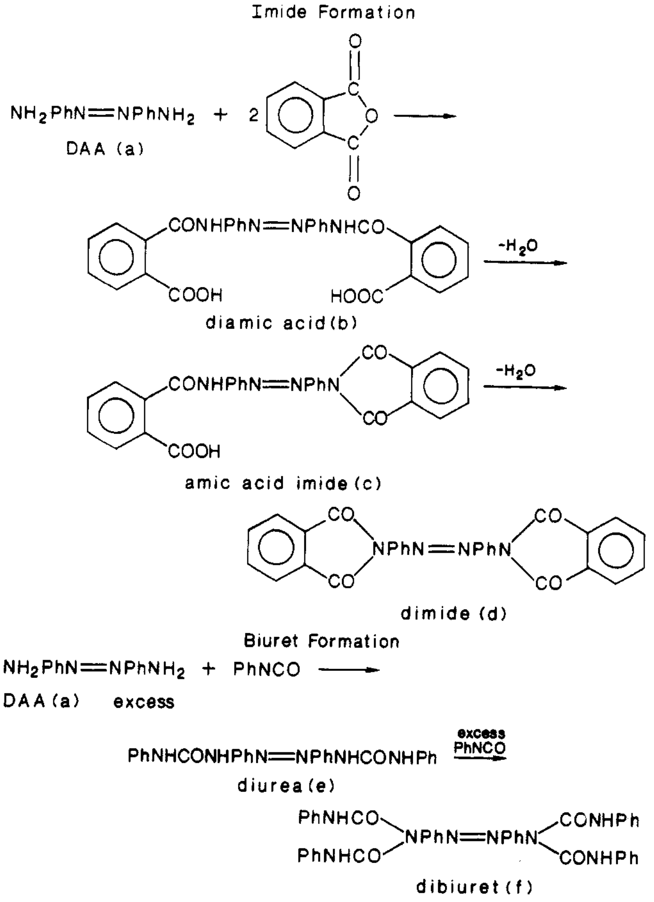
Scheme I



could be used so that even after blue-shifts occur the matrix absorption will not interfere with the label's absorption.

Acknowledgment. We acknowledge partial support of this research by the Army Research Office (Contract No. DAAG 29-85-K-0055) and the National Science Foundation, Polymers Program (Grant No. DMR 82-05897). Helpful discussions on organic reactions with Prof. Huang and the critical reading of the manuscript by Prof. Morawetz are also acknowledged.

Registry No. I, 107302-25-0; **II**, 107302-26-1; **b**, 107302-27-2; **c**, 107302-28-3; **d**, 107302-29-4; **e**, 74261-74-8; **f**, 107302-30-7; **DAA**, 538-41-0; PhNCO, 103-71-9; 4,4-$H_2NC_6H_4N{=}NC_6H_4NO_2$, 730-40-5; phthalic anhydride, 85-44-9.

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Synthesis and Cationic Polymerization of 3,9-Dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane

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Received September 16, 1986

Several spiro orthocarbonates, 1,5,7,11-tetraoxaspiro[5.5]undecane (**1**),[1] 3-methylene-1,5,7,11-tetraoxaspiro[5.5]undecane (**2**),[2] 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane (**3**),[3] and 8,10,19,20-tetraoxaspiro[5.2.2.5.2.2]henicosane (**4**),[4] undergo ring-opening transfer polymerization in the presence of cationic catalysts to give alternating copolymer, poly(ether carbonate). Bailey and Endo have shown that the spiro orthocarbonate (SOC) is one of the useful monomers that undertake expansion in volume upon polymerization.[5] Boron trifluoride and tin(IV) chloride are known to initiate cationic polymerization of SOCs at varying temperature.[1–4] On the other hand, we have carried out the polymerization of **1** with some sulfonium salts as thermal latent cationic catalysts at 80–120 °C.[6] Since the SOC might be a promising monomer as, e.g., a resin additive with enhancement of adhesion on curing,[7] it is important to make clear reactivity of SOCs for their functionalization or materialization. However, the SOCs hitherto used are fairly sensitive to moisture, so that scrutiny of the reactivity toward cationic catalysts has not been done yet.

Recently, we have prepared a SOC, 3,9-dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane (**5**), which is stable enough to moisture to study in detail. In this paper, synthesis of **5** and effectiveness of various cationic catalysts in the polymerization of **5** are described.

