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### Some Novel Conducting Polythiophene Derivatives: Theoretical Analysis, Synthesis, Characterization and Electroreological Properties

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# Some Novel Conducting Polythiophene Derivatives: Theoretical Analysis, Synthesis, Characterization and Electrorheological Properties

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A series of alternating phylene and symmetrically bithiophene containing repeat units and the respective homopolymers have been synthesized and characterized by combining FTIR, UV-Vis spectroscopy, four probe conductivity measurement, TGA and SEM analysis. Quantum mechanical calculations of the structures and infrared spectra of the monomers and respective dimers were compared with experimental results. The polymers are soluble in N-methyl-pyrrolidone (NMP). The samples have conductivities of  $10^{-5}$  S/cm levels. Thermal degradation analysis results indicated that poly-bithiophene derivatives have higher thermal stabilities than poly-monothiophene derivatives. All samples exhibited different surface morphologies. The electrorheological (ER) properties of polymer suspensions in silicone oil were prepared and ER behavior was investigated as a function of shear rate, electric field strength and frequency.

**Keywords:** Polythiophene derivatives, theoretical calculations, chemical synthesis, electrorheology

## 1 Introduction

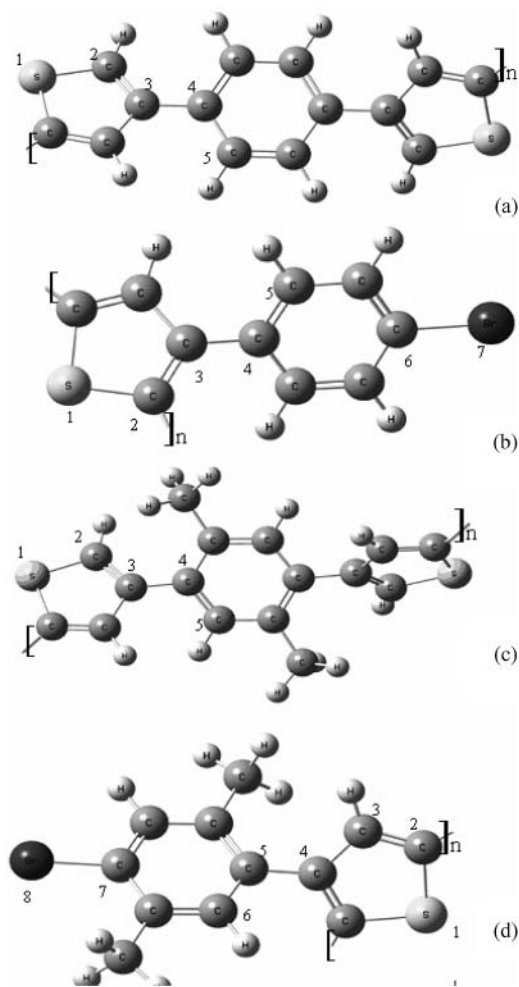
$\pi$ -Conjugated polymers, which have potential applications in microelectronics (1) and optics (2), comprise an interesting group of novel semi-conducting materials. As a result, intensive chemical, physicochemical and electronic investigations have been carried out on these materials. Among them, polythiophene (PT) and its derivatives are the most challenging class of conjugated polymers. Because of their environmental and thermal stabilities, they can be used as electrical conductors (3), non-linear optical devices (4), sensors (5), batteries (6), organic transistors (7) and electrochromic devices (8–10). In addition to the processability of these materials, it has been reported that the semi-conducting conjugated polymers exhibit fluorescent characteristics that make them potential materials for application as light emitting diodes (polymer LEDs) (11). Polythiophene becomes an electronically conducting material upon doping, but unfortunately it is insoluble. However,

it has been found that the attachment of alkyl groups of four or more carbon atoms to the third position of PT increases the solubility and processability of both the undoped and doped states of the polymer in many organic solvents (12). Poly (3-phenylthiophene) and poly (3-alkylthiophene) were the most studied polythiophene derivatives (13,14). The phenyl groups introduced into the backbone of PT stabilize the conjugated  $\pi$ -bonds and the gratified alkyl groups improve the solubility of the polymers.

A crucial step in the development of new conjugated polymers is to add the substituents in the monomers. Thus, the introduction of substituents has been widely used to induce changes in the structure and electronic properties, confer solubility, as well as improve the process ability of these materials. In this respect, the substitutional effects on the above-mentioned properties have been researched both experimentally and quantum mechanically (15a-b).

