J MATER SCI **41** (2006) 3159–3162 LETTERS

Synthesis of luminescent polyurethane with π-conjugated segment in main chain

ZHIJIAN ZHANG*, ZHUN MA, SHIXIANG XIE, ZHE ZHENG, XUQIONG XIAO, WEI WEI, WEI HUANG
Institute of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China
E-mail: zjzhang@fudan.edu.cn

On account of the excellent optical and electrical properties, polymers or oligomers which contain long π-conjugated units have been of intensive industrial and scientific attention since the discovery of the application of the poly(phenylene vinylene) (PPV) in polymeric light-emitting diodes [1]. Remarkable progresses have been achieved in the development of these kinds of conjugated polymers and oligomers, such as polyfluorenes (PFs), polythiophenes (PTs), and poly(para-phenylene)s (PPPs) with applications in organic light-emitting diodes (OLEDs), photo-diodes, transistors, biosensors, solar cells, and so on [2–4]. Recently, some blended systems of conjugated polymers and general polymers have been prepared by physical and mechanical methods, such as oligo(PPV)/LLDPE (liner low density polyethylene) and MEH-PPV/PMMA [5, 6].

Although the polyurethane (PU) is one of the most classic materials, it is still attractive for its wide diversity in structures and applications. For example, PU is blended with the conductive polyaniline (PAni) and the ultra high dielectric constant is afforded [7]. The $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$/PU composite exhibits a higher dielectric constant [8] while electrical conductivity of PU filled with carbon black yet presents significantly lower [9]. The thermo-responsive polyurethane was prepared from 2-methylaziridine and supercritical carbon dioxide [10]. Magnetic nano-particles containing PU were prepared by urethane and acrylic acid [11]. Most of other researches on the PU focus on changing their mechanical properties by adjusting the species or ratios of hard segments and soft ones. In this paper, one simple route is provided to introduce the PL property into general polymeric materials, PU.

Nuclear magnetic resonance (^1H NMR) spectra were collected on Varian Merculy Plus 400, with chloroformd as a solvent and tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu IR prestige-21 spectrometer. Ultraviolet-visible (UV-Vis) absorption and fluorescence property were measured by using a Shimadzu UV-3150 UV-Vis-NIR spectrophotometer and RF-5300PC luminescence spectrometer with a xenon lamp as light source, respectively. The GPC analysis was conducted on Shimadzu 10A in the eluent tetrahydrofuran (THF) with polystyrene as the standard.

2,7-Dibromofluorene, tetrakis (triphenylphosphine) palladium, 4-(hydroxymethyl) phenyl-boronic acid, triethylbenzylammonium chloride, 2,4-tolylene diisocyanate (TDI), and polyethylene glycol 400 (PEG) were purchased from Aldrich Chemicals Company. 1-bromo-dodecane was purchased from Shanghai Chemical Reagent Co. Ltd. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All chemicals used were further purified before use.

2,7-Dibromo-didodecyl-9*H*-fluorene was synthesized using 2,7-dibromofluorene (compound **1**) as the starting material. To a mixture of compound **1** (3.9 g, 12 mmol) and catalytic amounts of triethylbenzylammonium chloride in a 100 ml Schlenk tube was added DMSO (18 mL) under nitrogen. After half an hour, 1-bromo-dodecane was added to the reaction mixture, and then the mixture was treated with 5.5 mL of 50% aqueous NaOH at 60 °C stirred for 12 hr. After the mixture was cooled to room temperature, ether (500 mL) was added. The organic layer was washed with 100 mL of a 1.0 M hydrochloric acid solution and 150 mL of water. The organic layer was dried by $MgSO_4$ and concentrated under reduced pressure. The oily residue was purified by flash column chromatography to afford compound **2** (7.6 g, 96%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) spectra, δ (ppm) = 0.54–0.62 (m, 4H), 0.85–0.88 (t, 6H), 1.04–1.22 (m, 36H), 1.88–1.93 (m, 4H), 7.43–7.46 (m, 4H), 7.50–7.52 (m, 2H). Elem. Anal. Calcd for $C_{37}H_{56}Br_2$: C, 67.27; H, 8.54. Found: C, 67.42; H, 8.36.

Tpsta({4-[9,9-didodecyl-7-(4-hydroxymethyl-phenyl) -9*H*-fluoren-2-yl] -phenyl} -methanol) (compound **3**) was synthesized in advance through the Suzuki coupling

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* Author to whom all correspondence should be addressed.

