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Novel Poly[3-(*p*-substituted)benzoyl-2,5-thiophenes] via Nickel(0)-Catalyzed Coupling Polymerization

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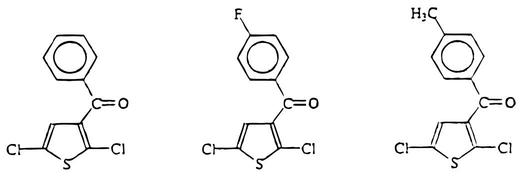
ABSTRACT: Three novel poly[3-(*p*-substituted)benzoyl-2,5-thiophene]s (**Ib**, **IIb**, and **IIIb**) were successfully prepared via nickel(0)-catalyzed coupling polymerization of 3-benzoyl-2,5-dichlorothiophene (**Ia**), 3-(*p*-fluoro)benzoyl-2,5-dichlorothiophene (**IIa**), and 3-(*p*-toluoyl)-2,5-dichlorothiophene (**IIIa**). To our knowledge, monomers (**IIa**) and (**IIIa**) are new compounds. On the basis of K and α values from the Mark−Houwink relationship, the $\langle M_v \rangle$ of the polymers were in the range 1.50×10^5 to 3.51×10^5 g/mol. The α value equal to 0.97 is close to unity indicating that the $\langle M_v \rangle$ is approximately equal to the $\langle M_w \rangle$. The high molecular weight polymers were soluble in common organic solvents. Their glass transition temperatures were all above 160 °C and showed no evidence of crystallinity by differential scanning calorimetry. All three polymers were thermally and thermooxidatively stable with 10% weight loss in nitrogen and air occurring above 430 °C. The UV−vis absorption λ_{max} for the three polymers greater than 465 nm is a further evidence of the high molecular weight and the long effective conjugation length.

1. Introduction

Substituted polythiophene derivatives are of considerable interest due to their unique combinations of electrical and electrooptical properties, thermal stability, and structural versatility.[1−3] The structures of the starting materials, the synthetic methods, the physical treatments, and the chemical modifications can significantly impact the performance of these materials. Hence, there is the possibility to produce tailor-made polythiophenes with properties for specific applications including electroluminescent devices, batteries and sensors, and electromagnetic interference shielding materials.[1−4]

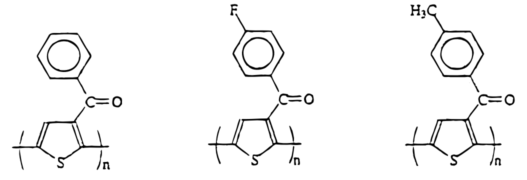
A number of chemical and electrochemical routes for synthesizing polythiophene and its derivatives have been described in the literature.[1−6] These include electrochemical polymerization, chemical polymerization with an oxidant such as iron trichloride, and polymerization by metal-catalyzed coupling of 2,5-dihalothiophenes. Our interest is in the latter, specifically nickel(0)-catalyzed coupling polymerization of 3-substituted-2,5-dichlorothiophenes. Previously, Yamamoto et al.[7,8] described. Ueda et al.[9] showed this method is suitable for the synthesis of poly(3-phenyl-2,5-thiophene) without the irregular coupling or branching sometimes seen in conventional electrochemical and chemical polymerization. We will utilize this technique to produce novel, functionalized poly(3-benzoyl-2,5-thiophene) and its derivatives (Figure 1). The solubility, thermal and thermooxidative stabilities, and film-forming ability of these materials will be discussed. In addition, UV−vis analysis will be utilized as an initial evaluation of the spectral properties and effective conjugation length. Our interest in the benzoylated materials was furthered by the synthetic work of Marrocco et al.[10] and the electrooptical studies of Okamoto et al.[11] of poly(benzoyl-1,4-phenylene) (PBP), the phenylene analogue of our materials.[12] Blue light-emitting diodes were successfully fabricated from PBP. In a future publication, the electrical and electrooptical properties of our polythiophenes will be reported. However, in this initial paper, we report the successful synthesis and characterization of high molecular weight poly(3-benzoyl-2,5-thiophene) (**Ib**),[13] poly [3-(*p*-fluoro)benzoyl-2,5-thiophene] (**IIb**),[14] and poly[3-(*p*-toluoyl)-2,5-thiophene] (**IIIb**).[14]

(a). Structures of Three Monomers



3-Benzoyl-2,5-dichlorothiophene (**Ia**)
3-(*p*-Fluoro)benzoyl-2,5-dichlorothiophene (**IIa**)
3-(*p*-Toluoyl)-2,5-dichlorothiophene (**IIIa**)

(b). Structures of Three Polymers



Poly(3-benzoyl-2,5-thiophene) (**Ib**)
Poly[3-(*p*-fluoro)benzoyl-2,5-thiophene] (**IIb**)
Poly(3-*p*-toluoyl-2,5-thiophene) (**IIIb**)

Figure 1. Structures of monomers and polymers.

