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Novel Polymers: Syntheses and Characterizations of Polyurethanes Derived from 2,5-Bis(4-isocyanatophenyl)-3,4-diphenylthiophene and Aliphatic Diols

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Recently, Imai et al. reported that the compound 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (Ia) reacts with aromatic dianhydrides, dialdehydes, and diacid chlorides to yield polyimides, polyazomethines, and polyamides, respectively.[1,2] These are linear high molecular weight polymers. Apparently, the high thermal stability and enhanced solubility of the polymers are partly due to a highly phenylated thiophene ring in Ia.

One of the most important classes of commercial polymers is the polyurethane. A number of reports describing the preparation of urethane polymers by the addition reactions of structurally modified diisocyanates with a variety of polyols have been documented.[3,4] The most widely utilized aromatic diisocyanates are 4-4′-methylenebis-(phenyl isocyanate) (MDI) and tolylene diisocyanate (TDI). However, neither the preparations of tetraphenylthiophene-substituted diisocyanates nor any polymerizations of these monomers have been reported. The object of this work is to synthesize a monomer of the type mentioned above, to synthesize a variety of urethane polymers from it, and to examine their solubilities rather than their thermal properties since the urethane linkage, NHC(O)=O, is thermally unstable. We report herein (i) the synthesis of 2,5-bis(4-isocyanatophenyl)-3,4-diphenylthiophene (I); (ii) conversion of I to model urethane monomers, 2,5-bis[4-(carbomethoxyamino)phenyl]-3,4-diphenylthiophene (IIa) and 2,5-bis[4-(carbethoxyamino)phenyl]-3,4-diphenylthiophene (IIb); (iii) the preparation of urethane polymers, poly-EG, poly-DEG, and poly-BG, from the reactions of I with ethylene glycol, diethylene glycol, and 1,4-butanediol, respectively; (iv) the characterizations and physical properties of these compounds.

Experimental Section

Materials. The following aliphatic diols were purified by the distillation through a 40-cm Vigreux column: 1,2-ethanediol (ethylene glycol) 53–54 °C (0.1 mmHg); 2,2′-oxydiethanol (diethylene glycol), 84–85 °C (0.15 mmHg); and 1,4-butanediol, 81–82 °C (0.11 mmHg). Solvents such as chlorobenzene, toluene, *N*,*N*-dimethylacetamide (DMAC), *N*,*N*-dimethylformamide (DMF), 2-methylpentanone (MIBK), and dimethyl sulfoxide (Me_2SO) were purified by the method described in the literature.[5] The starting material, 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (Ia) was synthesized by the method reported elsewhere.[1]

Methods of Characterization: Spectroscopy. Infrared (IR) spectra were recorded on Perkin-Elmer Model 283 and Model 983 spectrometers. The samples for IR spectra were run either in $CDCl_3$ solution or in the form of KBr pellets. Carbon-13 and proton-pulse Fourier transform NMR spectra at 50.3 and 200 MHz, respectively, were recorded on an IBM-200SY multinuclear NMR spectrometer. Mass spectral data were obtained on a Hewlett-Packard GC/MS system 5988A.

Molecular Weight Determination. The weight-average molecular weights (polystyrene equivalents) of the polymers were determined by gel permeation chromatography (GPC) using 50-Å (IBM 100-199 MW), PSM 60 S (Du Pont 10^2–10^4 MW), and PSM 300 S (Du Pont 3×10^3–3×10^5 MW) columns and a differential refractometer R403 detector with dimethylformamide (DMF) as the eluent at the rate of 1 mL/min.

Viscosity Measurements. Inherent viscosity measurements were made for a 0.5% solution of urethane polymer in DMAC at 30 °C using a Ubbelohde viscometer.

Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Synthetic Procedures: A. Monomer. Synthesis of 2,5-Bis(4-isocyanatophenyl)-3,4-diphenylthiophene (I). A 12% solution of phosgene, $COCl_2$, in toluene (40.0 mL) was added cautiously to a stirring solution of Ia (1.00 g, 2.39 mmol) in chlorobenzene (5.00 mL) at 0 °C under an argon atmosphere. The mixture was stirred overnight and then refluxed at 115 °C for 3 h. The clear solution was allowed to cool and excess phosgene was removed by purging the reactor with dry argon. After removal of solvents, a grey-white residue (1.10 g, 97.9% yield) was crystallized and then recrystallized from a mixture of benzene and hexane under an inert atmosphere to give ca. 1.00 g (88.9% yield) of pure I as a white solid.