Experimental Section

Materials. Commercially available *p*-toluenesulfonic acid monohydrate was dehydrated by heating at 100 °C for 6 h in vacuo, giving brown solid which was directly used as a catalyst. Boron trifluoride etherate, titanium(IV) chloride, and *n*-butyl iodide were purified by distillation just before use. Benzyltetramethylenesulfonium hexafluoroantimonate was prepared according to the method reported previously by us.[8] As for cationic catlysts other than those stated above, each extra pure grade reagent was used as first use without purification.

Characterization. Molecular weight and its dispersion were measured by Toyo Soda HPLC CCP&8000 using TSK gel G2500H and G3000H (solvent, THF). IR spectra were recorded with JEOL FT/IR-3. NMR spectra were obtained by JEOL PMX-60 (60 MHz) and FX-100 (100 MHz).

Diethyl Benzylmalonate (6). To sodium ethoxide solution prepared from sodium (10.8 g, 0.47 mol) and 450 mL of absolute ethanol, diethyl malonate (150 g, 0.94 mol) and then benzyl chloride (59.3 g, 0.47 mol) were added dropwise at room temperature. The resulting mixture was refluxed for 2 h. After cooling, the reaction mixture was diluted with water and subsequently extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by distillation to give 100 g (86%) of **6**, bp 129–130 °C/0.15 mmHg.

2-Benzyl-1,3-propanediol (7). To a suspension of $LiAlH_4$ (40.0 %, 1.1 mol) in absolute ether (1.3 L), the diester (**6** 100 g, 0.40 mol) was added dropwise at room temperature. After the addition, the mixture was refluxed for 4 h and stirred overnight at room temperature. A saturated sodium sulfate solution was slowly added into the reaction mixture. A white mass was filtered off, and the filtrate was evaporated. The residual white solid was recrystallized from benzene. Yield: 59.2 g (87%). Mp: 64–66 °C.

3,9-Dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane (5). Preparation of **5** followed the previously reported method for **1**.[9] A mixture of **7** (25.0 g, 0.75 mol), tetraethyl orthocarbonate (**8**,

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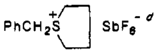
Table I
Polymerization of SOC by General Lewis Acids[a]

run	cat.	temp, °C	yield of polymer, %		conv., %
			insoluble[b]	soluble[b]	
1	none	140	0	0	0
2	BF_3OEt_2	120	74[c]	16	90
3		140	76	18	94
4		160	80	14	94
5	$BF_3{\cdot}2MeOH$	120	42	7	49
6	$AlCl_3$	120	4	0	4
7	$TiCl_4$	120	1	0	1
8	$SnCl_4$	120	85[d]	15	100
9	$GeCl_4$	120	0	0	0
10	$FeCl_3$	120	6	0	6
11	$ZnCl_2$	120	8	0	8

[a] Bulk polymerization using catalyst (2 mol %) for 24 h. [b] n-Hexane soluble or insoluble polymer. [c] $\bar{M}_n = 5500$, $\bar{M}_w/\bar{M}_n = 1.58$ (based on polystyrene by GPC). [d] $\bar{M}_n = 4600$, $\bar{M}_w/\bar{M}_n = 1.37$ (based on polystyrene by GPC).

Table II
Polymerization of SOC by Some Cationic Catalysts[a]

run	cat.	insoluble polymer[b,c]			soluble polymer[b] yield, %	conv., %
		yield, %	$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$		
1	n-BuI	2			0	2
2	n-BuCl	0			0	0
3	$MgCl_2$	0			0	0
4	$Mg(ClO_4)_2$	15			0	15
5	TsOH	2			0	2
6	$Ph_3C^+BF_4^-$	78	3.8	1.47	22	100
7	$Ph_3C^+SbCl_6^-$	72	2.8	1.37	28	100
8	 [d]	98	6.5	1.62	2	100

[a] Bulk polymerization using catalyst (2 mol %) at 120 °C for 24 h. [b] n-Hexane soluble or insoluble polymer. [c] $\bar{M}_n$, based on polystyrene by GPC. [d] Bulk polymerization using catalyst (2 mol %) at 120 °C for 12 h.