2. Experimental Section

2.1. Materials. All reagents were purchased from Aldrich and used as received except when reported. Bipyridine (99+%) and triphenylphosphine (99%) were purified by recrystallization from ethanol and dried under vacuum for 12 h at room temperature. Powdered (−100, +325 mesh) zinc (99.999%) was purchased from Cerac Specialty Inorganics and used as received. Benzoyl chloride (98%), methanol (reagent grade),

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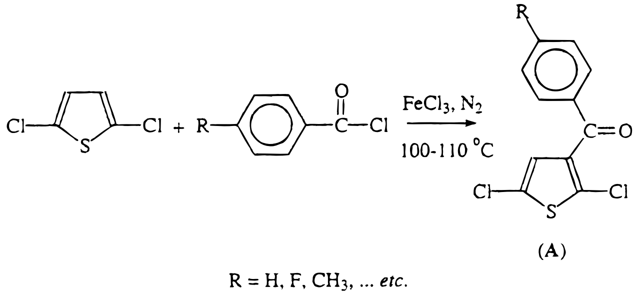
Scheme 1



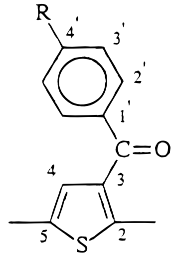
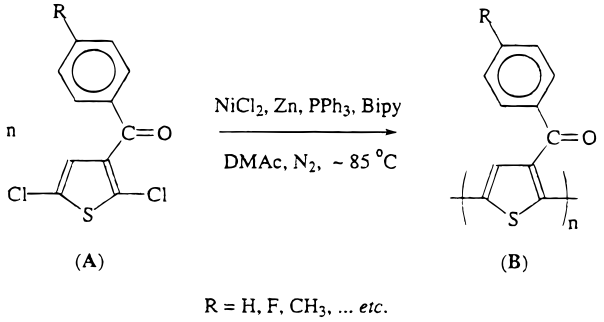

R = (**I**): H; (**II**): F; (**III**): CH$_3$

Figure 2. Labeling structure for NMR spectra.

Scheme 2



tetrahydrofuran (THF, HPLC grade), and sodium iodide were purchased from Fisher and used without further purification. Ultradry anhydrous nickel chloride (99.99%) (Alfa) and *N*-methyl-2-pyrrolidinone (NMP, HPLC grade) (Sigma-Aldrich) were also used as received.

2.2. Analytical Methods. A Bruker DRX-400 nuclear magnetic resonance spectrometer was utilized to perform ^{1}H, ^{13}C, and 2D NMR experiments. A Varian GC fitted with a Finnigan Mat Magnum mass spectrometer was used for monomer identification and purity examination. A high-resolution Kratos MS-50 mass spectrometer was used to further confirm the molar masses of **Ia**−**IIIa**. The glass transition temperatures and the melting point of **IIIa** were determined using a Perkin-Elmer Pyris Series 1 DSC. The T_g values reported were obtained from the inflection point of the second heating curve and the T_m value of **IIIa** was obtained from the peak value at a heating rate of 20 °C/min. Thermogravimetric analysis was performed on a Perkin-Elmer Pyris Series TGA-7. The molecular weights and molecular weight distributions were determined with a Waters gel permeation chromatograph and a Wyatt MiniDAWN laser light scattering system (GPC−LS online) in THF. The batch light scattering (LS) measurements in NMP were performed also using a Wyatt MiniDAWN system. Viscometry measurements were taken in NMP using a Cannon viscometer (Ubbelohde, 1C/D22) in a constant-temperature bath (Koehler, K234000) at 30.00 ± 0.01 °C. The UV−visible absorption spectra were determined using a Hewlett-Packard HP-8452 Diode Array UV−visible spectrometer with a quartz cell (CHCl$_3$ as a solvent). The FT-IR transmittance spectra were obtained using a BIO-RAD Digilab FTS-7 FTIR spectrometer with a pair of salt plates. Elemental analysis of the monomers and polymers was performed using a Perkin-Elmer model 2400 Series II CHN/S instrument.

2.3. Monomer Synthesis. A typical monomer synthesis is shown in Scheme 1 and follows. To a stirred solution of 2,5-dichlorothiophene (0.1 mol) and iron (III) chloride (0.025 mol) was added the desired benzoyl chloride (0.12 mol). The reactions were heated to 100−110 °C for 4 h and then cooled to room temperature. The products were treated by 5% HCl/H$_2$O, saturated NaCl/H$_2$O, 5% NaOH/H$_2$O, and cold water. After the reaction mixture was stirred with ethanol and decolorizing carbon, the monomers were isolated via rotary-evaporation, drying in a vacuum, and recrystallization from ethanol, then characterized.

3-Benzoyl-2,5-dichlorothiophene (Ia). A yellow liquid was obtained. Yield: 63%. **Ia** was >99% pure by GC. High-resolution MS: *m*/*e* = 255.95161 (calcd, 255.95164) for $C_{11}H_6OS^{35}Cl_2$, $M + 2$ = 257.94866 (calcd, 257.94869) for $C_{11}H_6OS^{35}Cl^{37}Cl$, and $M + 4$ = 259.94614 (calcd, 259.94617) for $C_{11}H_6OS^{37}Cl_2$. The deviation is less than 0.13 ppm. ^{1}H NMR (CDCl$_3$) (refer to Figure 2 for all NMR labels): δ 7.82 [d, 2H (2′)], 7.61 [t, 1H (4′)], 7.49 [t, 2H (3′)], 6.98 [s, 1H (4)]. ^{13}C NMR (CDCl$_3$): δ 188.86 (C=O), 137.04 (C-1′), 136.65 (C-3), 133.65 (C-4′), 130.97 (C-5), 129.88 (C-2′), 128.77 (C-3′), 127.59 (C-4), and 127.17 (C-2); IR: 1654.3 cm^{-1} (C=O stretching). Anal. Calcd for $C_{11}H_6SOCl_2$: C, 51.38; H, 2.35; S, 12.47. Found: C, 51.73; H, 2.54; S, 11.83.