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DOI: 10.1007/s10853-006-6409-y

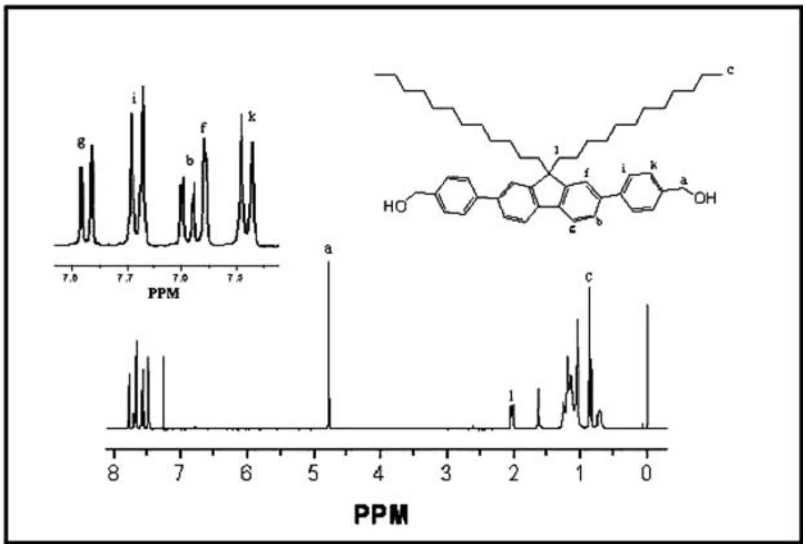


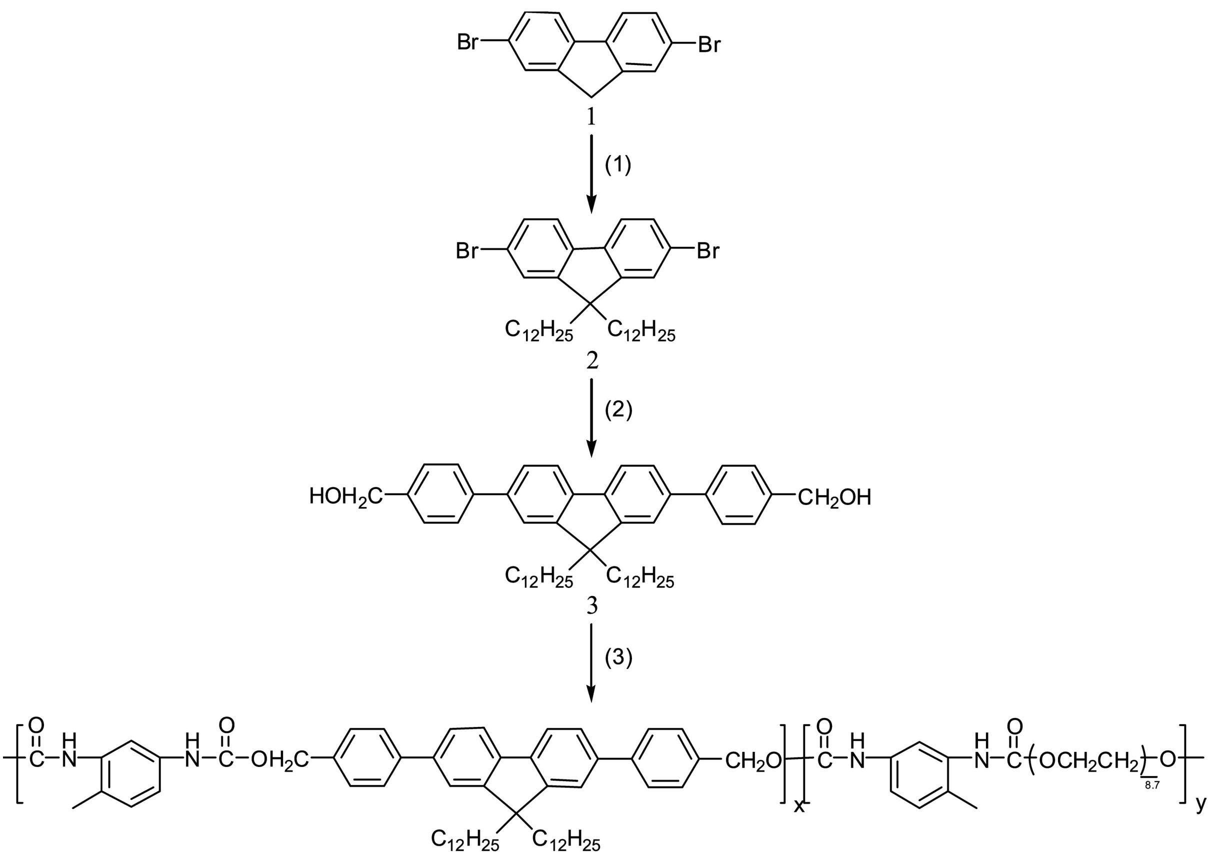
Figure 1 ^{1}H NMR spectra of monomer (compound **3**).

