

A Facile Approach to Prepare Organo-soluble Side-Chain Polyimides for Second-Order Nonlinear Optics

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ABSTRACT

A simple synthetic method to prepare poly(urethane-imide) (PUI) based nonlinear optical (NLO) polymers was developed. In this method, a side-chain PUI was synthesized via a NCO-terminated polyurethane prepolymer instead of poly(amic acid) prepolymer and a tedious synthesis of the chromophore-containing diamine monomers was avoided. The resulting polymers showed large second-order NLO activities with good temporal and thermal stability.

INTRODUCTION

Second-order nonlinear optical polymers offer great promise for use in electro-optic modulators, optical interconnects, and other devices due to their large linear electro-optic coefficients, low dielectric constants, flexibility in fabrication and processing techniques that are compatible with integrated circuit technology.^[1-5] However, a number of issues have to be thoroughly addressed before they have any commercial value and one of the most crucial issues is the high temporal stability of dipole orientation.^[4] Recent studies on side-chain polyimides (PI) show some encouraging results.^[6-8] It seems that high T_g polymers such as aromatic PIs have been the promising choice of matrix materials for NLO polymers that may be utilized to reduce the relaxation of aligned dipoles. A common synthetic route for those NLO polyimides is the condensation polymerization of dianhydrides with diamines containing an NLO chromophore via a poly(amic acid) prepolymer followed by a high-temperature imidization or a chemical imidization process.^[9, 10] This method, however, often involves a tedious synthesis of the chromophore-containing diamine monomers. Sometimes, the fact that few chromophores can survive the relatively harsh chemical conditions of the monomer synthesis and the imidization of the polymers and the difficulty in the synthesis of chromophore-containing diamine compounds limit the type of chromophores that may be incorporated into the polyimide backbone. To avoid the synthesis of chromophore-containing diamine compounds, an alternate synthetic route was developed by Jen et al.^[8, 11] They developed on-pot preparation of preimidized, hydroxy-containing polyimide, followed by the covalent attachment of a chromophore to the backbone of the polyimide via a Mitsunobu reaction. This approach allows some flexibility in the

selection of the polymer backbone and the chromophores. However, in this work the NLO chromophore was incorporated into the polyimide backbone only through a single bonding site, which can reduce the orientational stability at high temperatures relative to chromophores attached via multiple bonding sites. In addition, one-step polymerization between an NLO chromophore-containing diol and bis-imide compound via a Mitsunobu reaction to prepare polyetherimide derivatives was reported by Lee et al.^[12] Using this method, there is no need to synthesize NLO-diamine monomer. The poor solubility of the polymers synthesized however greatly limited the wide application of this method. To overcome the problems such as poor polymer solubility, and difficult synthesis of chromophore-containing diamine monomers, a new facile synthetic approach was described in this communication. In the present investigation, we prepare NLO polyimides via a NCO-terminated polyurethane prepolymer instead of a poly(amic acid) prepolymer. This new approach avoids the troublesome NLO-diamine synthesis. This technique also permits the versatility in selection of the chromophores to be incorporated into the polyimide backbone in addition to providing two bonding sites for chromophore attachment to give better orientational stability. The synthesized polyimides, or more precisely poly(urethane-imide)s (PUI) might be a better matrix material, as processibility and solubility are enhanced without losing the advantageous properties of polyimides. The conventional DR-19 dye which has di-hydroxy groups is just used as a test NLO chromophore to characterize the novel synthetic approach.

EXPERIMENTAL

PUI1: 0.9g (3.6 mmol) of MDI was dissolved in 5 mL anhydrous DMAc. To this solution was added slowly 0.560g (1.7 mmol) of DR-19, and the resulting reaction mixture stirred at 40°C and 75°C each for 1 h and 90°C for 2 h. On cooling in ice-bath, 0.526g (1.7 mmol) OPDA was added in the mixture. After further reaction at 40°C and 90°C each for 2 h, the mixture was refluxed overnight. The resultant product (PUI1) was precipitated into methanol and further purified by repeated dissolution in DMAc and precipitation into methanol. Yield 1.62g (85%). IR (KBr pellet, cm^{-1}) 3412 (N-H), 1777 and 1721 (C=O), 1372 (C-N), 1513 (N=O). UV-vis (10^{-4} mol/L DMAc solution) $\lambda_{\max} = 485 \text{ nm}$.