3-(*p*-Fluoro)benzoyl-2,5-dichlorothiophene (IIa). A yellow liquid with some crystals was obtained. Yield: 65%. **IIa** was >99% pure by GC; High-resolution MS: *m*/*e* = 273.94177 (calcd, 273.94222) for $C_{11}H_5FOS^{35}Cl_2$, $M + 2$ = 275.93877 (calcd, 275.93927) for $C_{11}H_5FOS^{35}Cl^{37}Cl$, and $M + 4$ = 277.93554 (calcd, 277.93607) for $C_{11}H_5FOS^{37}Cl_2$. The deviation is less than 1.63 ppm. ^{1}H NMR (CDCl$_3$): δ 7.84 [q, 2H (2′)], 7.15 [t, 2H (3′)], 6.95 [s, 1H (4)]. ^{13}C NMR (CDCl$_3$): δ 187.27 (C=O), 167.25 and 164.85 (C-4′), 136.48 (C-3), 133.30 (C-1′), 132.53 and 132.63 (C-2′), 130.71 (C-5), 127.44 (C-2), 127.38 (C-4), 115.88 and 116.10 (C-3′). IR: 1662.0 cm^{-1} (C=O stretching). Anal. Calcd for $C_{11}H_5FSOCl_2$: C, 48.02; H, 1.83; S, 11.65. Found: C, 48.35; H, 1.90; S, 10.86.

3-(*p*-Toluoyl)-2,5-dichlorothiophene (IIIa). A light yellow powder was obtained. Yield: 61%. Mp: 71.3 °C (peak value). **IIIa** was >99% pure by GC; High-resolution MS: *m*/*e* = 269.96731 (calcd, 269.96729) for $C_{12}H_8OS^{35}Cl_2$, $M + 2$ = 271.96433 (calcd, 271.96434) for $C_{12}H_8OS^{35}Cl^{37}Cl$, and $M + 4$ = 273.96479 (calcd, 273.96476) for $C_{12}H_8OS^{37}Cl_2$. The deviation is less than 0.04 ppm. ^{1}H NMR (CDCl$_3$): δ 7.75 [d, 2H (2′)], 7.29 [d, 2H (3′)], 6.98 [s, 1H (4)], 2.45 [s, 3H (methyl)]. ^{13}C NMR (CDCl$_3$): δ 188.54 (C=O), 144.83 (C-4′), 137.05 (C-3), 134.50 (C-1′), 130.50 (C-5), 130.19 (C-2′), 129.55 (C-3′), 127.62 (C-4), 127.19 (C-2), 22.00 (methyl). IR: 1656.3 cm^{-1} (C=O stretching). Anal. Calcd for $C_{12}H_8OSCl_2$: C, 53.15; H, 2.97; S, 11.82. Found: C, 53.28; H, 2.94; S, 11.62.

2.4. Polymer Synthesis. The polymerization reactions are described in Scheme 2. A detailed description of the synthesis of polymer **Ib** follows. Into a 250 mL three-necked pear flask equipped with an overhead stirrer, a nitrogen inlet, and a gas outlet were added **Ia** (7.45 g, 2.9×10^{-2} mol), nickel chloride (0.28 g, 2.175×10^{-3} mol), zinc (6.06 g, 8.99×10^{-2} mol), triphenylphosphine (7.61 g, 2.9×10^{-2} mol), bipyridine (0.34 g, 2.175×10^{-3} mol), and *N*,*N*-dimethylacetamide (DMAc) (12 mL) under nitrogen. The reactions were stirred at 85 °C for 4 h. Sodium iodide (9.78 g, 6.525×10^{-2} mol) was added and the reaction allowed to stir for an additional 2 h. In each case, the very viscous gels produced were diluted with four times the original amount of DMAc. The products were precipitated into a large excess of 20% HCl/methanol solution. The dark red solids that remained were washed with methanol, water, and methanol sequentially, collected and dried under vacuum at 100 °C for 12 h. The yields of the polymers after complete workup were greater than 90%.

Poly(3-benzoyl-2,5-thiophene) (Ib). ^{1}H NMR (CDCl$_3$): δ ~7.80 (2′), ~7.57 (4′), ~7.40 (3′), ~6.99 (4). ^{13}C NMR (CDCl$_3$): δ ~191.2 (C=O), ~140.2 (C-3), ~137.4 (C-1′), ~133.7 (C-4′), ~132.8 (C-5), ~131.2 (C-2), ~130.1 (C-2′), ~129.6 (C-4), ~128.7 (C-3′). IR: 1653.1 cm^{-1} (C=O stretching). Anal. Calcd for $(C_{11}H_6SO)_n$: C, 70.94; H, 3.23; S, 17.21. Found: C: 71.66, H: 3.67, S: 14.67.