The physical properties and characterizations of I are as follows: mp 166 °C; moderately stable in air for a brief period of time; solubility, at room temperature, highly soluble in most organic solvents; the electron impact (EI) mass spectrum of I exhibits a parent grouping with the most intense peak at *m*/*z* 470.15 that corresponds to the parent ion $[^{12}C_{30}H_{18}{}^{14}N_2{}^{16}O_2{}^{32}S]^+$. Anal. Calcd for $C_{30}H_{18}N_2O_2S$: C, 76.59; H, 3.86; N, 5.95; S, 6.80. Found: C, 76.33; H, 3.94; N, 5.81; S, 7.00. NMR ($CDCl_3$) ^1H (relative to external Me_4Si) δ 7.12, 6.93, 6.90 [m, aromatic protons]; ^{13}C (relative to external Me_4Si) δ 139.98 [s, C(4)], 137.45 [s, C(5)], 136.05 [s, C(9)], 132.47 [s, C(10)], 131.76 [s, C(6)], 130.70 [d, $^1J(^{13}C-^1H]$ = 160 Hz, C(11)], 130.19 [d, $^1J(^{13}C-^1H)$ = 168 Hz, C(12)], 128.01 [d, $^1J(^{13}C-^1H)$ = 161 Hz, C(7)], 126.91 [d, $^1J(^{13}C-^1H)$ = 166 Hz, C(13)], 124.92 [s, N=C(14)=O], 124.68 [d, $^1J(^{13}C-^1H)$ = 165 Hz, C(8)]. IR ($CDCl_3$ vs. $CDCl_3$) 2270 cm^{-1}(vvs) (νN=C=O).

B. Model Compounds. Synthesis of 2,5-Bis[4-(carbomethoxyamino)phenyl]-3,4-diphenylthiophene (IIa). Compound I (0.47 gm 1.00 mmol) was allowed to react with dry absolute methanol (20.0 mL) in a round-bottom flask of 50 mL capacity, containing a magnetic stirring bar and equipped with an argon inlet and a reflux condensor with a $CaCl_2$ guard tube. After the solution was stirred at room temperature for 0.5 h and then at the reflux temperature of methanol for 2 h, it was cooled to room temperature. Excess methanol was removed by using a rotary evaporator to give a brown solid. Upon charcoal treatments and recrystallizations of the solid from methanol, 0.416 g (0.779 mmol, 78% yield) of IIa was isolated as pure white crystals. The physical properties and characterizations of IIa are as follows: mp 236 °C; reasonably stable in air; solubility, at room temperature, highly soluble in polar solvents and less soluble in nonpolar solvents; the EI mass spectrum of IIa exhibits a parent grouping with the most intense peak at *m*/*z* 534 that corresponds to the parent ion $[^{12}C_{32}H_{26}{}^{14}N_2{}^{16}O_4{}^{32}S]^+$; NMR ($CDCl_3$, relative to external Me_4Si) ^1H δ 7.22–7.10, 6.94, and 6.55 [m and s, 10 H, aryl CH and aryl NH], 3.73 [s, 3 H, CH_3], ^{13}C δ 153.85 [s, C=O], 139.26, 137.67, 136.90, 136.49, 129.48 [s, aryl C], 130.82 [d, aryl CH, $^1J(^{13}C-^1H)$ = 151 Hz], 129.81 [d, aryl CH, $^1J(^{13}C-^1H)$ = 161 Hz], 127.86 [d, aryl CH, $^1J(^{13}C-^1H)$ = 155 Hz], 126.6 [d, aryl CH, $^1J(^{13}C-^1H]$ = 162 Hz], 118.40 [d, aryl CH, $^1J(^{13}C-^1H)$ = 161 Hz], 52.36 [q, CH_3, $^1J(^{13}C-^1H)$ = 147 Hz]. Anal. Calcd for $C_{32}H_{26}N_2O_4S$: C, 71.89; H, 4.90; N, 5.24; S, 6.00. Found: C, 71.94; H, 4.99; N, 5.29; S, 6.43: IR ($CDCl_3$ vs. $CDCl_3$) 3440 (m)(NH), 1735 cm^{-1} (s) (NHC(O)=O).