PUI2: PUI2 was synthesized with the procedure similar to that used in the synthesis of PUI1 apart from replacing MDI with TDI. Yield 88%. IR (KBr pellet, cm^{-1}) 3366 (N-H), 1779 and 1721 (C=O), 1365 (C-N), 1513 and 1338 (N=O). UV-vis (10^{-4} mol/L DMAc solution) $\lambda_{\max} = 482 \text{ nm}$.

PUI3: PUI3 was synthesized with the procedure similar to that used in the synthesis of PUI1 apart from replacing OPDA with 6FDA. Yield 81%. IR (KBr pellet, cm^{-1}) 3354 (N-H), 1783 and 1725 (C=O), 1376 (C-N), 1512 and 1338 (N=O). UV-vis (10^{-4} mol/L DMAc solution) $\lambda_{\max} = 483 \text{ nm}$.

PUI4: PUI4 was synthesized with the procedure similar to that used in the synthesis of PUI2 apart from replacing OPDA with 6FDA. Yield 82%. IR (KBr pellet, cm^{-1}) 3365 (N-H), 1785 and 1727 (C=O), 1371 (C-N), 1514 and 1339 (N=O). UV-vis (10^{-4} mol/L DMAc solution) $\lambda_{\max} = 483 \text{ nm}$.

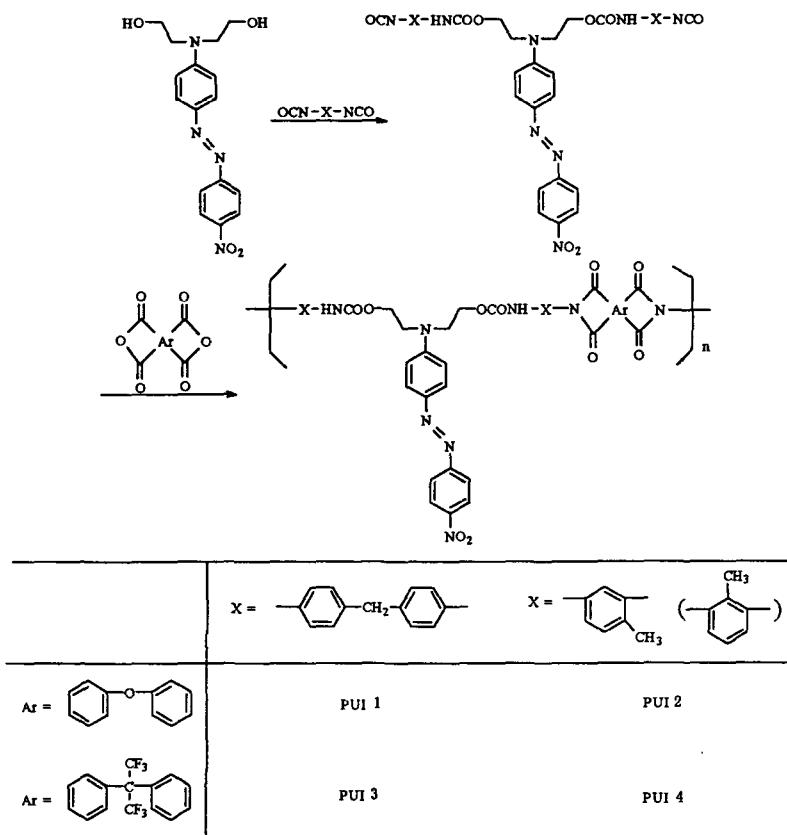


Fig. 1 Synthetic scheme of PUIs

RESULTS AND DISCUSSION

The synthetic procedure for formation of the polymers is shown in Fig. 1. The reaction was performed in a two step process. Initially, the NCO-terminated polyurethane prepolymer was synthesized using an excess of diisocyanate (4,4'-diphenylmethane diisocyanate (MDI) or 2,4-toluylene diisocyanate (TDI)) and DR-19. Then, the condensation polymerization reaction between a dianhydride (4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) or 3,3',4,4'-diphenylether-tetracarboxylic acid dianhydride (OPDA)) and a NCO-terminated polyurethane prepolymer was executed in anhydrous N,N-dimethylacetamide (DMAc) solvent. The obtained polymers were further purified by repeated dissolution in DMAc and precipitation into methanol. The present simple synthetic route may be applied to many kinds of NLO chromophores which have di-hydroxy functional groups.

