Preparation of Poly(2,5-thienyleneethylene) and Poly(2,5-furyleneethylene) by Vapor Phase Pyrolysis of (5-Methyl-2-thienyl)methyl Benzoate and (5-Methyl-2-furyl)methyl Benzoate

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ABSTRACT: The synthesis of poly(2,5-thienyleneethylene) and poly(2,5-furyleneethylene) by vapor deposition polymerization is presented. (5-Methyl-2-thienyl)methyl benzoate and (5-methyl-2-furyl)methyl benzoate were subjected to vapor phase pyrolysis above 650 °C to form 2,5-dimethylene-2,5-dihydrothiophene and 2,5-dimethylene-2,5-dihydrofuran. Upon condensation, both compounds spontaneously polymerize, respectively, at a temperature higher than −25 °C to produce poly(2,5-thienyleneethylene) and poly(2,5-furyleneethylene). The obtained poly(2,5-thienyleneethylene) is soluble in chloroform above 60 °C. It is a semicrystalline polymer and displays a glass transition at around 25 °C and a melting transition at around 160 °C. The synthesized poly(2,5-furyleneethylene) is insoluble in tetrahydrofuran, chloroform, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) at room temperature and only swells in DMF and DMOS above 100 °C. Solid-state NMR studies show that the poly(2,5-furyleneethylene) is cross-linked. The poly(2,5-furyleneethylene) is also a semicrystalline polymer exhibiting a glass transition at around 20 °C and a melting transition at around 110 °C. Solution polymerizations of 2,5-dimethylene-2,5-dihydrothiophene and 2,5-dimethylene-2,5-dihydrofuran were also carried out, respectively, in THF to yield poly(2,5-thienyleneethylene) and poly(2,5-furyleneethylene). Finally, the relative merits for the polymerization of 2,5-dimethylene-2,5-dihydrothiophene and 2,5-dimethylene-2,5-dihydrofuran by both methods are compared.

Introduction

Preparation of poly(*p*-xylylene) and substituted poly(*p*-xylylene) film by the vacuum pyrolysis of di-*p*-xylene and substituted di-*p*-xylene was first reported by Gorham in 1996.[1] Thereafter, extensive studies[2−4] have been underway on either the chemistry of the polymerization or the properties and applications of the paralene polymers formed by the vacuum pyrolysis process. Besides di-*p*-xylylene, a limited number of highly ring strain substituted compounds, such as octafluoro[2.2]paracyclophane,[5] [2.2]-(2,5)-thiophenophane,[6] 1,9-dichloro[2.2]paracyclophane,[7] and dispiro[2.2.2.2]-deca-4,9-diene,[8] have been subjected to vapor deposition polymerization to form poly(tetrafluoro-*p*-xylene), poly(2,5-thienyleneethylene), poly(1,4-phenylenechloroethylene), and poly(1,4-phenylene-1,2-dimethylethylene) films, respectively. From a practical perspective, this polymerization technique has been well established and widely utilized in the area where vacuum deposition of a polymer plays a prominent role. This methodology has been used recently by Moore et al. to generate organic polymer films with a low dielectric constant for microelectronic interconnection applications.[9−12]

Recently, Chou et al.[13,14] reported the vapor phase pyrolysis of (5-methyl-2-thienyl)methyl benzoate **(1)** and (5-methyl-2-furyl)methyl benzoate **(2)** to form 2,5-dimethylene-2,5-dihydrothiophene **(3)** and 2,5-dimethylene-2,5-dihydrofuran **(4)**. The generated compounds **3** and **4** are known to behave chemically as diradicals **(5, 6)** and undergo cyclization to form mostly cyclic dimers and trimers in THF in the presence of hydroquinone (Scheme 1).[15−17] Compounds **3** and **4** are ideal monomers for vapor deposition polymerization.

In this study, we synthesize poly(2,5-thienylethylene) and poly(2,5-furyleneethylene) by vapor deposition and solution polymerizations of 2,5-dimethylene-2,5-dihydrothiophene and 2,5-dimethylene-2,5-dihydrofuran as prepared by vapor phase pyrolysis of (5-methyl-2-thienyl)methyl benzoate and (5-methyl-2-furyl)methyl benzoate. Also, the chemical structures and thermal properties of the obtained polymers are characterized by IR, NMR, differential scanning calorimetry, and X-ray diffraction.