14.5 g, 0.38 mol),[10] and anhydrous p-toluenesulfonic acid (0.15 g, 0.87 mmol) in dry xylene (40 mL) was heated at 110 °C for 10 h. During the reaction, ethanol was distilled off. The collection of theoretical amount of ethanol was followed by addition of triethylamine (1 mL) after cooling. The mixture was allowed to stand overnight at room temperature. Thereafter, removal of xylene under vacuum afforded a white precipitate which was recrystallized from cyclohexane. Yield: 83%. Mp: 100–102 °C. IR (KBr) cm^{-1}: 1013, 702. ^1H NMR ($CDCl_3$): δ 2.00–2.30 (m, 2 H, 2 C*H*), 2.35–2.72 (d, 4 H, 2 $PhCH_2$), 3.60–4.24 (m, 8 H, 4 CH_2O), 7.10–7.40 (s, 10 H, 2 Ph). MS, m/z (relative intensity): 341 (M + 1, 0.24%). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 73.82; H, 7.25.

Polymerization of 5. A Typical Procedure. The monomer (5, 0.5 g, 1.47 mmol) and one of the catalysts (2 mol %) were mixed in a tube in a glovebox under the atmosphere of dry nitrogen. The tube was degassed by repeated cooling and pumping, sealed, and heated at a set temperature (see Tables I–III) for 24 h. The polymerization of 5 was terminated by addition of triethylamine (0.7 mL) after cooling and opened. The mixture was dissolved in methylene chloride (2 mL) and reprecipitated by pouring the solution into n-hexane (400 mL). n-Hexane was removed by decantation. The residual viscous oil was dried under vacuum to give insoluble polymer in n-hexane. n-Hexane layer was concentrated under reduced pressure, yielding soluble polymer in n-hexane which was dried in vacuo. Insoluble polymer: IR (neat) cm^{-1}: 1250, 1130, 702. ^1H NMR ($CDCl_3$): δ 1.88–2.48 (br, 2 H, 2 CH), 2.48–2.92 (br, 4 H, 2 CH_2Ph), 2.92–3.61 (br, 4 H, CH_2OCH_2), 3.68–4.43 (br, 4 H, $CH_2OC(=O)OCH_2$), 7.19–7.82 (br, 10 H, 2 Ph).

Results and Discussion

Synthesis of 5. In order to prepare moisture-insensitive SOC, we designed the synthesis of SOC 5 with introduction of two benzyl groups into the 3- and 9-positions of SOC 1, respectively, which possibly stabilize the SOC structure by enhanced hydrophobicity and ring fixation. By the reaction of benzyl chloride with 2 equiv of diethyl malonate,[11] diethyl benzylmalonate (6) was obtained in 86% yield and then reduced with $LiAlH_4$ to corresponding diol 7 (2-benzyl-1,3-propanediol, 87%). According to the previously reported condensation method,[9] 3,9-dibenzyl-1,5,7,11-tetraoxaspiro[5.5]undecane (5) was prepared by the reaction of tetraethyl orthocarbonate (8)[10] with 2 equiv of diol 7 in xylene at 110 °C using p-toluenesulfonic acid as catalyst. The SOC 5 was obtained in 83% yield as

Table III
Effect of H_2O in Cationic Polymerization of SOC[a]

run	cat.	insoluble polymer[b,c]			soluble polymer[b] yield, %	conv., %
		yield, %	$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$		
1	H_2O	0			0	0
2	$AlCl_3$	4			0	4
3	$AlCl_3$–H_2O (1:24)	17			46	63
4	$TiCl_4$	1			1	1
5	$TiCl_4$–H_2O (1:24)	13			68	81
6	$SnCl_4$[d]	69	3.2	1.29	13	82
7	$SnCl_4$–H_2O (1:1)[d]	80	3.6	1.32	8	88
8	$SnCl_4$ (open)[d,e]	82	3.2	1.29	9	91
9	$SnCl_4$[f]	85	4.6	1.37	15	100
10	$SnCl_4$–H_2O (1:17)[f]	73	1.4	1.40	27	100

[a] Bulk polymerization using catalyst (2 mol %) at 120 °C for 24 h. [b] n-Hexane soluble or insoluble polymer. [c] $\bar{M}_n$, based on polystyrene by GPC. [d] From Wako Pure Chemical Ind. [e] The catalyst was treated in the presence of atmosphere moisture. [f] From Yotsuhata Kagaku Kogyo.