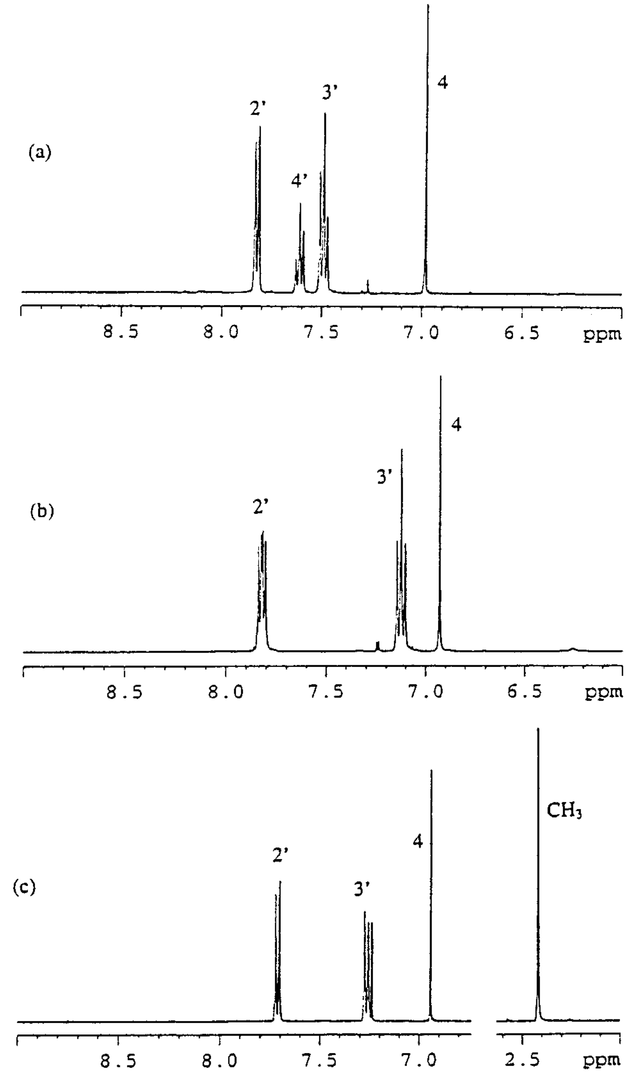


Figure 3. ^{1}H NMR of monomers: (a) **Ia**; (b) **IIa**; (c) **IIIa**.

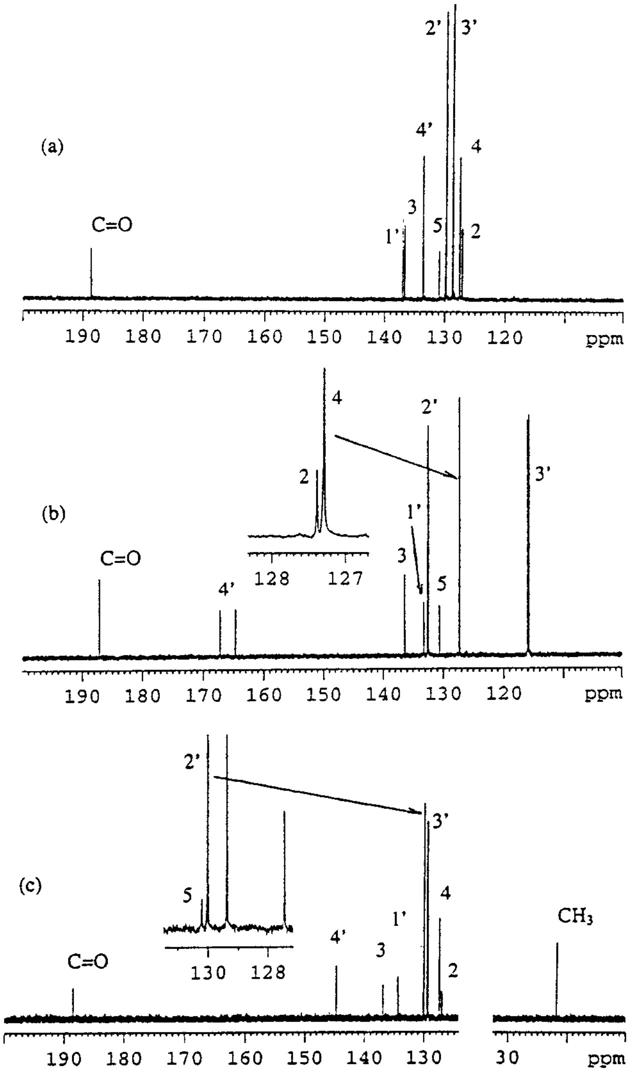


Figure 4. ^{13}C NMR of monomers: (a) **Ia**; (b) **IIa**; (c) **IIIa**.

Poly[3-(*p*-fluoro)benzoyl-2,5-thiophene] (IIb). ^{1}H NMR ($CDCl_3$): δ ~7.80 (2′), ~7.12 (3′), ~6.93 (4). ^{13}C NMR ($CDCl_3$): δ ~189.66 (C=O), 164.95 and 167.30 (C-4′), ~140.01 (C-3), ~136.95 (C-1′), ~133.73 (C-5), ~132.42 (C-2′), ~131.15 (C-2), ~128.71 (C-4), ~115.85 (C-3′). IR: 1652.9 cm^{-1} (C=O stretching). Anal. Calcd for $(C_{11}H_5FSO)_n$: C, 64.71; H, 2.45; S, 15.69. Found: C, 66.90; H, 3.09; S, 13.35.