In this study, we synthesized 3-[(2,5-dimethyl-4-tienyl)phenyl] tiyofen, 3-[(2,5-dimetil-4-brom)fenil] tiyofen, 3-[(4-tiyenil)fenil] tiyofen and 3-[4-brom fenil] tiyofen monomers and polymerized them chemically using  $\text{FeCl}_3$  as an oxidant. The resultant polymers were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), Ultraviolet-Visible Spectroscopy (UV-Vis) and conductivity measurements. Theoretical analysis of structures

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**Fig. 1.** The optimized geometries of monomers of (3-substitute) thiophenes. Brackets in each figure represents the polymerization linkages.

and infrared spectra on four monomers and homodimers of 3-substituted thiophenes shown in Figure 1(a-d) are also reported. The theoretical FTIR vibration frequencies were verified by comparison with experimental results on four soluble poly(3-substitutedthiophenes). Furthermore, we have attempted to use new substituted polythiophenes in electroreological suspensions. Conducting polymers, polypyrrole (PPy), polyaniline (PANI), polythiophene (PT), and similar polymers are promising materials for piratical applications because of their high electrical conductivity and good environmental stability. Because of their poor polymers are widely investigated in combination with other polymers or inorganic materials as composites or blends (16). It is well known that ring substituents on the polythiophene backbone leads to a decrease in the conductivity (13). Thus, the synthesized substituted polythiophene particles may be used without further treatment of dedoping. The rheological properties of these ER fluids were measured by rotantional rheometer equipped with a high-voltage generator.

## 2 Experimental

### 2.1 Materials

1,4-dibromobenzene, 2,5-dimethyl-1,4-dibromobenzene, 3-bromothiophene,  $\text{NiCl}_2(\text{diphenylphosphino propane})$  were purchased from a domestic chemical company and used without further purification. All of the solvents were analytic reagents and purified by standart distillation methods. All reactions given below were carried out under nitrogen atmosphere. 3-[(2,5-dimethyl-4-tienyl)phenyl] tiyophene, 3-[(2,5-dimethyl-4-brom)phenyl] tiyophene, 3-[(4-tienyl)phenyl] tiyophene and 3-[4-brom phenyl] tiyophene were synthesized according to Grignard method (17). Reagent ferric chloride,  $\text{FeCl}_3$ , obtained from Riedel de Haen, was used as an oxidizing agent for chemical polymerization of monomers. Chloroform ( $\text{CHCl}_3$ ) (Riedel de Haen) and ethanol (EtOH) (Merck) were used without further purification. Silicone oil was used after drying at  $130^\circ\text{C}$  for 3 h in a vacuum oven, to remove any moisture present ( $\rho = 0.97 \text{ g/cm}^3$ ,  $\eta = 1000 \text{ mPas}$ ,  $\varepsilon = 2.61$ ).

### 2.2 Synthesis of Monomers

#### 2.2.1. Synthesis of 3-(2,5-dimethyl-4-tienyl)phenyl tiyophene (3DMTPT)

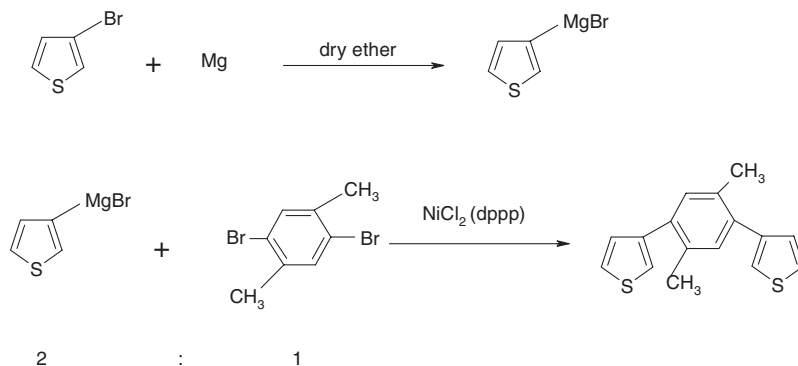
3.48 g (21.3 mmol) of 3-bromothiophene in 100 mL of tetrahydrofuran (THF) was slowly added to a cold solution of 1.2164 g (50 mmol) of magnesium in 100 mL THF at  $0^\circ\text{C}$ . The reaction mixture was then heated to reflux for 48 h and cooled to room temperature. Consequently, the Grignard reagent was formed and it was added to a solution of (4.720 g, 20 mmol) of 1,4-dibromobenzene in 70 mL of THF with a catalytic amount of  $\text{NiCl}_2$  (diphenylphosphino propane). The reaction mixture was heated to reflux for 24 h. Then the reaction mixture was cooled, terminated with 2 M HCl aqueous solution, extracted with dichloromethane three times. The combined organic layer was washed with water and dried with anhydrous magnesium sulfate. Finally, the solvent was removed by rotary evaporation. The product was a yellow crystal. Yield was 48%. Melting point (m.p.)  $206^\circ\text{C}$ .