[12]. A typical procedure was described as following. Compound **2** (4.6 g, 7.0 mmol), 4-(hydroxymethyl)phenyl boronic acid, (3.0 g, 21.0 mmol), and catalytic amount of $Pd(PPh_3)_4$ were mixed in a three-neck flask which was desecrated and filled with nitrogen. Toluene (30 mL) and 2 M sodium carbonate (18 mL) were added. The mixture was refluxed under nitrogen for 48 hr. After cooling, the organic layer was separated and washed with brine and dried by $MgSO_4$. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum to afford compound **3** (2.86 g, 57%) as a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) spectra was shown in Fig. 1. δ (ppm) = 0.72 (m, 4H), 0.77–0.81 (t, 6H), 1.06–1.26 (m, 36H), 2.02–2.06 (m, 4H), 4.77 (s, 4H), 7.47–7.49 (d, 4H), 7.56 (s, 2H), 7.58–7.60 (m, 2H), 7.67–7.69 (m, 4H), 7.77–7.79 (d, 2H). Elem. Anal. Calcd for $C_{51}H_{70}O_2$: C, 85.66; H, 9.87. Found: C, 85.84; H, 9.68. There was no signal of OH in $CDCl_3$; FT-IR was used to further identify the prepared compound **3**. The peaks at 3610 and 1040 cm^{-1} could be indexed as OH end groups in compound **3**. Preparation of compound **3** containing bi-functional end groups was very useful, because many kinds of polymeric materials could be produced, such as PU, polyester.

The title PU was prepared according to the reaction sequence outlined in the Scheme 1. The reaction between the OH group and isocyanate (group NCO) to produce PU is classic and facile. One three-neck flask containing 2, 4-tolylene diisocyanate (TDI, 0.285 mL, 2.0 mmol) was desecrated and filled with pure nitrogen. Then compound **3** (0.47 g, 0.5 mmol) was dissolved in 5 ml anhydrous xylene and added dropwise under vigorously stirring in half an hour. The reaction mixture was stirred at 50 °C for 1 hr before adding dropwise polyethylene glycol 400 (PEG, 0.60 g, 1.5 mmol, M = 400) in 5 ml anhydrous xylene and then the resulting mixture was heated to 80 °C. [The molar ratio of (compound **3** + PEG)/TDI is 1/1, the ratio PEG/compound **3** (y/x) is 3/1] The reaction lasted 12 hr and the viscidity of the reaction system increased obviously. The freshly prepared PU was dissolved in THF, precipitated by adding methanol, filtered, and dried. The target polyurethane was obtained (1.32 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) spectra, δ (ppm) = 0.64–1.44 (m, 46x H), 2.02–2.14 (m, 4x H), 2.34–2.48 (m, 12x H), 3.34–3.76 (m, 92x H), 4.22–4.34 (m, 12x H), 4.65–4.84 (m, 4x H), 7.35–7.90 (m, 26x H). Elem. Anal. Calcd for $C_{139x}H_{204x}O_{39x}N_{8x}$: C, 63.94; H, 7.87; N, 4.29. Found: C, 64.14; H, 7.68; N, 4.38.

The FT-IR spectrum of the reaction mixture was applied to monitor the completeness of polymerization process. From Fig. 2, the peak at about 2280 cm^{-1} disappeared, indicating that the group of NCO from the monomer of TDI had been reacted completely [7]. The broad peak at 3300 cm^{-1} and the relatively small peak at 1600 cm^{-1} made sure the existence of NH group while the peaks at 1720 and 1230 cm^{-1} also confirmed the presence of the group of C=O in the product. Therefore, it could be safely concluded that PU had been produced. The product was an elastic solid with a light yellow color after the solvent was removed, rather than the thermoplastic PU, mainly because the monomer of PEG 400 was very flexible and decreased the rigidity of compound **3** significantly. In addition, the hard segment in the prepared PU main chain is not long enough to influence the mechanical properties. If other types of luminescent PU are expected, such as the luminescent PU plastics, or luminescent PU fibers, longer rigid, and even different molecular structure, such as star-like or dendron, π-conjugated segments in PUs shall be employed and be reported in the future publications.

The molecular weight measurement was performed by gel permeation chromatography (GPC) in the eluent THF using the calibration curve of polystyrene standards. From the GPC curve, it could be seen that the number-average molecular weight (Mn) and the weight-average



Luminescent Polyurethane

(1) n-$C_{12}H_{25}Br$, triethylbenzylammonium, 50% NaOH aqueous solution, 12 h;
(2) 4-(hydroxymethyl)phenyi-boronic acid, $Pd(PPh)_3$, 2M Sodium carbonate, 48 h;
(3) TDI, PEG 400, 80°C, 12 h.