Poly(3-toluoyl-2,5-thiophene) (IIIb). ^{1}H NMR ($CDCl_3$): δ ~7.66 (2′), ~7.23 (3′), ~6.98 (4), ~2.40 (methyl). ^{13}C NMR ($CDCl_3$): δ ~190.97 (C=O), ~144.56 (C-4′), ~137.20 (C-3), ~134.71 (C-1′), ~132.21 (C-5), 130.83 (C-2), ~130.22 (C-2′), ~129.35 (C-3′), ~128.49 (C-4), ~21.86 (methyl). IR: 1652.9 cm^{-1} (C=O stretching). Anal. Calcd for $(C_{12}H_8SO)_n$: C, 71.96; H, 4.03; S,16.01. Found: C, 73.17; H, 4.49; S, 14.00.

3. Results and Discussion

3.1. Synthesis and Characterization of Monomers. The choice of monomers was based upon the previous indication from polyphenylene-based materials[12] that the benzoyl sidegroup was sufficient to give amorphous, soluble polymers. In addition, it was necessary that the substituents on the phenylene ring be compatible with the nickel catalyst to be utilized. For these purposes, 3-benzoyl-2,5-dichlorothiophene (**Ia**), 3-(*p*-fluoro)benzoyl-2,5-dichlorothiophene (**IIa**), and 3-(*p*-toluoyl)-2,5-dichlorothiophene (**IIIa**) were chosen. All three monomers were synthesized by the iron(III) chloride catalyzed acylation of 2,5-dichlorothiophene with unsubstituted and substituted benzoyl chlorides (Scheme 1). Although some of each monomer was lost in undesired polymerization during the reaction and during work up and purification, a yield of 60−65% was obtained. This is a significant improvement over previously reported results[15,16] for 3-benzoyl-2,5-dichlorothiophene, in which 26.2 and 13.5% yields were obtained. To our knowledge, this is the first report of monomers **IIa** and **IIIa**.

The chemical structures of the monomers were verified by NMR (refer to Figure 2 for all NMR labels). In ^{1}H NMR (Figure 3), the hydrogen on the thiophene ring at δ 6.95, which remains unchanged for all three derivatives, is clearly identified. Other key features in the spectra include the doublets splitting into quartet and triplet affected by fluorine[17] in monomer **IIa** (Figure 3b), the singlet of methyl hydrogens of **IIIa** at δ 2.45 (Figure 3c), and the correct integration ratios of all three monomers. ^{13}C NMR was also used to verify the structures (Figure 4). Correct assignments were made with the aid of 2D NMR. The carbonyl carbons of the three monomers were found at $\delta \sim 188$. The carbon bound to fluorine in monomer **IIa** appears as a doublet at δ 167.4 and 164.7 (Figure 4b). The carbon of the methyl group in monomer **IIIa** gave a signal at δ 22.0 (Figure 4c). All intensities of the carbon signal for these monomers were reasonable. The purity of the mono-

Table 1. Effects of Polymerization Conditions

entry	polymers	*T* (°C)	*t* (h)	$NiCl_2$	Bipy	PPh_3	DMAc	NaI	yield (%)	[η]^a (dL/g)	T_g (°C)	10% wt loss (°C)^b
1	**Ib**	80	6 (6)^c	0.1^d	0.1^d	0.4^d	12.5^d	3.0^d	78	0.031	138.5	402.5
2	**Ib**	85	6 (2)	0.075	0.075	1.0	4.5	3.0	90.6	0.132	167.4	462.1
3	**Ib**	85	5 (0)	0.075	0.075	1.0	5.0		93.6	0.15	155.1	463.7
4	**Ib**	85	5 (0)	0.075	0.075	1.0	5.0		92.3	0.128	142.6	449.1
5	**Ib**	85	6 (2)	0.075	0.075	1.0	4.5	3.0	95.7	0.138	157.5	457.4
6	**Ib**	90	8 (2)	0.1	0.1	1.5	4.5	3.0	87	0.065	147	447.4
7	**Ib**	100	5 (2)	0.075	0.075	1.0	5.0	3.0	98.7	insoluble	127	387.1
8	**Ib**	100	5 (0)	0.075	0.075	1.0	5.0		99.9	insoluble	153.8	389.3
9	**IIb**	80	24 (17)	0.075	0.075	1.0	5.0	3.0	80.3	insoluble	149	393.3
10	**IIb**	85	7 (2)	0.075	0.075	1.0	5.0	3.0	93	0.145	146.6	421.4
11	**IIb**	85	7 (2)	0.075	0.075	1.0	4.5	3.0	93.3	0.14	137.3	445.5
12	**IIb**	85	6.5 (2)	0.075	0.075	1.0	4.5	3.0	97.7	0.325	170.2	463.5
13	**IIIb**	85	8 (2)	0.075	0.075	1.0	5.0	3.0	90	0.114	164.1	425
14	**IIIb**	85	7.5 (2)	0.075	0.075	1.0	4.5	3.0	95	0.365	150	437.5
15	**IIIb**	90	18 (2)	0.075	0.075	1.0	8.0	3.0	83	0.105	140	397

[a] Measured in *N*-methyl-2-pyrrolidnone (NMP) at 30.0 °C. [b] Determined in N_2 environment. [c] The values in parentheses are the time (hours) after added NaI in to the completion of the polymerization. [d] All are molar ratios based on the monomer as 1.0.

mers was confirmed by GC−MS, which showed only one peak from gas chromatography for each monomer and the characteristic molecular ion and fragment peaks for **Ia**−**IIIa** in the mass spectra. Additionally, the high-resolution mass spectrometry gave the expected molecular ion peak values, $M + 2$ and $M + 4$ values, which were almost equal to the calculated values with very small deviations of 0.04−1.63 ppm. Furthermore, the elemental analysis confirmed the chemical compositions of the three monomers.