FTIR  $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$ : 2970 (C-H stretching), 2960, 2935, 2880, 2350, 1760, 1480 ( $-\text{CH}_2$  bending), 1440, 1380 ( $-\text{CH}_3$  bending), 1350, 1260, 1200, 1140, 1060, 1040, 985, 880 ( $\beta$ -H thiophene), 760 ( $\alpha$ -H thiophene).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ -ppm): 7.51 (m,  $\alpha$ -2H,Th), 7.41 (m,  $\beta$ -2H,Th), 7.32 (m,  $\alpha$ -2H,Th), 6.93 (s, 2H, aromatic), 2.35 (s, 6H, aliphatic).

The scheme of synthesis is demonstrated in Scheme 1.

#### 2.2.2. Synthesis of 3-(2,5-dimethyl-3-brom)phenyl tiyophene (3DMBPT)

The synthetic procedure was similar to 3-(2,5-dimethyl-4-tienyl)phenyl tiyophene, but it was synthesized by a coupling reaction of 3-bromothiophene with 2,5-dimethyl-1,4-

**Sch. 1.** Synthesis of 3DMTPT.

dibromobenzene(1:1) in THF using  $\text{NiCl}_2$  (diphenylphosphino propane) as catalyst. Yield is 50%. m.p.  $202.7^\circ\text{C}$ .

FTIR  $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$ : 3060, 2925, 2855, 2360, 2350, 1500, 1440, 1380, 1350, 1200, 1140, 1060, 900, 725, 700 (C-Br).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ -ppm): 7.55 (m,  $\alpha$ -2H,Th), 7.38 (m,  $\beta$ -2H,Th), 7.27 (m,  $\alpha$ -2H,Th), 7.06 (s, 1H, aromatic), 6.81 (s, 1H, aromatic), 2.84 (s, 3H, aliphatic), 2.04 (S, 3H, aliphatic).

The synthesis is demonstrated in Scheme 2.

### 2.2.3. Synthesis of 3-(4-tienyl) phenyl thiophene (P3TPT)

The synthetic procedure was similar to 3-(2,5-dimethyl-4-tienyl)phenyl thiophene, except that the refluxing time was 1.5 h. Yield is 52%; m.p.  $170.52^\circ\text{C}$

IR  $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$ : 3100 (aromatic C-H), 2375, 2350, 1480 ( $-\text{CH}_2$  bending), 1400, 1265 (disubstitue benzene), 1075, 1000, 810 (p-disubstitue benzene).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ -ppm): 7.62 (m,  $\alpha$ -2H,Th), 7.27 (m,  $\beta$ -2H,Th), 7.04 (m,  $\alpha$ -2H,Th), 7.38 (s, 4H, aromatic).

The synthesis is represented in Scheme 3.

### 2.2.4. Synthesis of 3-(4-bromo)phenyl thiophene (3BPT)

The synthetic procedure was similar to 3-(4-tienyl) phenyl thiophene, but it was synthesized by a coupling reaction of 3-bromothiophene with 1,4-dibromobenzene (1:1) in

THF using  $\text{NiCl}_2$  (diphenylphosphino propane) as catalyst. Yield is 59%; m.p.  $193^\circ\text{C}$ .

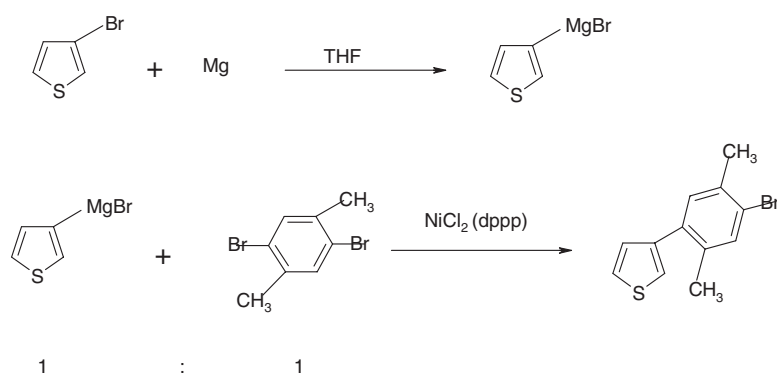
IR  $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$ : 3050 (aromatic C-H), 2360, 2325, 1450 ( $-\text{CH}_2$  bending), 1450, 1200 (disubstitue 1,4-), 1150, 1000, 740, 700 (C-Br).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ -ppm): 7.65 (m,  $\alpha$ -2H,Th), 7.18 (m,  $\beta$ -2H,Th), 7.00 (m,  $\alpha$ -2H,Th), 7.45 (m, 2H, aromatic), 7.22 (m, 2H, aromatic).