The structures of the polymers were confirmed by conventional spectroscopic techniques such as FT-IR and UV-vis spectroscopy. The solubility of the obtained polymers in various solvents is listed in Table 1. It is observed that all PUIs are soluble in strong polar organic solvents such as DMAc, N-Methyl-2-pyrrolidone (NMP), N,N-dimethyl formamide (DMF), dimethylsulfoxide (DMSO) and 1,4-butyrolactone and show certain solubility in some low boiling point solvents such as

Table 1 Solubility of PUIs in various solvents at 25°C

Solvent	PUI1	PUI2	PUI3	PUI4
NMP	+	+	+	+
DMAc	+	+	+	+
DMF	+	+	+	+
DMSO	+	+	+	+
1,4-Butyrolactone	+	+	+	+
THF	+−	+−	+−	+−
Acetone	+−	+−	+−	+−
CHCl ₃	+−	+−	+−	+−
Toluene	−	−	−	−
Cyclohexane	−	−	−	−

+ : soluble; +− : partially soluble, − : insoluble

tetrahydrofuran (THF), chloroform and acetone. The high organo solubility of PUIs results from the existence of both the flexible urethane moiety and the side-chain diazo chromophores, which leads to loose chain packing and large free volume. PUI4 shows the best solubility and can even be dissolved in THF. The better solubility of PUI4 may be attributed to the existence of both the hexafluoroisopropylidene moiety and the asymmetry structure of TDI.

Thermal properties of PUIs are listed in Table 2. Differential scanning calorimetry (DSC) analysis showed T_g values in the range between 171°C and 211°C for the four PUIs. Although these are relatively low values compared to those of common rigid aromatic polyimides, which are attributed to the flexible urethane linkage and bulky side-chain chromophore, they are somewhat higher than those of many polyimides synthesized using unconventional methods.^[12, 13] PUIs based on more rigid 6FDA and TDI possess higher T_g values than those based on OPDA and MDI. Thermogravimetric analysis (TGA) shows that initial weight loss in the polymers begins at ca. 300°C, which represents the onset of decomposition of the NLO chromophore and the urethane segments. The breakdown of the polymer main chain occurs at around 540°C.

Table 2 Physical properties of PUIs

PUI	PUI1	PUI2	PUI3	PUI4
T _g (°C) ^a	171	184	196	211
T _{d1} (°C) ^b	298	313	304	314
T _{d2} (°C) ^c	542	564	544	549
d ₃₃ (pm/V) ^d	52.5	51	51	34

^a Measured with DSC under the protection of N₂ with a scan rate of 20 °C/min.

^b Initial thermal decomposition (on-set) temperature measured with TGA under the protection of N₂ with a scan rate of 20 °C/min.

^c Thermal decomposition (on-set) temperature of polymer backbone measured with TGA under the protection of N₂ with a scan rate of 20 °C/min.

^d SHG susceptibility coefficient measured with Maker Fringe method (+/- 5)

PUIs exhibit excellent film-forming properties and good optical quality films were easily obtained by spin coating. Thin films with a thickness of about 1 μm were spin-coated onto silica substrates from a 0.5 μm micro-filtered DMAc solution. Subsequently, the samples were baked at 60°C for half an hour and 120°C for 12 hours to remove most of the residual solvent. The films obtained appeared very smooth and highly translucent. The microscopic characteristics of the film surface were analyzed with a scanning atomic force microscope (AFM) working in constant force contact mode. A typical three-dimensional (3D) plot of the surface topology is presented in Figure 2. It can be seen that the film surface was quite flat and the root-mean-square value of the microscopic surface roughness was calculated as $\sigma_{\text{RMS}} = 0.323 \text{ nm}$.