Experimental Section

Materials. 5-Methylthiophene-2-carbaldehyde, 5-methyl-2-furfural, lithium aluminum hydride, and benzoyl chloride were obtained from Tokyo Kaisei Inc. and used as received. Tetrahydrofuran (THF) used in the reduction and polymerization was distilled in a nitrogen atmosphere over sodium benzophenone ketyl just before use. 2,2′-Azobis(isobutyronitrile) (AIBN; Fluka) was freshly recrystallized from methanol.

Techniques. ^{1}H and ^{13}C NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer and infrared spectra were measured with a Nicolet 520 FT-IR spectrometer. Elemental analysis was determined using a Heraeus elementary analyzer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were 10 °C/min. Thermogravimetric analysis was performed on a Seiko TG/DTA 200 thermal analyzer at 10 °C/min. The thermal decomposition temperature (T_d) was read at a temperature at which 5% weight loss occurred. Gel permeation chromatog-

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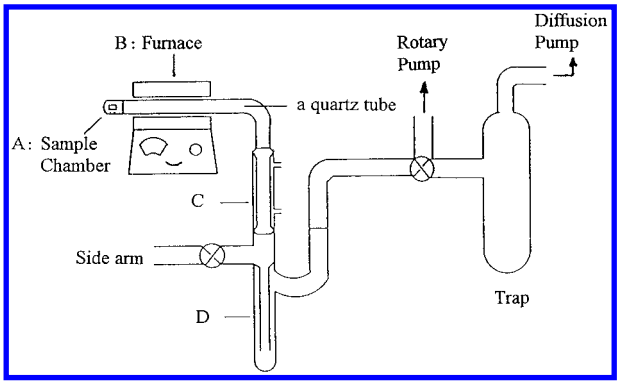
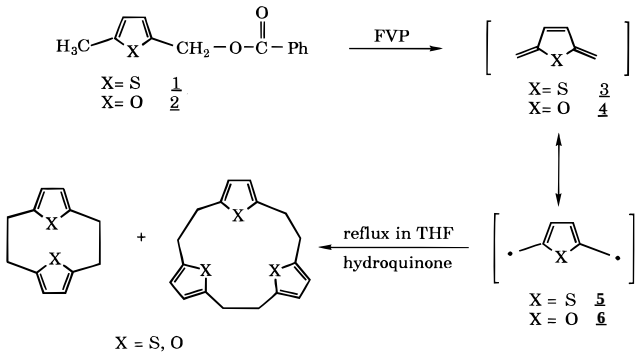


Figure 1. Apparatus for the vapor deposition polymerization: A, sample chamber; B, 800-W furnace; C, ice-water-cooled condenser; D, liquid-nitrogen-cooled deposition chamber.

Scheme 1



raphy (GPC) was run on an Applied Biosystems 400 LC instrument equipped with a differential refractometer, a UV detector, and a set of PL gel columns of 10^2, 5×10^2, 10^3, and 10^4 Å. The molecular weight calibration curve was obtained by using standard polystyrenes. X-ray diffraction measurements were taken with nickel-filtered Cu Kα radiation with a Rigaku powder diffractometer.

Synthesis of (5-Methyl-2-thienyl)methyl Benzoate (1) and (5-Methyl-2-furyl)methyl Benzoate (2). Both **1** and **2** were prepared from 5-methylthiophene-2-carbaldehyde and 5-methyl-2-furfural according to the synthetic procedures reported in the literature.[13,14]

Synthesis of 2,5-Dimethylene-2,5-dihydrothiophene (3) and 2,5-Dimethylene-2,5-dihydrofuran (4). Compounds **3** and **4** were prepared by the flash vacuum pyrolysis method[13,14] using the apparatus shown in Figure 1.

Vapor Deposition Polymerization of 2,5-Dimethylene-2,5-dihydrothiophene (Runs 1−5) and 2,5-Dimethylene-2,5-dihydrofuran (Runs 10−14). Vapor deposition polymerizations of 2,5-dimethylene-2,5-dihydrothiophene and 2,5-dimethylene-2,5-dihydrofuran were carried out, respectively, under a pressure of 2×10^{-3} Torr at temperatures of −78, −25, 0, 20, and 60 °C (see Tables 1 and 5). Run 3 is described below.