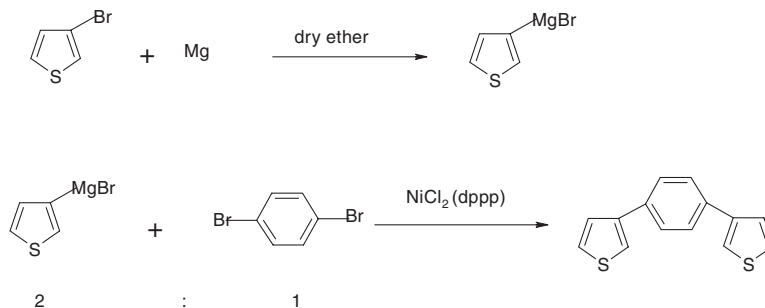
The synthesis is demonstrated in Scheme 4.

## 2.3 Synthesis of Polymers

### 2.3.1. Synthesis of poly-[3-(2,5-dimethyl-4-tienyl)phenyl thiophene] (P3DMTPT)

3-(2,5-dimethyl-4-tienyl)phenyl thiophene ( $1.1 \times 10^{-3}$  mol, 0.297 g) was dissolved in 50 mL  $\text{CHCl}_3$ . The solution was shaken for 10 min in an ultrasonic bath which resulted in a good dispersion of 3-(2,5-dimethyl-4-tienyl)phenyl thiophene. The polymerization of 3-(2,5-dimethyl-4-tienyl)phenyl thiophene] was initiated by the drop wise addition of ( $2.77 \times 10^{-3}$  mol, 0.45 g) ferric (III) chloride as oxidizing agent under constant stirring at  $25^\circ\text{C}$ . The molar ratio of oxidizing agent to monomer was taken as 2.5, it was then reacted at the same temperature for 24 h. At the end of polymerization, precipitated polymer were filtered and washed with  $\text{CHCl}_3$  until the filtrate was colorless.

**Sch. 2.** Synthesis of 3DMBPT.



**Sch. 3.** Synthesis of 3TPT.

Finally, the polymer was dried at 50°C for 24 h under vacuum environment.

The synthesis is demonstrated in Scheme 5.

Poly-[3-(2,5-dimethyl-3-brom)phenyl thiophene] (P3DMBPT), poly[3-(4-tienyl)phenyl thiophene] (P3TPT) and poly [3-(4-bromo)phenyl thiophene] (P3BPT) were prepared by using the same procedure as (P3DMTPT).

## 2.4 Characterization of Samples

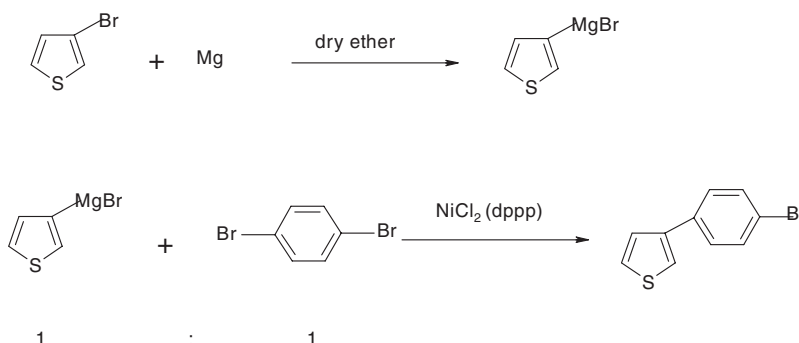
FTIR spectra of the polymers were recorded on a Perkin-Elmer model spectrometer (Beaconsfield, Beuckinghamshire, HP91QA, England). NMR spectra were taken using Bruker Avance DPX-400 MHz NMR spectroscopy into  $\text{CDCl}_3$ . Scanning electron microscopy (SEM) studies of the polymers were performed using a Phillips XL-30S FEG model scanning electron microscope. UV-Vis spectra were recorded between 250 and 900 nm using a 1 cm path length quartz cuvette, and pure NMP were used as the reference on a Perkin-Elmer Lambda 20 UV-Vis spectrophotometer. Thermograms of the polymers were recorded by using a Perkin-Elmer (Beaconsfield, Beuckinghamshire, HP91QA, England) thermogravimetric analyzer in the presence of  $\text{O}_2$  atmosphere from 20 to 900°C with a heating rate of  $10^\circ\text{C min}^{-1}$ . The electrical conductivity of polymers was measured using the standard four-probe technique. The direct current electrical conductivity of samples was measured by a standard four-probe method

using PCI-DAS6014 for a current source, voltmeter and temperature controller. For the measurements, pellets were prepared from dry powdered samples by using a steel die having 13 mm diameter in a hydraulic press under a pressure of 200 MPa. All samples were in the pellet forms and the thicknesses of the pellets were measured by a digital micrometer. Electrical conductivity of the polymer samples was measured by four-probe system with PCI-DAS6014 connected to a computer. Conductivity values of samples were calculated according to the van der Pauw equation (13).