Synthesis of 2,5-Bis[4-(carbethoxyamino)phenyl]-3,4-diphenylthiophene (IIb). In a procedure identical with that employed in the synthesis of IIa, 1.80 mmol of I was allowed to react with 20.0 mL of anhydrous ethanol to yield 0.747 g (1.33 mmol, 74% yield) of IIb as transparent, cubic crystals. The physical properties and characterization of IIb are as follows: mp 210 °C; reasonably stable in air; solubility, at room temperature, highly soluble in polar solvents and less soluble in nonpolar solvents; the EI mass spectrum of IIb exhibits a parent grouping with the most intense peak at *m*/*z* 562 that corresponds to the

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Table I
Synthesis and Physical Properties of the Polyurethanes

A. Synthesis of Poly-EG[a]

solvent	polymer yield, %	viscosity[c] η_{inh}, dL/g	nature of reactn mixture
N,*N*-dimethylacetamide	95.86	0.10	soln
dimethyl sulfoxide	97.46	0.16	soln
2-methylpentanone	93.80	0.08	ppt
dimethyl sulfoxide + 2-methylpentanone (1/1)	96.61	0.13	soln

B. Synthesis of Poly-BG[a,b]

time	viscosity[c] η_{inh}, dL/g
5.0 min	0.1586
1.0 h	0.1506
2.0 h	0.1521
7.0 h	0.1549

C. Physical Properties of the Polyurethanes

aliphatic dialcohol	polymer code	yield, %	η_{inh}, dL/g	MW[d]	mp, °C
ethylene glycol	poly-EG	96.61	0.13	10 800	220-224
diethylene glycol	poly-DEG	96.35	0.15	14 200	200-205
1,4-butanediol	poly-BG	95.50	0.15	14 500	207-210

[a] Polymerization was carried out by allowing 2.00 mmol of I to react with 2.00 mmol of ethylene glycol or 1,4-butanediol in 5.0 mL of the solvent at 115 °C for 2.0 h under an inert atmosphere of dry argon. [b] A 50:50% mixture of Me_2SO and MIBK was used as the solvent. [c] Measured at a concentration of 0.5 g/dL in DMAC at 30 °C. [d] Weight-average molecular weight obtained from the gel permeation chromatography (GPC) calibration curve.

Table II
Solubilities of Urethane Polymers[a]

solvent	polymer EG	DEG	BG
N,*N*-dimethylacetamide	++	++	++
N,*N*-dimethylformamide	++	++	++
dimethyl sulfoxide	++	+	+
tetrahydrofuran	++	++	++
chloroform	–	±	++
acetone	–	–	–
2-methylpentanone	±	±	±
benzene	–	–	–
conc sulfuric acid	++	++	++

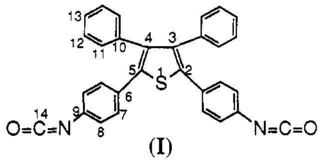
[a] (++) soluble at room temperature; (+) soluble at higher temperatures; (±) partially soluble at higher temperatures; (–) insoluble.

parent ion $[^{12}C_{34}H_{30}{}^{14}N_2{}^{16}O_4S]^+$; NMR ($CDCl_3$, relative to external Me_4Si) ^1H δ 7.23–7.10, 6.94, 6.54 [m and s, 10 H, aryl CH and aryl NH], 4.18 [q, 2 H, CH_2, $^3J(^1HCC^1H)$ = 7.33 Hz], 1.27 [t, 3 H, CH_3, $^3J(^1HCC^1H)$ = 7.33 Hz]; ^{13}C δ 153.42 [s, C═O], 139.22, 137.69, 137.02, 136.51, 129.34 [s, aryl C], 130.82 [d, aryl CH, $^1J(^{13}C-^1H)$ = 152 Hz], 129.79 [d, aryl CH, $^1J(^{13}C-^1H)$ = 161 Hz], 127.84 [d, aryl CH, $^1J(^{13}C-^1H)$ = 155 Hz], 126.58 [d, aryl CH, $^1J(^{13}C-^1H)$ = 162 Hz], 118.34 [d, aryl CH, $^1J(^{13}C-^1H)$ = 162 Hz], 61.27 (t, CH_2, $^1J(^{13}C-^1H)$ = 147 Hz], 14.32 [q, CH_3, $^1J(^{13}C-^1H)$ = 126 Hz]. Anal. Calcd for $C_{34}H_{30}N_2O_4S$: C, 72.58; H, 5.37; N, 4.98; S, 5.70. Found: C 72.22; H, 5.49; N, 4.82; S, 5.66. IR ($CDCl_3$ vs. $CDCl_3$) 3440 (m) (NH), 1730 cm^{-1} (s) (NHC(O)═O). The detailed X-ray analysis of IIb is reported elsewhere.[6]