Compound **1** (1.0 g, 4.31 mmol) was pyrolyzed at 650 °C in the normal manner to form 2,5-dimethylene-2,5-dihydrothiophene, which was trapped in the liquid-nitrogen-cooled deposition chamber. After the pyrolysis was completed, the deposition chamber was warmed to 0 °C and then maintained under vacuum for 6 h. The polymeric film was subsequently formed in the deposition chamber. A large quantity of THF (0 °C) was introduced into the deposition chamber through the sidearm to stop the polymerization. Finally, the polymeric film was peeled from the wall, washed twice with THF, and dried at 100 °C under vacuum.

Solution Polymerizations of 2,5-Dimethylene-2,5-dihydrothiophene (Runs 6−9) and 2,5-Dimethylene-2,5-dihydrofuran (Runs 15−19). Runs 6−9 and 15−19 were carried out using a similar procedure. The reaction conditions are reported in Tables 3 and 7. The detailed synthetic procedure for run 19 is described below.

Scheme 2

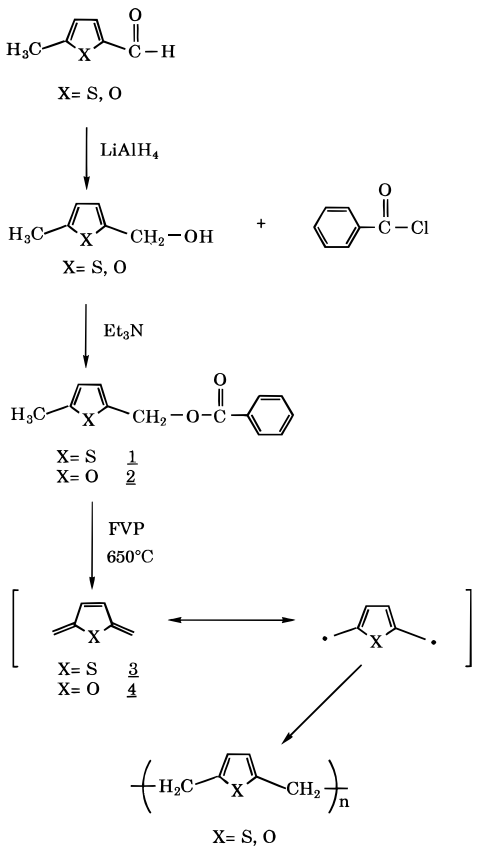


Table 1. Vapor Deposition Polymerization of 2,5-Dimethylene-2,5-dihydrothiophene

run	polym temp (°C)	time (h)	yield (%)
1	−78	6	0
2	−25	6	53
3	0	6	68
4	20	6	78
5	60	6	70

Compound **2** (1.0 g, 4.63 mmol) was pyrolyzed at 650 °C in the normal manner to form 2,5-dimethylene-2,5-dihydrofuran, which was trapped in the liquid-nitrogen-cooled deposition chamber. After the pyrolysis was completed, 10 mL of THF was introduced into the trap through a sidearm. The liquid-nitrogen-cooled deposition chamber was gradually warmed to room temperature. AIBN (3.0 mg) was added to the solution obtained, which was then heated to 60 °C for 15 h under a nitrogen atmosphere. The solution was cooled to room temperature, and the polymer began to precipitate. The precipitated product was recovered by filtration, washed twice with THF, and dried under vacuum at 70 °C. The product obtained was extracted with THF to 60 °C to yield soluble (19B) and insoluble (19A) fractions.

Results and Discussion

Vapor Deposition Polymerization of 2,5-Dimethylene-2,5-dihydrothiophene (Runs 1−5). Vapor deposition polymerization of monomer **3** was carried out under a pressure of 2×10^{-3} Torr at temperatures of −78, −25, 0, 20, and 60 °C. The experimental results are summarized in Table 1. When **3** was polymerized at −78 °C (run 1), no polymer was obtained. When the temperature was raised to −25 °C (run 2), a colorless transparent film was obtained in the deposition chamber with a yield of 53.2%. The total conversion to polymers increased basically as the polymerization temperature increased. However, the maximum yield was obtained at 20 °C.