Electrorheological properties of the suspension were determined with a Termo-Haake RS600 parallel plate electroreometer (Germany). The gap between the parallel plates was 1.0 mm and the diameters of the upper and lower plates were 35 mm. The voltage used in these experiments was also supplied by a 0–12.5 kV (with 0.5 kV increments) dc electric field generator (Fug Electronics, HCl 14, Germany), which enabled resistivity to be created during the experiments.

## 2.5 Computational Details

The structures of neutral 3DMTPT, 3DMBPT, 3TPT, 3BPT and their homodimers were optimized by using DFT/B3LYP level calculations with 6-31G(d) basis sets. All optimized structures were then subjected to frequency calculations to ensure that they were in true minima. The aim of the computational calculations is for a quick check



**Sch. 4.** Synthesis of 3BPT.

**Table 1.** Some of the selected bond distances ( $r$ , Å) and angles ( $a$ , deg) for the monomers and homodimers of P3DMTPT, P3DMBPT, P3TPT, P3TPT. The numbers show the atoms that are labeled in Figure 1(a-d)

Fig. 1-a	Monomer	Dimer	Fig. 1-c	Monomer	Dimer
r(1-2)	1.7311	1.7306	r(1-2)	1.7328	1.7566
r(2-3)	1.3763	1.3762	r(2-3)	1.3756	1.3874
r(3-4)	1.4766	1.4766	r(3-4)	1.4834	1.4890
r(4-5)	1.4030	1.4052	r(4-5)	1.4035	1.4051
a(2-3-4-5)	-149.32	-149.06	a(2-3-4-5)	-136.01	-136.28
Fig. 1-b	Monomer	Dimer	Fig. 1-d	Monomer	Dimer
r(1-2)	1.7305	1.7300	r(1-2)	1.7354	1.7290
r(2-3)	1.3761	1.3760	r(2-3)	1.3648	1.3649
r(3-4)	1.4771	1.4773	r(4-5)	1.4850	1.4891
r(4-5)	1.4052	1.4049	r(5-6)	1.4030	1.4013
r(6-7)	1.9121	1.9116	r(7-8)	1.9182	1.9183
a(2-3-4-5)	-148.38	-147.92	a(3-4-5-6)	-128.19	-122.95

of the observed FTIR spectra of monomers and polymers. Therefore, we did not attempt to search potential energy surface (PES) of monomers and dimers. Within our computational capacity, we have only done calculations on homodimers to represent the polymer structures that are subject to the current manuscript. All the calculations were performed using the Gaussian 03 program (18).

## 3 Results and Discussion

### 3.1 Theoretical Results: Structure and Spectra

The optimized geometries of 3DMTPT, 3DMBPT, 3TPT, and 3BPT monomers are shown in Figure 1(a-d) and some of the bond lengths and angles are listed in Table 1. There are no dramatic changes in bond lengths going from monomer to dimer except in the dimerization part. It should be noted here that substitution of backbone ring with side phenyl group affects the backbone planarity (not shown) due to the steric effects.

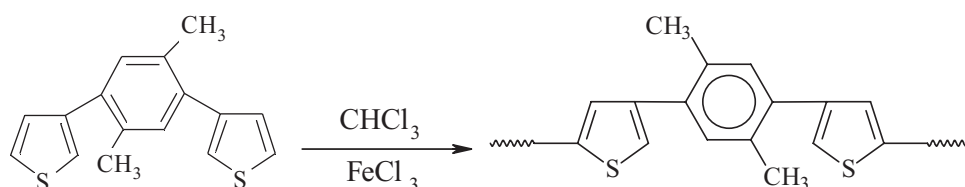
The calculated vibrational spectra are demonstrated in Figure 2 for heterodimers of 3DMTPT (a), 3DMBPT (b), 3TPT (c), and 3BPT (d) and some of the characteristic peaks are also listed in Table 2. As was stated in the methodology part, the dimer structures were assumed to represent the polymer structures. Considering the similarities between the observed and calculated spectra (Figs. 2 and 3), this assumption is convincing. All dimer structures con-

sidered here contains  $\alpha - \alpha$  linkages. It should be noted here also that although the experimental spectra contains dominantly  $\alpha - \alpha$  linkages, it is impossible to eliminate the cross linkages (i.e.  $\alpha - \beta$  or  $\beta t\beta$ ) during the polymerization reactions.