3.2. Synthesis of Poly[3-(*p*-substituted)benzoyl-2,5-thiophenes]. For the polymerization of the monomers, we referred to previous reports[9,10,18] describing nickel(0) catalysis as a polymer-forming reaction for aromatic dichlorides. The nickel(0) catalyst was generated in situ from nickel chloride, triphenylphosphine, zinc, and bipyridine (Scheme 2).

The reaction conditions for our 3-benzoyl-2,5-dichlorothiophenes were investigated by varying the reaction solvent volumes, catalyst ratios, temperatures, and time. Polymerization results of the monomers (**Ia**−**IIIa**) are reported in Table 1. It was found that 0.075 molar equiv of nickel chloride relative to the monomer gave the best results. Reactions with greater than 0.075 equiv of nickel chloride relative to the monomer lowered the yield and reduced the intrinsic viscosities by nearly half (entries 1 and 6 in Table 1). An equimolar amount of bipyridine relative to nickel chloride was necessary in these reactions to suppress the main side reaction and the transfer of aryl groups from triphenylphosphine to metal.[9,19] In addition, it was found that a molar equivalent of triphenylphosphine and 3.1 molar equiv of zinc relative to the monomer were necessary to obtain the best result. A lower or higher molar ratio of triphenylphosphine did not allow us to obtain high molecular weight materials and lowered the yield to 78% (entries 1 and 6 in Table 1). It was also found that sodium iodide (molar ratio of 3:1 based on monomer) had a positive effect on the reaction when added during the final 2 h of polymerization and at a reaction temperature lower than 90 °C. The amount of DMAc found to be appropriate for the reactions was approximately 1:5 of monomer/solvent (molar ratio). This volume of solvent provided the necessary solubility and mobility of the reaction system and led to reasonable reaction time.

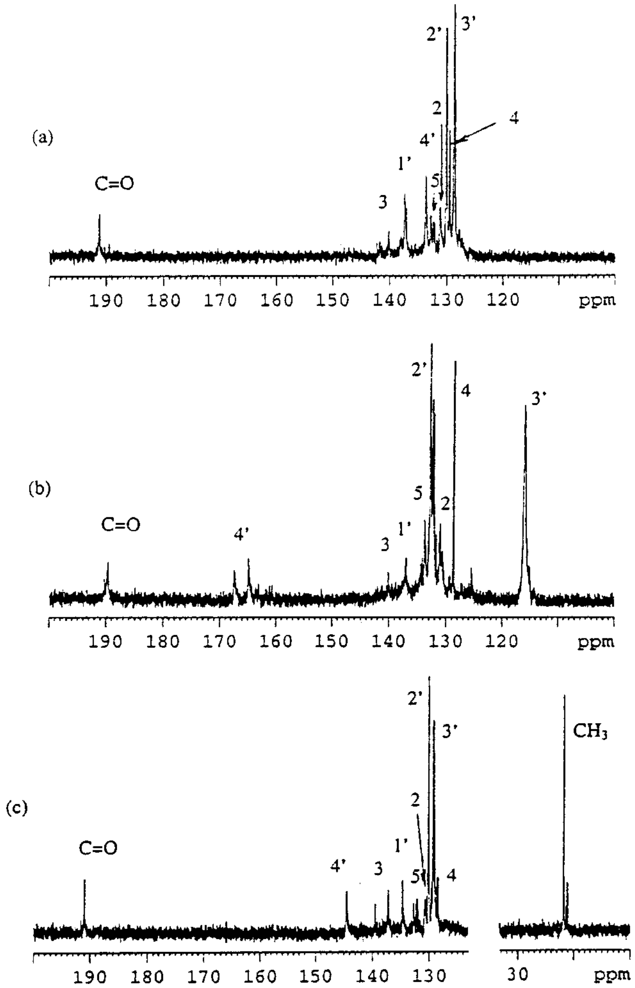


Figure 5. ^{13}C NMR of polymers: (a) **Ib**; (b) **IIb**; (c) **IIIb**.

The effect of the reaction temperatures was examined at 80, 85, 90, 100 °C for the three polymers. It was found that 85 °C was the optimal polymerization temperature. At 80 and 90 °C, the reaction yields and molecular weights were significantly lower. In the case of polymer **Ib**, a temperature of 100 °C gave mixed results (entries 7 and 8 in Table 1). The required polymerization time was shortened, giving viscous gels after 4 h and a nearly quantitative yield. However, the products were insoluble in solvents such as NMP, chloroform, and tetrahydrofuran, and the thermal stabilities (10% weight loss in nitrogen) were approxi-