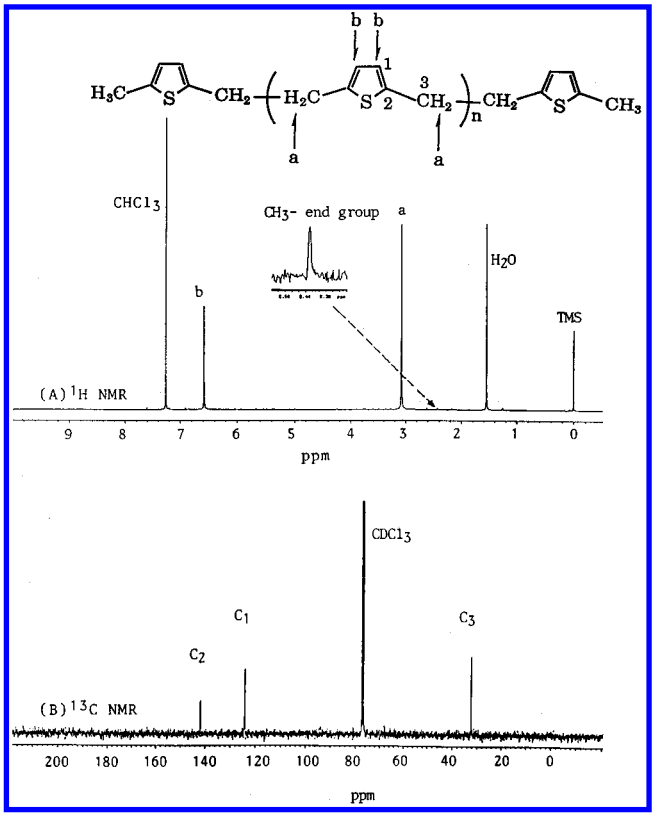


Figure 2. (A) ^{1}H NMR ($CDCl_3$) spectrum and (B) ^{13}C NMR ($CDCl_3$) spectrum of the polymer film obtained in run 2 of Table 1.

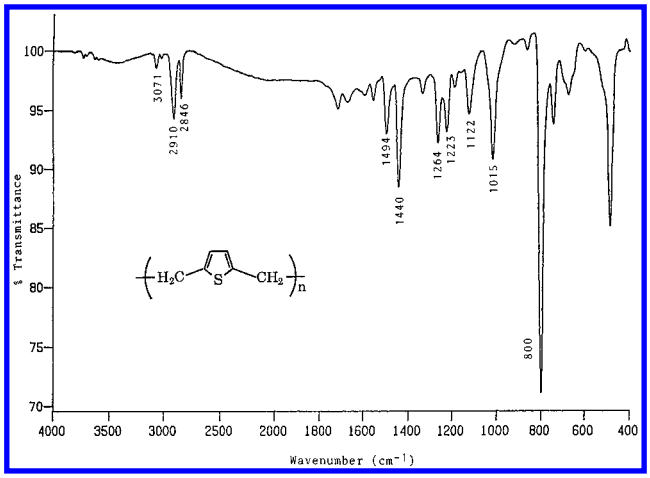


Figure 3. FT-IR spectrum of the poly(thienyleneethylene) film obtained in run 2 of Table 2.

The tough films obtained in the deposition chamber were soluble in chloroform at 60 °C. Figures 2A and 2B show respectively the ^{1}H and ^{13}C NMR spectra of the polymers obtained from run 2. Figure 2A exhibits a singlet peak at 3.08 ppm due to the methylene protons, a singlet peak at 6.58 ppm due to the protons on the thiophene rings, and a small singlet peak at 2.43 ppm due to chain end methyl protons, while Figure 2B displays three carbon peaks at 32.30, 124.11, and 141.80 ppm. The NMR data demonstrate a perfectly linear poly(2,5-thienyleneethylene) structure. The number-average molecular weights of the obtained polymers were determined according to the relative intensity of the end-group methyl protons peak and the methylene protons peak. Figure 3 presents the IR spectrum of poly(2,5-thienyleneethylene). Table 2 summarizes the molecular weights and the thermal analysis results of

Table 2. Characterization of Polymers Obtained in Runs 2−5

		DSC (°C)		TG (°C)
run	$\bar{M}_n$[a]	T_g	T_m	T_d[b]
2	10738	26	162	398
3	19945	28	163	402
4	15611	23	160	390
5	12267	24	169	393

[a] Data obtained from the ^{1}H NMR end-group analysis. [b] T_d = temperature at which weight loss of 5% occurred.