One of the main differences in the spectra going from 3DMTPT (a), 3DMBPT (b), 3TPT (c), and 3BPT (d) is the bands due to the  $\text{CH}_3$  groups in the structure in 3000–3500  $\text{cm}^{-1}$  region. This region also contains C-H stretching that belongs to the aromatic ring (i.e., benzene and thiophene). The similar trend is observed in experimental spectra shown in Figure 3. The peaks around 1600–1400  $\text{cm}^{-1}$  are the C-C stretching the ring (Table 2) in all spectra shown in Figure 2.

### 3.2 FTIR Results of Polymers

The FTIR spectra of P3DMTPT, P3DMBPT, P3TPT and P3BPT are presented in Figure 3. Characteristic peak values for poly(3-substituted) thiophenes are listed in Table 3 (19–21). The bands at 1606, 1616 and 1617  $\text{cm}^{-1}$  are attributed to the vibrations of C=C asymmetric ring stretching of benzene. The bands at 1585 and 1586  $\text{cm}^{-1}$  are assigned to the C=C asymmetric ring stretching vibrations, while the 668 and 665  $\text{cm}^{-1}$  bands are ascribed to the C-S-C ring deformation of the thiophene ring. The presence of these bands may indicate the formation of poly(3-substituted)thiophenes (Fig. 3).

**Sch. 5.** Synthesis of P3DMTPT.

**Table 2.** Some of the calculated characteristic infrared frequencies of homodimers of P3DMTPT, P3DMBPT, P3TPT, P3BPT

Mode	P3DMTPT	P3DMBPT	P3TPT	P3BPT
C-H stretching				
Thiophene	3224 (13.6)	3226 (12.8)	–	–
Benzene	3182 (60.3)	3192 (22.7)	3198 (8.1)	3224 (2.8)
CH <sub>3</sub>	3132 (32.4)	3132 (42.6)	3129 (19.4)	3226 (7.3)
C-C ring stretching (benzene)	1544 (63.7)	1530 (94.9)	1535 (53.4)	1555 (201.2)
C-C ring stretching (thiophene)	1477 (12.6)	1442 (4.5)	1495 (12.2)	1473 (12.6)
	1402 (20.7)			
C-H out of plane deformation (thiophene)	731 (33.2)	730 (36.5)	729 (27.3)	840 (58.7)
	802 (65.8)			

The experimental and calculated spectra are different in the bending region. This might be because of phase difference of the two compared systems and the size of the calculated models with respect to measured ones. In general, the deviation between the calculated and experimental spectra might be due to the general tendency of the quantum mechanical methods to overestimate the force constants at the equilibrium, anharmonicity of the system and phase difference between the observed and calculated structures. Nevertheless, the results seem encouraging.

### 3.3 TGA Results

The thermal properties of polymers were studied by TGA and the curves of poly(3-substituted) polythiophenes are shown in Figure 4. P3TPT and P3BPT indicate weight loss with 55% wt. in the range of 50–180°C temperatures, whereas P3DMTPT has weight loss with 40% wt.

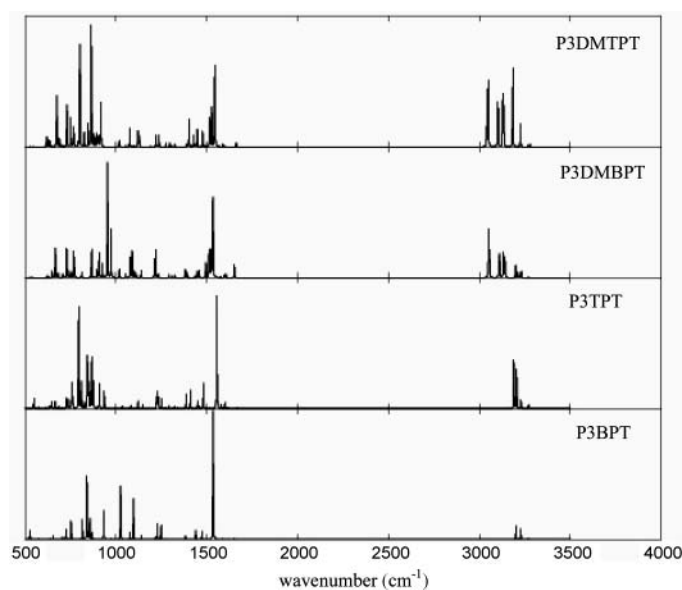
P3DMBPT has the lowest weight loss in the same temperature range. These steps indicate the expulsion of adsorbed solvents, monomers and oligomers with low molecular weights from the polymer matrix (22). After 400°C, P3TPT and P3BPT have the second decomposition step showing the side chain and the polymer backbone decomposition. Among poly(3-substitutedthiophenes), P3DMTPT has the second high decomposition temperature. The phenyl ring into the polythiophene backbone could increase thermal stability due to its role in the conjugation length. These decomposition temperatures are higher than those of poly(3-phenylthiophene) given in literature (23). The high decomposition temperatures of these polythiophene derivatives indicate that they can be applied in a wide temperature scale.