Table 2. Molecular Weights of Polymers

polymer	$\langle M_w \rangle$ (GPC−LS) (THF)	$\langle M_n \rangle$ (GPC−LS) (THF)	$\langle M_w \rangle$ (LS) ($CHCl_3$)	$\langle M_w \rangle$ (LS) (NMP)	[η] (dL/g) (NMP)	$\langle M_v \rangle$ (NMP)
Ib	6.33×10^4	5.27×10^4	6.00×10^4	3.11×10^4	0.031	3.10×10^4
Ib	9.81×10^4	7.96×10^4	8.14×10^4	6.68×10^4	0.065	6.67×10^4
Ib	1.56×10^5	1.21×10^5	2.06×10^5	1.34×10^5	0.132	1.39×10^5
Ib	1.74×10^5	1.44×10^5		1.60×10^5	0.150	1.58×10^5
IIb	1.65×10^5	1.30×10^5			0.145	1.53×10^5
IIb					0.325	3.51×10^5
IIIb	1.06×10^5	8.08×10^4			0.114	1.19×10^5
IIIb					0.365	3.95×10^5

mately 60 °C lower than those of the polymers made at 85 °C. We also found no obvious melting evidence for these insoluble products by DSC. Ueda et al.[9] and Fahey et al.[20] have suggested that polymerizations at 100 °C give inferior results due to the transfer of aryl groups from triphenylphosphine. The polymer obtained at 100 °C continues to be investigated.

The reaction time was also an important parameter for these polymerizations. The most suitable reaction time was determined to be 6−8 h for each of the monomers. Longer polymerization times (12−24 h) were attempted (entries 9 and 15). However, the results were polythiophenes with lower yields, lower solubilities, and lower thermal stabilities. Uegaki et al.[21] and Granel et al.[22] found similar results which they attributed to the decomposition of the complex $NiCl_2(PPh_3)_2$ held at temperatures above 60 °C for an extended time.

3.3. NMR Characterization. The proton NMR (not shown) of the three polymers showed little change in chemical shift with respect to the corresponding monomers except for some broadening and overlap due to the long chain structure of the polymers.[23] The ^{13}C NMR spectra provide a clearer structural picture (Figure 5). The carbonyl carbons of the three polymers were all seen at $\delta \sim 190$. The fluorine effect in polymer **IIb** is seen by the splitting the bound carbon into δ 167.4 and 164.7 (Figure 5b). The methyl carbon at δ 21.9 (Figure 5c) is also identified. These characteristics are consistent with the results of the respective monomers. Small shoulders accompanied with the proton's main peaks on the thiophene ring in ^1H NMRs of three polymers (not shown) and small shoulders on the three carbonyl carbons (Figure 5) and on the methyl carbon (Figure 5c) provided some information of regiostructures in the polymers, i.e., head−tail (H−T) and head−head (H−H) or tail−tail (T−T) linkages between repeat units. It appears that the polymers contain approximately 85% of H−T structure and 15% of H−H or T−T structure based on the ratio estimations of these main peaks relative to their corresponding small shoulders. These results are consistent with the similar conclusion by Souto Maior et al.[24] Furthermore, no signal due to the unsubstituted carbon (C-2) of the thiophene ring was observed at δ 120, which indicates that the C-2 and C-5 carbons on thiophene ring are involved completely in the coupling polymerization and that no branching occurred in the polymer main chain structure.[9] The detailed structural studies by ^1H NMR, ^{13}C NMR, 2D NMR, and solid CP/MAS NMR for these novel materials will be reported in a future publication.[25]

3.4. Thermal Characterizations. The glass transition temperatures of the three polymers, **Ib**, **IIb**, and **IIIb** are 167.4, 170.2, and 164.1 °C, respectively. The high T_g is an indication that their main polymer chains are rather rigid. The 10% weight loss values obtained from thermogravimetric analysis of 463.7 and 463.5 °C for poly(3-benzoyl-2,5-thiophene) (**Ib**) and poly[3-(*p*-fluoro)benzoyl-2,5-thiophene] (**IIb**) in nitrogen are comparable. However, in air, polymer **IIb** has a lower thermooxidative stability (10% weight loss at 443.5 °C vs 460.5 °C for **Ib**). The thermal stability and thermooxidative stability (437.5 °C in N_2 and 430.6 °C in air) of poly(3-toluoyl-2,5-thiophene) (**IIIb**) all lower than those for either of the other two polymers. This may be due to the methyl group, which is easily lost during heating. In general, these polymers possess thermal stabilities and properties comparable to those of other high performance polymers.

3.5. Molecular Weight Characterization. According to our previous research,[13] *N*-methyl-2-pyrrolidinone (NMP) is a better solvent than tetrahydrofuran (THF) for these polythiophene derivatives. Therefore, NMP (30.0 °C) was the solvent of choice for light scattering batch measurements to set up a Mark−Houwink relationship for our polymers[26]

$$[\eta]\ (\mathrm{dL/g}) = 1.36 \times 10^{-6}\ \langle M_v \rangle^{0.97}$$

where [η] is the intrinsic viscosity from the diluting viscometric method and $\langle M_v \rangle$ is the viscosity average molecular weight from the batch measurement of light scattering. $K = 1.36 \times 10^{-6}$ dL/g and $\alpha = 0.97$ are constants in above conditions. They were determined by the intercept and the slope of the plot of log[η] vs log$\langle M_v \rangle$ respectively. The α value is consistent with the value ($\alpha = 0.96$) of poly(3-hexylthiophene) in THF at 25 °C reported by Holdcroft.[27] The value of α close to unity indicates that the $\langle M_v \rangle$ is approximately equal to $\langle M_w \rangle$ and the polymer chain is rather rigid.[27] The results of molecular weight measured in different solvents and different methods are summarized in Table 2. In general, the molecular weights via viscometry are comparable with the results via light scattering. These polymers have a high viscosity average molecular weight ($>1.1 \times 10^5$) which should provide a long enough effective conjugation length for further electrooptical applications. Weight average molecular weights above 2.5×10^4 for polythiophenes are usually required for such applications.[1,28]