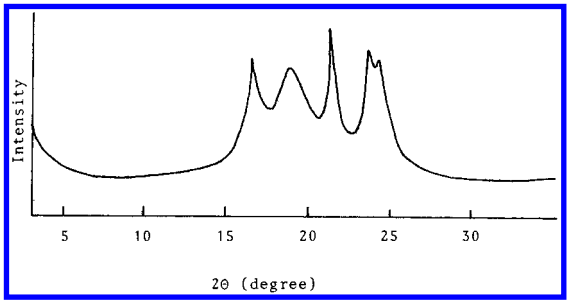


Figure 4. X-ray diffraction diagram of the poly(thienyleneethylene) film obtained in run 2 of Table 1.

Table 3. Solution Polymerization of 2,5-Dimethylene-2,5-dihydrothiophene

run	concn (g/mL)	polym temp (°C)	reacn time (h)	yield (%)
6	0.016	20	15	64.1
7	0.024	20	15	55.0
8	0.048	20	15	59.1
9	0.024	0	15	2.5

all polymers obtained. All polymers exhibit, respectively, a glass transition at around 25 °C and a melting temperature at around 160 °C. The prepared poly(2,5-thienyleneethylene) is obviously a semicrystalline material, which was further verified by X-ray diffraction measurement (Figure 4). Comparing the thermal behavior of the synthesized poly(2,5-thienyleneethylene) with that (T_g = 80 °C, T_m = 400 °C) of poly(*p*-xylene)[1] apparently reveals that both polymers are semicrystalline in nature. However, poly(2,5-thienyleneethylene) exhibits much lower glass transition and melting temperatures than poly(*p*-xylylene).

Solution Polymerization of 2,5-Dimethylene-2,5-dihydrothiophene (Runs 6−9). 2,5-Dimethylene-2,5-dihydrothiophene was also polymerized in THF at 0 and 20 °C, and the experimental results (Table 3) were used to compare with those of the polymers obtained by vapor deposition polymerization. At 0 °C, most of the monomer **3** was converted to cyclic dimers and trimers. The total conversion to polymer was only 2.5%. When the polymerization temperature was raised to 20 °C, the polymer yields were higher than 55%. The number-average molecular weights of the polymers were also measured by ^{1}H NMR end-group analysis. According to those results, the number-average molecular weights of the obtained polymers increased as the monomer concentration increased. Again, both ^{1}H and ^{13}C NMR spectra also verified the polymers obtained by solution polymerization were perfectly linear poly(2,5-thienyleneethylene).

Comparing results obtained by solution polymerization and vapor deposition polymerization reveals that a higher polymer yield can be obtained by vapor deposition polymerization. However, better control of the molecular weight can be achieved by solution polymerization. Table 4 summarizes the thermal analysis results of the polymers obtained in runs 6−9. The

Table 4. Characterization of Polymers Obtained in Runs 6−9

		DSC (°C)		TG (°C)
run	$\bar{M}_n$[a] ($\times 10^{-4}$)	T_g	T_m	T_d[b]
6	0.86	18	166	406
7	1.24	21	164	404
8	1.53	23	163	390
9	1.27	19	164	402

[a] Data obtained from the ^{1}H NMR end-group analysis. [b] T_d = temperature at which weight loss of 5% occurred.

Table 5. Vapor Deposition Polymerization of 2,5-Dimethylene-2,5-dihydrofuran

run	polym temp (°C)	polym time (h)	yield (%)
10	−78	6	0
11	−25	6	18.2
12	0	6	74.3
13	20	6	61.2
14	60	6	53.6

polymers show a quite similar thermal behavior to those obtained in runs 1−5.

Vapor Deposition Polymerization of 2,5-Dimethylene-2,5-dihydrofuran (Runs 10−14). Vapor deposition polymerization of **4** was also carried out under a pressure of 2×10^{-3} Torr at temperatures of −78, −25, 0, 20, and 60 °C. The experimental results are summarized in Table 5. When polymerization was carried out at −78 °C (run 10), no polymer was obtained. When the polymerization temperature was raised to −25 °C (run 11), a colorless transparent film was obtained in the deposition chamber with 18.2% yield. The total conversion to polymers increased as the polymerization temperature increased from −25 to 0 °C. The maximum yield was obtained at 0 °C.