### 3.4 Conductivity Results

The conductivities of synthesized poly(3-substitute) thiophenes are given in Table 4. As seen from Table 4, the conductivity values of synthesized poly(3-substitute) thiophenes are moderate, at the order of  $\sim 10^{-5}$  S cm<sup>-1</sup>. These conductivity values are in very good agreement with the literature (24,25). It can be seen that there is not a big difference among conductivities ( $10^{-5}$  S/cm level) of the substituted polymers. This result could confirm that there is no great contribution to the electronic structure of the trimeric system when compared to 3-substituted phenyl group. It could be confirmed from UV-Vis and theoretical results that P3DMTPT and P3TPT have more conjugated backbones and planarity than those of P3BPT and P3DMBPT. This could affect thermal and morphological properties, whereas the conductivity values are close to each other. Additionally, conductivity values of polymers are adequate for either electro-rheological or diode applications.

### 3.5 SEM Results

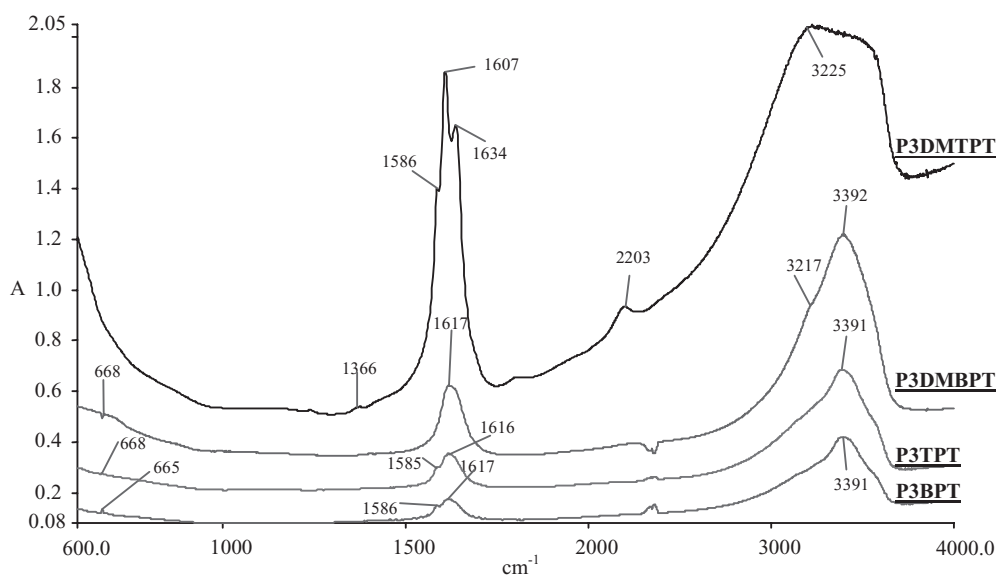
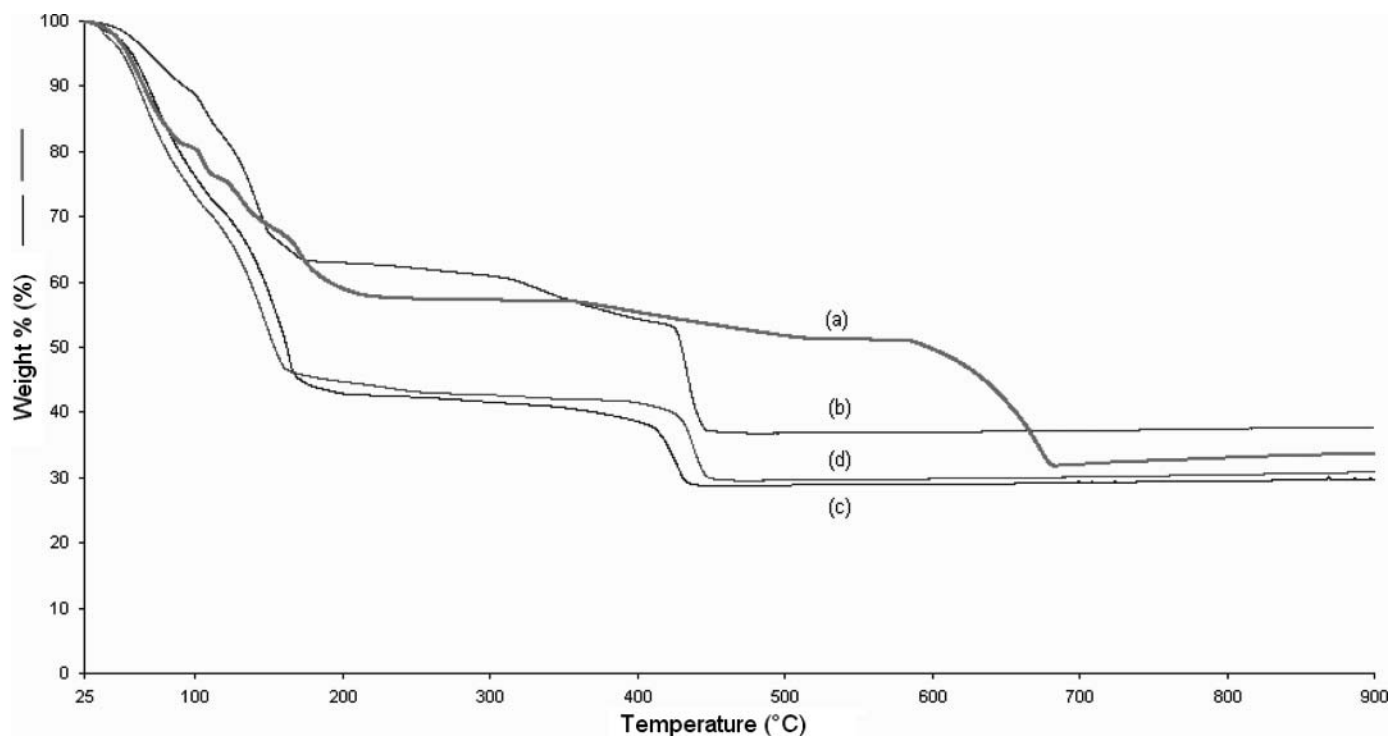
The morphologies of obtained substituted polymers depend on the structure of the monomer, and nature of the substituted groups. SEM images showed that P3DMTPT