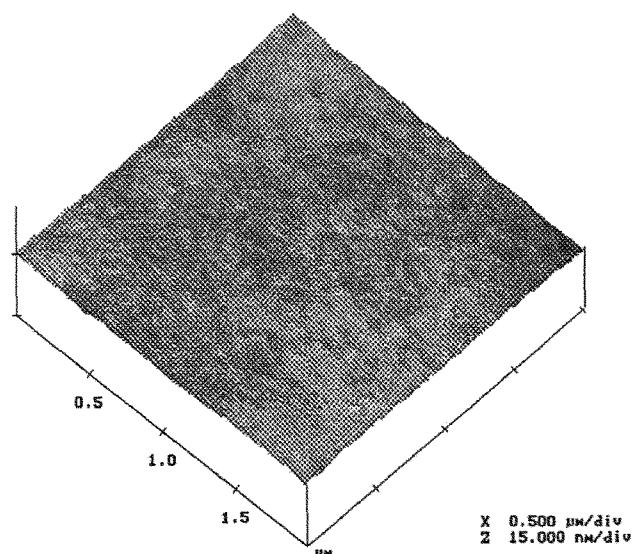


Fig. 2 Typical 3D plot of the film surface topology measured by AFM

The second-order nonlinear optical activity of the polymer films on the indium tin oxide (ITO) glass was produced by using a corona discharge poling process. The *in situ* SHG measurement experimental arrangement described before^[14, 15] was used to pole and investigate the orientational process of the chromophore at the same time. Fig.3 plotted the changes of normalized SHG intensities $I_{\text{sample}}/I_{\text{quartz}}L^2$ versus temperature of PUI2 during the poling process, where I_{sample} and I_{quartz} are SHG intensity of sample and single crystal quartz reference ($d_{11}=0.46 \text{ pm/V}$), respectively, and L is the film thickness. The poling voltage began to apply from the room temperature. Upon the application of high voltage across the samples, SHG signal was observed which we believed mainly due to the electric field induced second harmonic (EFISH) contributions. As the poling temperature reached T_A , the SHG intensity began to increase with the increase of the poling temperature. However, above the critical temperature T_B , the SHG intensity decreased rapidly until eventually to the same level as before T_A . This is mainly caused by the coaction of the three factors: (1) as the temperature increases, the free volumes of the side-chain polymer also increase and thus the NLO dipoles get more freedom to align in the direction of the electric

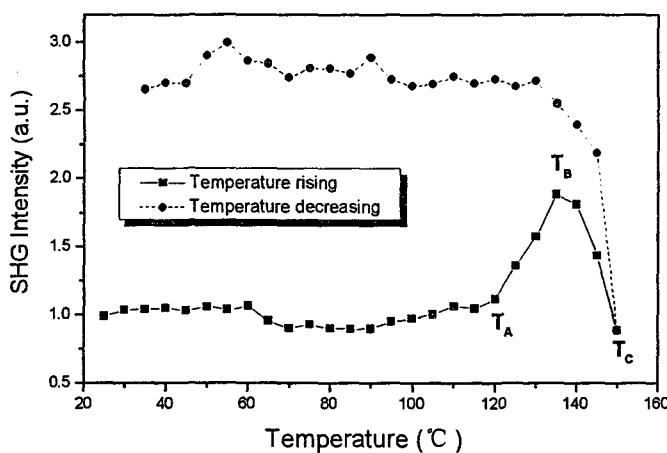


Fig. 3 *In situ* SHG intensities versus temperature of PUI2 during corona poling (heating rate about 1 °C/min)

poling field; (2) high temperature imparts high thermal randomization energy for the NLO dipoles, which can compete with the electric poling field; (3) as the temperature increases, the conductivity of the polymer films increases and thus the effective electric field decreases. The first factor will help increase the SHG intensity while the last two act contrarily. Below T_B , the first factor is dominant, so the SHG intensity increased with the increase of the poling temperature. At the critical temperature T_B , the three factors reach a balance and a maximum SHG intensity was then observed. Above T_B , the last two factors became dominant and the SHG intensity decreased rapidly. To our common knowledge, the glass transition temperature is the temperature when the oriented amorphous NLO dipole moments are usually randomized and the resultant SHG activity is largely depressed. So T_c in Fig.3 should be comparable to T_g of the polymer. However, the values of T_c are about 30°C lower than the T_g values obtained from DSC. The same phenomena were also appeared in many other systems although with no further explanation.^[16-18] We thought it mainly due to the different heating rate of the measurements (20°C/min for DSC and 1°C/min for *in situ* SHG measurement). When the temperature is reduced, the effects of the last two factors can be minimized as shown in the cooling curve. As the cooling occurs, physical aging causes the free volume of the polymer to shrink, thus restricting the chromophore motion and stabilizing the alignment. The SHG signal is higher during the cooling stage than the heating stage. It might due to the better alignment of the NLO dipoles after the heating process. T_c in Fig.3 can be considered as the optimum poling temperature since it is the lowest temperature, at which sufficient chromophore mobility is achieved. The macroscopic d_{33} values of PUIs are measured at $\lambda = 1064$ nm using Maker Fringe method after the corona poling (see Table 2).