The tough films obtained in the deposition chamber were insoluble in tetrahydrofuran, chloroform, DMF, and DMSO at room temperature and only swelled in DMF and DMSO above 100 °C. Measurements of the molecular weights were not possible owing to the polymer's poor solubility. Figure 5 shows the solid-state ^{13}C NMR spectrum of the polymer obtained. As indicated in this figure, the C_1 and C_1' resonances are clearly resolved at 106.4 and 107.5 ppm, respectively. This occurrence seems to imply that the obtained polymer is cross-linked.

Table 6 summarizes the thermal analysis results of all obtained polymers. The polymers obtained by vapor deposition polymerization display, respectively, a glass transition at around 20 °C followed by a melting transition at around 110 °C on the DSC heating scan. It is also a semicrystalline material, which was further verified by X-ray diffraction measurement.

Solution Polymerization of 2,5-Dimethylene-2,5-dihydrofuran (Runs 15−19). Solution polymerization of **4** was carried out in THF with or without AIBN. The experimental results are summarized in Table 7. Both runs 15 and 16 were carried out in THF without AIBN. Under these polymerization conditions, most of the pyrolysis product **4** was converted to cyclic dimers and trimers.[13] The total conversion to polymer was only around 25%. The polymer yield slightly increased with a decrease in the added amount of THF. Runs 17−19 were carried out in THF in the presence of AIBN. The polymer yield increased monotonically with an increase in the added amount of AIBN.

The obtained polymers were further fractionated into hot THF (60 °C) insoluble fractions 15A−19A and soluble fractions 15B−19B. The weight percentages of

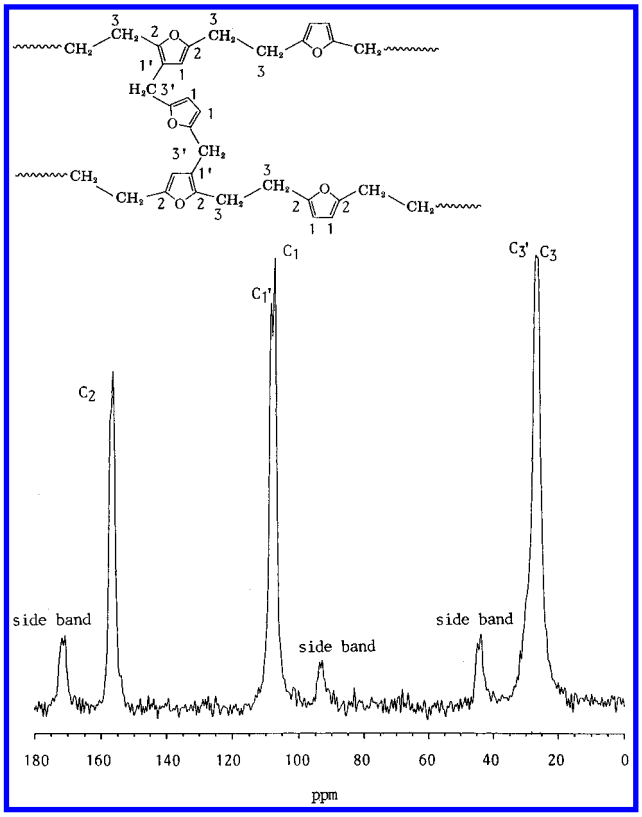


Figure 5. Solid-state ^{13}C NMR spectrum of the polymer film obtained in run 12 of Table 5.

Table 6. Characterization of Polymers Obtained in Runs 11−14

		DSC (°C)		TG (°C)
run	polym temp (°C)	T_g	T_m	T_d[a]
11	−25	23	120	372
12	0	27	103	362
13	20	21	109	370
14	60	22	113	364

[a] T_d = temperature at which weight loss of 5% occurred.

Table 7. Solution Polymerization of 2,5-Dimethylene-2,5-dihydrofuran[a]

			yield (%)		
run	concn (g/mL)	AIBN (mg)	total[b]	frac A	frac B
15	0.044		28.0	10.2	17.8
16	0.022		25.5	9.5	16.0
17	0.044	3	39.7	11.5	28.2
18	0.044	6	49.3	13.9	35.4
19	0.044	12	52.2	16.1	36.1

[a] Fraction A: hot THF (60 °C) insoluble fraction; fraction B: hot THF (60 °C) soluble fraction; reaction temperature: 60 °C; reaction time: 15 h. [b] Total = fraction A + fraction B.

hot THF soluble fractions increased with increasing added AIBN. Figures 6A and 6B present the ^{1}H and ^{13}C NMR spectra of 15B. Both spectra prove that fraction 15B is a perfectly linear poly(2,5-furyleneethylene). The molecular weight of 15B was determined by GPC to be 2.24×10^4 using hot THF as an eluent and standard polystyrenes as references. According to Table 8, the hot THF soluble fractions show higher molecular weights and lower polydispersity values in the cases when AIBN was added in the polymerization. The solid-state ^{13}C NMR spectrum of the hot THF insoluble fraction (15A) is quite similar to that in Figure 4. This observation seems to suggest that polymer 15A is cross-linked.

