  $A_1$  and  $A_0$  are the absorbance before and after poling, respectively.<sup>4</sup> The order parameter of PPUI(1) film immediately after poling was found to be 0.30.

The NLO property of the PPUI(1) film was measured at the fundamental wavelength of 1064 nm. This polymer has high coefficient of optical nonlinearity: The  $d_{33}$  value immediately after poling was 23.6 pm/V.

Relaxation of the NLO chromophore alignment in the poled PPUI(1) film is illustrated in Figure 4, expressed as the temporal behavior of the order parameter ratio  $\phi(t)/\phi(0)$  for the poled polymer film at 150°C, since the order parameter can describe the degree of the chromophore alignment and the dipole orientation and correlate to the NLO properties of the polymer.<sup>4</sup> It was observed that the poled PPUI(1) film had good temporal stability of NLO properties and the  $\phi(t)/\phi(0)$  remained 71% after 1300 h at 150°C. The good thermal stability of NLO properties might be ascribed to the comparatively high  $T_g$  of the polymer.

The authors would like to express their appreciation to the Ministry of Education of China and the Shanghai Science and Technology Commission for their financial support.

#### REFERENCES

1. Eaton, D. F. *Science* 1991, 253, 281.
2. Marder, S. R.; Perry, J. W. *Science* 1994, 263, 1706.
3. Marder, S. R.; Kippelen, B.; Jen, A. K.; Peyghambarian, N. *Nature* 1997, 388, 845.
4. Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem Rev* 1994, 94, 31.
5. Marks, T. J.; Ratner, M. A. *Angew Chem Int Ed Engl* 1995, 34, 155.
6. Lin, J.; Hubbard, M.; Marks, T. *Chem Mater* 1992, 4, 1148.
7. Yu, D.; Gharavi, A.; Yu, L. *Macromolecules* 1996, 29, 6139.
8. Chen, T.; Jen, A.; Cai, Y. *J Am Chem Soc* 1995, 117, 7295.
9. Sotoyama, W.; Tatsuura, S.; Yoshimura, T. *Appl Phys Lett* 1994, 64, 2197.
10. Verbiest, T.; Burland, D.; Jurich, M.; Lee, V.; Miller, R.; Volksen, W. *Science* 1995, 268, 1604.
11. Tsutsumi, N.; Morishima, M.; Sakai, W. *Macromolecules* 1998, 31, 7764.
12. Sakai, Y.; Ueda, M.; Fukuda, T.; Matsuda, H. *J Polym Sci Part A Polym Chem* 1999, 37, 1321.
13. Jiang, H.; Kakkar, A. *Macromolecules* 1998, 31, 4170.
14. Sui, Y.; Liu, Y. G.; Yin, J.; Gao, J.; Zhu, Z. K.; Huang, D. Y.; Wang, Z. G. *J Polym Sci Part A Polym Chem* 1999, 37, 4330.

15. Liu, Y. G.; Sui, Y.; Yin, J.; Gao, J.; Zhu, Z. K.; Huang, D. Y.; Wang, Z. G. *J Appl Polym Sci* 2000, 76, 290.
16. Wang, C.; Zhang, C.; Wang, P.; Zhu, P.; Wu, W.; Ye, C.; Dalton, L. *Polymer* 2000, 41, 2583.
17. Kim, E.; Moon, I.; Kim, H.; Lee, M.; Han, S.; Yi, M.; Choi, K. *Polymer* 1999, 40, 6157.
18. Lee, K. S.; Moon, K. J.; Woo, H. Y.; Shim, H. K. *Adv Mater* 1997, 9, 978.
19. Woo, H. Y.; Shim, H. K.; Lee, K. S.; Jeong, M. Y.; Lim, T. K. *Chem Mater* 1999, 11, 218.
20. Van den Broeck, K.; Verbiest, T.; Degryse, J.; Van Beylen, M.; Persoons, A.; Samyn, C. *Polymer* 2001, 42, 3315.
21. Sui, Y.; Guo, X.; Yin, J.; Liu, Y.; Gao, J.; Zhu, Z.; Huang, D.; Wang, Z. *J Appl Polym Sci* 2000, 76, 1619.
22. Wang, N. P.; Leslie, T. M.; Wang, S.; Kowel, S. T. *Chem Mater* 1995, 7, 185.
23. Hou, Z.; Liu, L.; Xu, L.; Chen, J.; Xu, Z.; Wang, W.; Li, F.; Ye, M. *Thin Solid Films* 1999, 354, 232.