In addition to the *in situ* poling studies, temperature-dependent SHG experiments on prepoled samples were also carried out *in situ* by monitoring the SHG signal while heating at a rate of 1°C/min. The SHG intensity of PUI2 as a function of

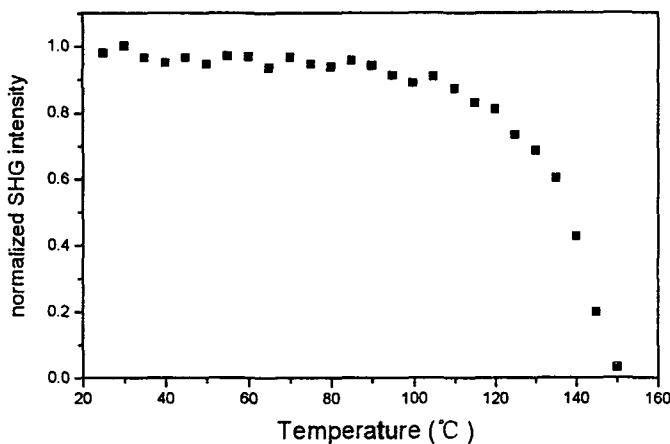


Fig. 4 SHG signal of PUI2 as a function of temperature

temperature was shown in Fig.4. The SHG intensity remained stable until close to the glass transition temperature where the SHG signal starts decay rapidly. It completely disappeared as the temperature went above T_g .

References

- [1] D. F. Eaton, *Science*, **1991**, *253*, 281
- [2] S. R. Marder, J. W. Perry, *Science*, **1994**, *263*, 1706
- [3] S. R. Marder, B. Kippelen, A. K. Jen, N. Peyghambarian, *Nature*, **1997**, *388*, 845
- [4] D. M. Burland, R. D. Miller, C. A. Walsh, *Chem. Rev.* **1994**, *94*, 31
- [5] T. J. Marks, M. A. Ratner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155
- [6] T. Verbiest, D. M. Burland, M. C. Jurich, V. Y. Lee, R. D. Miller, W. Volksen, *Science*, **1995**, *268*, 1604
- [7] D. Yu, A. Gharvi, L. Yu, *Macromolecules*, **1996**, *29*, 6139
- [8] T. A. Chen, A. K. Jen, Y. Cai, *J. Am. Chem. Soc.*, **1995**, *117*, 7295
- [9] Z. Peng, L. Yu, *Macromolecules*, **1994**, *27*, 2638
- [10] Y. Sui, Y. G. Liu, J. Yin, J. Gao, Z. K. Zhu, D. Y. Huang, Z. G. Wang, *J. Polym. Sci, Part A: Polym. Chem.*, **1999**, *37*, 4330
- [11] T. A. Chen, A. K. Jen, Y. Cai, *Macromolecules*, **1996**, *29*, 535
- [12] K. S. Lee, K. J. Moon, H. Y. Woo, H. K. Shim, *Adv. Mater.*, **1997**, *9*, 978
- [13] H. Y. Woo, H. K. Shim, K. S. Lee, M. Y. Jeong, T. K. Lim, *Chem. Mater.*, **1999**, *11*, 218
- [14] Z. Hou, L. Liu, L. Xu, J. Chen, Z. Xu, W. Wang, F. Li, M. Ye, *Thin Solid Films*, **1999**, *354*, 232
- [15] Z. Hou, L. Liu, L. Xu, Z. Xu, W. Wang, F. Li, M. Ye, *Chem. Mater.* **1999**, *11*, 3177
- [16] R. Inaba, M. Sagawa, M. Isogai, A. Kakuta, *Macromolecules*, **1996**, *29*, 2954
- [17] N. Tsutsumi, O. Matsumoto, W. Sakai, *Macromolecules*, **1997**, *30*, 4584
- [18] H. Saadeh, A. Gharavi, D. Yu, L. Yu, *Macromolecules*, **1997**, *30*, 5403