C. Urethane Polymers. Synthesis of Polyurethanes (Poly-EG, Poly-DEG, and Poly-BG): General Procedure. A solution of I (0.94 g, 2.00 mmol) in dimethylacetamide (DMAC) (4.00 mL) was stirred in a flame-dried round-bottom flask of 50-mL capacity, equipped with a magnetic stirring bar, an argon inlet, a thermometer, and a reflux condensor with a $CaCl_2$ guard tube. To this, a solution of ethylene glycol, diethylene glycol, or 1,4-butanediol (2.00 mmol) in DMAC (1.00 mL) was added while stirring was maintained. The solution was stirred again at room temperature for approximately 5–10 min and then heated to 115 °C with stirring for 2 h, during which time the colorless solution turned to pale yellow. Upon cooling to room temperature, the solution turned to a viscous liquid that was then poured onto 200 mL of water with constant stirring. The resulting precipitate was separated from the mixture and redissolved in fresh DMAC, and the procedure was repeated to isolate a light-brown solid. This solid was dried by using a water aspirator and then in a vacuum oven at 50 °C for 24 h to collect the corresponding polyurethane as a light-brown powder of high purity. Molecular weights and physical properties of polyurethanes poly-EG, poly-DEG, and poly-BG are given in Tables I and II.

Results and Discussion

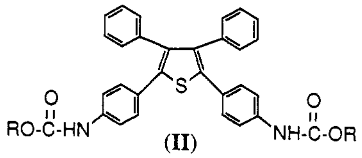
Polyurethane Precursor and Model Compounds. 2,5-Bis(4-isocyanatophenyl)-3,4-diphenylthiophene (I), a polyurethane precursor, was prepared in almost quantitative yield by the method described elsewhere.[7] The electron impact (EI) mass spectrum of I exhibits a parent grouping with the most intense peak at *m/z* 470.15 that corresponds to the parent ion $[^{12}C_{30}H_{18}{}^{14}N_2{}^{16}O_2{}^{32}S]^+$. The infrared spectrum (see Experimental Section) shows a strong stretching mode of vibration due to N═C═O bonds. The proton-coupled and proton-decoupled ^{13}C pulse Fourier transform NMR data (Experimental Section) of I confirm the presence of six singlets and five doublets corresponding to the six carbon atoms that are not attached to hydrogens and five aromatic CH groups, respectively. The assignments of all the carbon atoms in I (Figure 1) were in close agreement with those of similar compounds reported in the literature.[8] The ^1H NMR spectrum shows only the presence of hydrogens on the phenyl rings. The IR, NMR, and mass spectroscopic data along with the assignments for I are all consistent with the structure proposed in Figure 1. This was further supported by the reactions of I with methanol, ethanol, ethylene glycol, diethylene glycol, and 1,4-butanediol. The crystal structure of both 2,5-bis(4-nitrophenyl)-3,4-diphenylthiophene,[9] a precursor to I, and a model urethane monomer derived from I, 2,5-bis[4-(carbethoxyamino)phenyl]-3,4-diphenylthiophene (IIb)[6], unambiguously confirmed that the 4-isocyanatophenyl moieties in I are at the 2 and 5 positions of the thiophene ring. Furthermore, it also provided indirect evidence that the repeated urethane linkages in polyurethanes are at the same positions as in I. The synthesis and characterization of the model compounds IIa and IIb were straightforward and deserve no special comment. The ^{13}C NMR spectral assignments of the model compounds were made by comparing the data of these compounds with those of I (Experimental Section) and of similar compounds reported elsewhere.[8] The most significant feature in the infrared spectrum of each of the model compounds is the disappearance of the band near 2270 cm^{-1} due to N═C═O bonds and the presence of a stretching mode of vibration near 1730 cm^{-1} due to a carbonyl group in the urethane linkage.



(I)

Figure 1. Proposed structure of I.

The IR spectra, mass spectra, and NMR spectra (Experimental Section) of IIa and IIb are consistent with the structure shown in Figure 2, and this was confirmed by X-ray crystallography.[6]



(II)

R = CH_3, IIa ;

CH_2-CH_3, IIb .

Figure 2. Structure of II.