Scheme 1 Synthetic route of the luminescent PU.

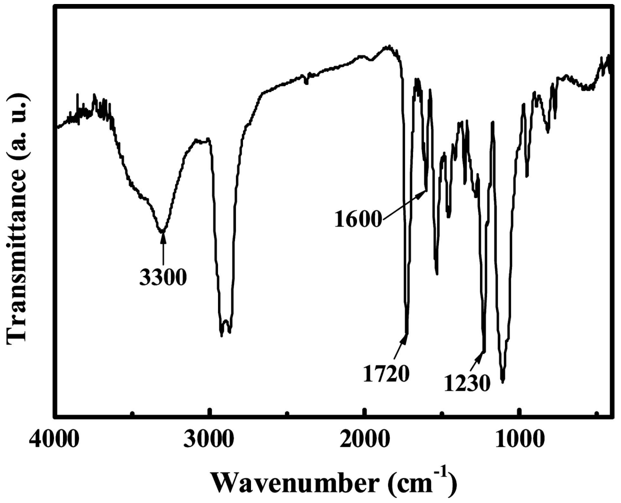


Figure 2 FT-IR spectra of reaction system after being lasted 12 hr.

molecular weight (Mw) of the resulted PU were 17,200 and 26,300 Da respectively, and the polymerization degree **x** and **y** could be calculated as around 6.6 and 19.8, respectively.

The absorption peak at 330 nm (3.76 eV) of the as-prepared PU as the thin film was related to π–π^* transition of π-conjugated fluorenyl and phenyl segment, and observed in many other reported π-conjugated polymers and oligomers [13, 14]. The PL properties of the thin film were determined on the RF-5300PC (Shimazhu), shown in Fig. 3. It could be seen that the maximum emissions of compound **3** and the as-obtained PU were at 363 nm (3.41 eV) and 365 nm (3.40 eV), with shoulder peak at 386 nm (3.21 eV) and 387 nm (3.20 eV), respectively. This indicated that the semiconductor properties (including luminescence) had been introduced to PU; moreover, there was even no difference between their PL spectra which was maybe due to no influence of enough flexible PEG chain on the conformation of short length rigid conjugated units. In fact, it was important that modification or functionalization of luminescence segments would not induce much change in the PL spectrum. Herein, we provide such a method to induce functional block chain with enough length and flexibility but not affect the optical properties of original luminescence units. Furthermore, it could be also observed that the overlap between UV-Vis absorption and PL was very small,

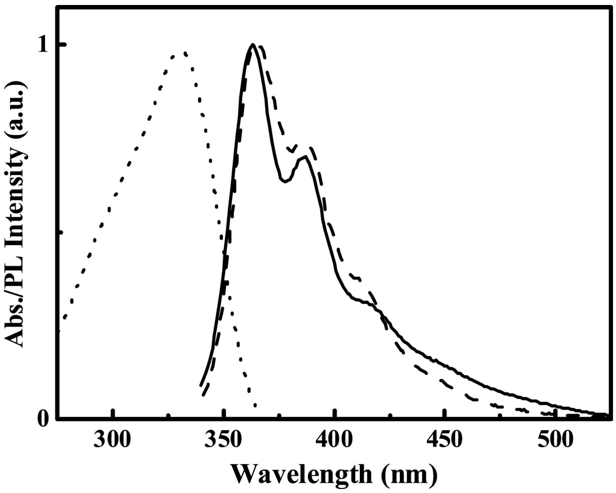


Figure 3 PL spectra of the compound **3** (*solid line*) as films; UV-Vis absorption (*dotted line*) and PL spectra (*dashed line*) of the prepared PU as films at room temperature.

which indicated the self-absorption of this kind of PU was very low. It was in favor of the improvement of the PL efficiency.

In conclusion, we have succeeded in synthesizing a luminescent PU with π-conjugated segments. The present approach provides a very simple method to combine general polymers functionalities, such as elasticity and mechanical property, with optical activity fluorescence. It could be also possible to afford PUs with conductivity by introducing suitable π-conjugated semiconducting segments. These functionalized general PUs could be further made into coatings, fibers, and plastics with interesting applications.

Acknowledgments

This work was financially supported by Shanghai Commission of Science and Technology under Grants 022261042 and National Nature Science Foundation of China NO. 60544001, we also would like to thank Dr. Feng Wang, Dr. Xuhui Zhu for their beneficial discussions.

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Received 19 July
and accepted 1 September 2005