3.6. UV−Visible and FTIR. The UV absorption $\lambda_{max} = 260$ nm of monomers and the λ_{max} of the polymers in $CHCl_3$ shifted to 470 nm (Figure 6), indicate the presence of an extended π-conjugation system along the polythiophene backbone, resulting in a longer wavelength shift (red-shift) of the absorption band. The value of 470 nm implies that these polymers could be good candidates for electrical or electrooptical applications because they have long enough effective conjugation length to provide the necessary electron mobility along the polymer chain for conductivity.[29] We also found that the absorption maximum of polymers was

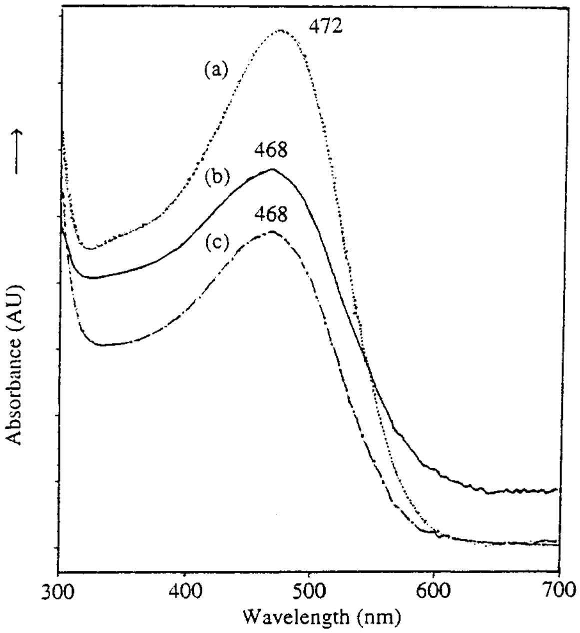


Figure 6. UV–Visible spectra of polymers: (a) **Ib**; (b) **IIb**; (c) **IIIb**.

Table 3. Solubility of Polymers

polymers	$CHCl_3$	NMP	DMAc	THF	acetone	methanol
Ib	S[a]	S	S	PS[a]	NS[a]	NS
IIb	S	S	S	S	PS	NS
IIIb	S	S	S	PS	NS	NS

[a] S, soluble; PS, partially soluble; NS, not soluble.

shifted to longer wavelength with increasing molecular weight. Low molecular weight ($\langle M_v \rangle = 2 \times 10^4$) polymer only obtained a flat plateau from 350 to 450 nm; moderate molecular weight ($\langle M_v \rangle = 6 \times 10^4$) polymer has a $\lambda_{max} = 464$ nm; and high molecular weight ($\langle M_v \rangle = 1.5 \times 10^5$) polymer possesses a $\lambda_{max} = 470$ nm. This result is consistent with the findings of Osawa et al.,[26] in which no obvious influence of molecular weight on the conjugation length was observed once a weight average molecular weight of approximately 25 000 for alkyl-substituted polythiophenes was reached. The carbonyl group characteristic C=O stretching around 1653 cm^{-1} for the three polymers was observed in FTIR spectra, which is consistent with the value of 1655 cm^{-1} for the monomers and further confirm the results of ^{13}C NMR.

3.7. Solubility and Film-Forming Ability of Polymers. The polymers are dark-red powders. They are soluble in a variety of solvents including NMP, DMAc, DMPU, DMF, DMSO, chloroform, methylene chloride, tetrahydrofuran, etc. Their solubilities are shown in Table 3. Poly[3-(*p*-fluoro)benzoyl-2,5-thiophene] (**IIb**) possesses better solubility than the other two polymers. It can be partially dissolved in acetone. The solubility of the polymers also depends on their molecular weights. Very high molecular weights ($\langle M_v \rangle > 3.0 \times 10^5$) are less soluble. These polymers produce red transparent thin films when solution cast from the above solvents. However, the films are rather brittle.

4. Conclusions

We have successfully synthesized three 3-(*p*-substituted)benzoyl-2,5-dichlorothiophenes via iron(III) chloride catalyzed Friedel–Crafts acylation in 60–65% yield. Two of the monomers, the fluoro- and the methyl-substituted derivatives, are new organic compounds. The yield of the unsubstituted monomer has been significantly improved from the previously reported 12–23%. At 85 °C for 6–8 h, the nickel-catalyzed coupling polymerizations yielded three high molecular weight, soluble, amorphous polythiophenes in nearly quantitative yields. Each of these polymers was found to be thermally and thermooxidatively stable with glass transistion temperatures from 165 to 170 °C and 10% weight loss values in both air and nitrogen above 430 °C. Higher reaction temperatures and longer reaction times yielded insoluble polymers with lower thermal properties. In further investigations, the composition of these products will be analyzed thoroughly. The ultraviolet absorption maxima of the polymers of approximately 470 nm is an indication of a sufficient effective conjugation length for future electrical and electrooptical applications.

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