Urethane Polymers. Although a general synthetic route to urethane polymers is known,[4] the polyurethanes prepared in this study are novel and are obtained in quantitative yields. These polymers are of great interest since highly phenylated thiophene rings are incorporated in them. Because of this backbone the physical properties of these polyurethanes should differ substantially from those containing aliphatic chains and one or two aromatic ring(s) as in 4,4′-methylenebis(phenylisocyanate) (MDI) and tolylene diisocyanate (TDI). The polymerization of I at 115 °C in different solvents such as *N*,*N*-dimethylacetamide (DMAC), dimethyl sulfoxide (Me_2SO), and 2-methylpentanone (MIBK) has also been investigated and the results are given in Table I. Although the polymerization of I occurred in all three solvents, a 1/1 mixture of Me_2SO and MIBK was found to be the most ideal solvent to optimize the polymer synthesis. However, the reaction in MIBK produced low molecular weight polyurethanes. This is probably due to a limited solubility of the resulting polymer during the initial stage of the polymerization. The rate of polymerization in terms of inherent viscosity was measured during the polymerization of I with 1,4-butanediol, and the results are shown in Table I. The polymerization appeared to be complete within 5 min at 115 °C in the ideal solvent (1/1 mixture of Me_2SO and MIBK) since there was little or no change in the inherent viscosity values of the polymers between the periods of 2.0 and 7.0 h. Therefore, we conclude that the polymerization of I with aliphatic diols in an ideal solvent mixture, at 115 °C, could be completed within the first 2.0-h period.

The infrared spectrum of each polymer shows several characteristic stretching modes of vibrations due to N—H, C=O, and C—H bonds in the regions, 3390, 1710, and 2900 cm^{-1}, respectively. However, the most significant feature in the IR spectra of these polymers is the disappearance of νN=C=O near 2300 cm^{-1}, which indicates the complete utility of this moiety in I during the polymerization. The inherent viscosity measurements and molecular weight determinations (see Table I) showed that the polyurethanes are low molecular weight species. Perhaps, the lower reactivity of I is responsible for the low molecular weights of the polyurethanes. However, our results are comparable to those of polyurethanes derived from sterically crowded diisocyanates.[4] All the polyurethanes prepared in this study melt to form a brownish mass in the temperature range around 200–220 °C. With the exception of broad resonances, the ^1H and ^{13}C NMR spectra of poly-EG, poly-DEG, and poly-BG are identical with those of model compounds IIa and IIb (see Experimental Section).

The solubility tests in various organic solvents have been conducted and the results are given in Table II. At room temperature, all the polyurethanes are highly soluble in DMAC, DMF, and THF. However, only two polymers, poly-DEG and poly-BG, are soluble in Me_2SO at elevated temperatures, and only poly-BG is highly soluble in chloroform. The urethane polymers prepared in our study are low molecular weight species and are highly phenylated. Considering these facts, it is not at all surprising that the polymers are highly soluble in many organic solvents. However, none of these polymers either dissolve or swell in benzene and acetone.

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Registry No. I, 107711-78-4; **I9**, 92996-46-8; **II9**, 107711-79-5; **IIb**, 105854-91-9; poly-EG (copolymer), 107711-85-3; poly-EG (SRU), 107711-80-8; poly-DEG (copolymer), 107711-86-4; poly-DEG (SRU), 107711-81-9; poly-BG (SRU), 107711-82-0; $COCl_2$, 75-44-5.

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Phase-Mixing Effect in Styrene–Butadiene Block Copolymers

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For a number of years, workers in this laboratory have studied the decrease in the glass transition temperatures of low molecular weight styrene microphases in phase-separated block copolymers below those of polystyrene homopolymers of comparable molecular weight both in styrene–dimethylsiloxane[1,2] and in styrene–butadiene block copolymers.[3,4] The glass transition temperature, T_g, of the styrene microphases in styrene–dimethylsiloxane block copolymers became equal to that of comparable molecular weight polystyrene homopolymers at a block molecular weight of about 1.8×10^4;[1,2] no effect of dimethylsiloxane block molecular weight on styrene (S) microphase T_g was found. In the case of styrene microphases in styrene–butadiene block copolymers, the T_g of the styrene microphases remained below that of polystyrene homopolymers of comparable molecular weight up to the highest molecular weight styrene block investigated, $M_n^s = 1.2 \times 10^5$;[4] the butadiene block molecular weight did not affect the

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