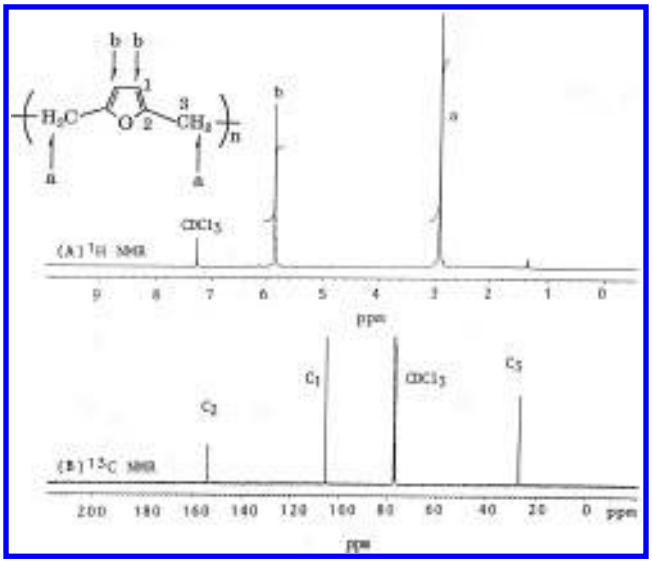


Figure 6. (A) ^1H NMR ($CDCl_3$) spectrum and (B) ^{13}C NMR ($CDCl_3$) spectrum of the hot THF-soluble fraction obtained in run 19 of Table 7.

Table 8. Characterization of Polymers Obtained in Runs 15 and 16

				DSC (°C)		TG (°C)
run	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$	T_g	T_m	T_d[a]
15A				22	105	342
15B	8.03	2.24	3.59	20	103	329
16A				23	110	330
16B	9.08	2.81	3.23	21	102	325
17A				25	114	354
17B	9.22	3.57	2.58	26	120	338
18A				31	109	326
18B	9.17	3.79	2.42	28	118	355
18A				25	118	334
19B	7.56	3.52	2.15	22	121	350

[a] T_d = temperature at which weight loss of 5% occurred.

Comparing results obtained by vapor deposition and solution polymerizations seems to suggest that vapor deposition polymerization of 2,5-dimethylene-2,5-dihydrofuran yields only a cross-linked polymer while solution polymerization of 2,5-dimethylene-2,5-dihydrofuran forms primarily a linear polymer.

Table 8 lists the thermal transitions of the hot THF soluble and insoluble fractions obtained in runs 15−19. The THF insoluble fractions show slightly higher glass transition temperatures and melting points than those of the THF soluble fractions. Eventually, all fractions reveal a quite similar thermal behavior to those of polymers obtained in vapor deposition polymerization (runs 10−14).

Conclusions

(5-Methyl-2-thienyl)methyl benzoate and (5-methyl-2-furyl)methyl benzoate have been subjected to vapor phase pyrolysis at 650 °C to produce 2,5-dimethylene-2,5-dihydrothiophene **(3)** and 2,5-dimethylene-2,5-dihydrofuran **(4)**. The obtained compounds **3** and **4** are able to be spontaneously polymerized on condensation at a temperature higher than −25 °C to form tough polymeric films. The prepared poly(2,5-thienyleneethylene) film has been proven to be a perfectly linear polymer, while the obtained poly(2,5-furyleneethylene) film has been verified by solid-state NMR spectroscopy to be cross-linked. Solution polymerizations of both **3** and **4** primarily yield, respectively, the perfectly linear poly(2,5-thienyleneethylene) and poly(2,5-furyleneethylene). The synthesized poly(2,5-thienyleneethylene) and poly(2,5-furyleneethylene) are semicrystalline in nature, and they exhibit much lower glass transition and melting temperatures than poly(*p*-xylylene).

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