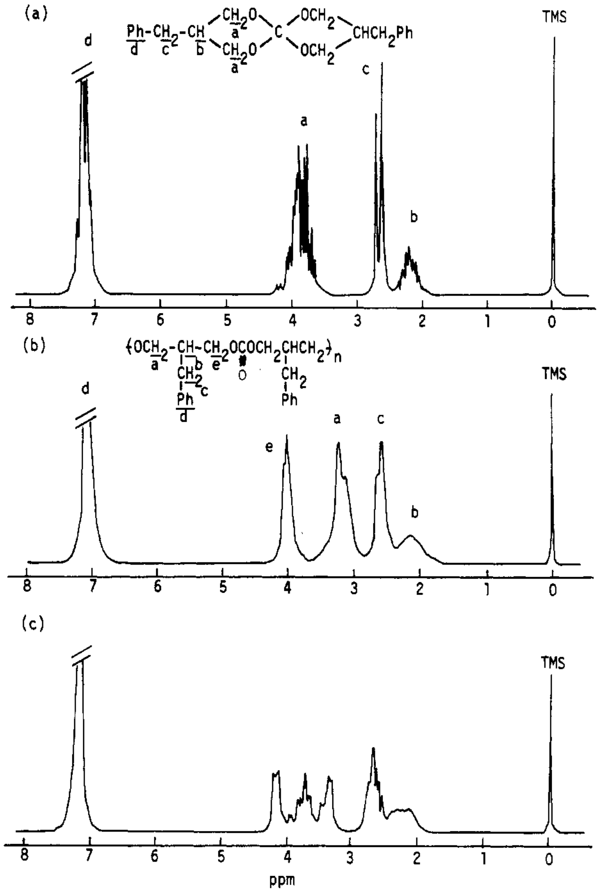
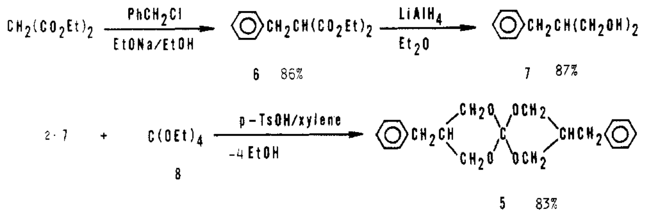


Figure 1. ^1H NMR spectra (100 MHz, δ, $CDCl_3$, Me_4Si). (a) SOC 5, (b) insoluble polymer in n-hexane, and (c) soluble polymer in n-hexane (obtained in the polymerization of SOC 5 with BF_3OEt_2 (2 mol %) at 120 °C for 24 h).

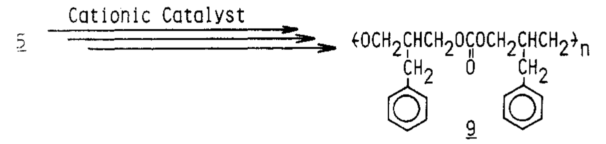
Scheme I



colorless crystals (mp 100–102 °C). The structure of 5 was confirmed by elemental analysis, IR, ^{1}H NMR (Figure 1a), ^{13}C NMR, and MS spectra.

The preliminary test of the moisture sensitivity of the SOC 5 was carried out by the hydrolysis catalyzed by acetic-d_4 acid (9 mol %) at 60 °C in 89% acetone-d_6. The hydrolysis of 5 was about 20 times slower than that of 1, revealing the desired moisture stability. In fact, the crystals of 5 showed no deliquescence in the presence of the atmospheric moisture, unlike the other SOCs (Scheme I).

Polymerization of 5. The bulk polymerization of 5 was carried out at 120–160 °C for 24 h in a sealed tube in the presence of a cationic catalyst (2 mol %). Both soluble and insoluble polymers in n-hexane were viscous colorless oils each of which was assigned to have structure 9 by IR and ^{1}H NMR spectra. IR spectrum showed a characteristic carbonate C=O absorption band at 1747–1743 cm^{-1} and two absorptions attributable to ether linkage (1250 (COC(=O)OC) and 1110 (COC) cm^{-1}). The ^{1}H NMR spectrum of each polymer was shown in parts b and c of Figure 1. In accordance with the proposed structure 9, two doublets of methylene groups adjacent to ether and carbonate oxygens appeared at 2.92–3.61 and 3.68–4.43 ppm, respectively, in the ^{1}H NMR spectrum of insoluble polymer. As shown in Figure 1c, in the soluble polymer chemical shift of methylene adjacent to ether, oxygen was clearly moved to a lower field (3.16–3.90 ppm) than that of insoluble polymer. This is obviously due to difference of degree of polymerization (DP). Generally, $\bar{M}_n$ of the insoluble polymer ranged from 3000 to 7000 depending on the polymerization condition. The insoluble polymer obtained by the use of BF_3OEt_2 was found to cause no or small shrinkage (0–3%) on polymerization by measurement of the density (average densities: 5, 1.218; 9, 1.232 g/cm^3).



Activity of Cationic Catalysts. The activity of various cationic catalysts, Lewis and protic acids listed in Tables I and II, was examined in the polymerization of 5 at 120 °C for 24 h. As indicated in Table I, 5 was not polymerized at 140 °C without catalyst at all, being recovered quantitatively. Table I indicates activities of typical Lewis acids. Among them, $SnCl_4$ and BF_3OEt_2 had higher activity. However, the other catalysts showed no or little activity except for $BF_3{\cdot}2MeOH$. The polymerization temperature was determined to be 120 °C, because there was no critical difference of the conversion of 5 between 120 and 160 °C. Alkyl halides (n-BuI, n-BuCl) gave almost no polymer. It is notable that p-TsOH is a very poor catalyst for 5. The effect of counteranion was examined with $MgCl_2$ and $Mg(ClO_4)_2$. High degree of charge separation in $Mg(ClO_4)_2$ than $MgCl_2$ might be effective. Carbocationic catlyst, trityl tetrafluoroborate and hexachloroantimonate, had quite high efficiency.

Meanwhile, use of sulfonium salt as developed by us as a thermal latent cationic catlyst,[8] resulting in the highest yield of the insoluble polymer (98%) with 100% conversion. Accordingly, $\bar{M}_n$ of the obtained insoluble polymer (6500) was higher than those (3800, 2800) given by both trityl tetrafluoroborate and hexachloroantimonate. This indicates that the sulfonium salt is the most effective catalyst. These results mentioned above are closely similar to those reported by us in the effect of the catalysts of the polymerization of bicyclo ortho ester.[12]

In cationic polymerization, it is well-known that H_2O plays an important role as cocatalyst. In this system, we further studied the effect of H_2O on the polymerization of 5 with a few Lewis acids. The results are summarized in Table III. The SOC 5 was not polymerized by H_2O alone (2 mol %). Although $AlCl_3$ or $TiCl_4$ showed little activity on polymerization of 5 when it was used alone, addition of H_2O (48 mol %) to the reaction system brought about a dramatic increase of the yield of polymer (runs 2–5). Combination with a suitable amount of H_2O (2 mol %, run 7) or feeding of $SnCl_4$ in the open (run 8) indeed caused increase of both the yield of insoluble polymer and the conversion of 5, in comparison with $SnCl_4$ alone (run 6). However, the insoluble polymer decreased by use of a large excess (34 mol %) of H_2O (runs 9 and 10). In this case, as expected, clear decrease of DP was also observed ($\bar{M}_n$ 4600 → 1400). This is in sharp contrast to the reverse DP change in the presence of a small amount of H_2O (runs 6–8). These observations are in good agreement with the important role of water well-known in the cationic polymerization. Since BF_3OEt_2 can act as a proton or Et^+ source in the polymerization, its high activity as initiator is acceptable, if the ring-opening reaction is initiated by H^+ or Et^+. However, $SnCl_4$ does not have the ability to generate cationic species in itself. Therefore, contamination of small or proper amount of water into $SnCl_4$ used (Table I, run 8, or Table III, run 9) is conceivable. In fact, activity change was confirmed with the use of another $SnCl_4$ supplied from a different source (Table III, run 6–8). Water as cocatalyst has been well-established in the polymerization of styrene with $SnCl_4$.[13] On the other hand, as for p-toluenesulfonic acid as protic initiator (Table II, run 5), much less activity may be attributed to lower acidity, probably in the presence of trace water.

Registry No. 5, 107711-17-1; 6, 607-81-8; 7, 2612-30-8; 8, 78-09-1; 9, 107711-20-6; $PhCH_2Cl$, 98-88-4; $EtO_2CCH_2CO_2Et$, 105-53-3; $BF_3{\cdot}2MeOH$, 2802-68-8; $FeCl_3$, 7705-08-0; $ZnCl_2$, 7646-85-7; BuI, 542-69-8; $Mg(ClO_4)_2$, 10034-81-8; TsOH, 104-15-4; $Ph_3C^+BF_4^-$, 341-02-6; $Ph_3C^+SbCl_6^-$, 1586-91-0; $PhCH_2S^+(CH_2)_4SbF_6^-$, 87301-55-1; H_2O, 7732-18-5; $AlCl_3$, 7446-70-0; $TiCl_4$, 7550-45-0; $SnCl_4$, 7646-78-8; BF_3OEt_2, 109-63-7.

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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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