**Fig. 2.** The calculated FTIR spectra of poly(3-substitute) thiophenes.

**Table 3.** Assignments of IR bands of poly(3-substituted) thiophenes

Band	P3DMTFT	P3DMBFT	P3TFT	P3BFT
O-H stretching (moisture from KBr)	3225	3392	3391	3391
C-H aromatic stretching		3217		
C=C asymmetric ring stretching (benzene)	1634,1609	1617	1616	1617
C=C asymmetric ring stretching (thiophene)	1586	–	1585	1586
C-S-C ring deformation	–	668	668	665

**Fig. 3.** The experimental FTIR spectra of poly(3-substituted) thiophenes.**Fig. 4.** TGA curves of poly(3-substituted) thiophenes (a) P3DMTPT, (b) P3DMBPT, (c) P3TPT, (d) P3BPT.



**Table 4.** Conductivity values of poly(3-substitute thiophenes)

Polymer	Conductivity ( $S\ cm^{-1}$ )
Poly-[3-(2,5-dimethyl-4-tienyl)phenyl thiophene] (P3DMTPT)	$2.33 \times 10^{-5}$
Poly-[3-(2,5-dimethyl-3-bromo)phenyl thiophene] (P3DMBPT)	$6.98 \times 10^{-5}$
Poly [3-(4-tienyl) phenyl thiophene] (P3TPT)	$1.53 \times 10^{-5}$
Poly [3-(4-bromo)phenyl thiophene] (P3BPT)	$1.95 \times 10^{-5}$

(5a) P3DMBPT (5b), P3TPT (5c), P3BPT (5d) and homopolymers prepared under similar conditions had quite different morphologies (Fig. 5). P3DMTPT (5a) has porous and fibre-like structure similar to polythiophene structure (26). The SEM micrograph of P3DMBPT and P3TPT indicated sponge-like and porous structure whereas P3BPT has laminar structure. P3TPT and P3BPT are more stacked neatly those of P3DMTPT and P3DMBPT.

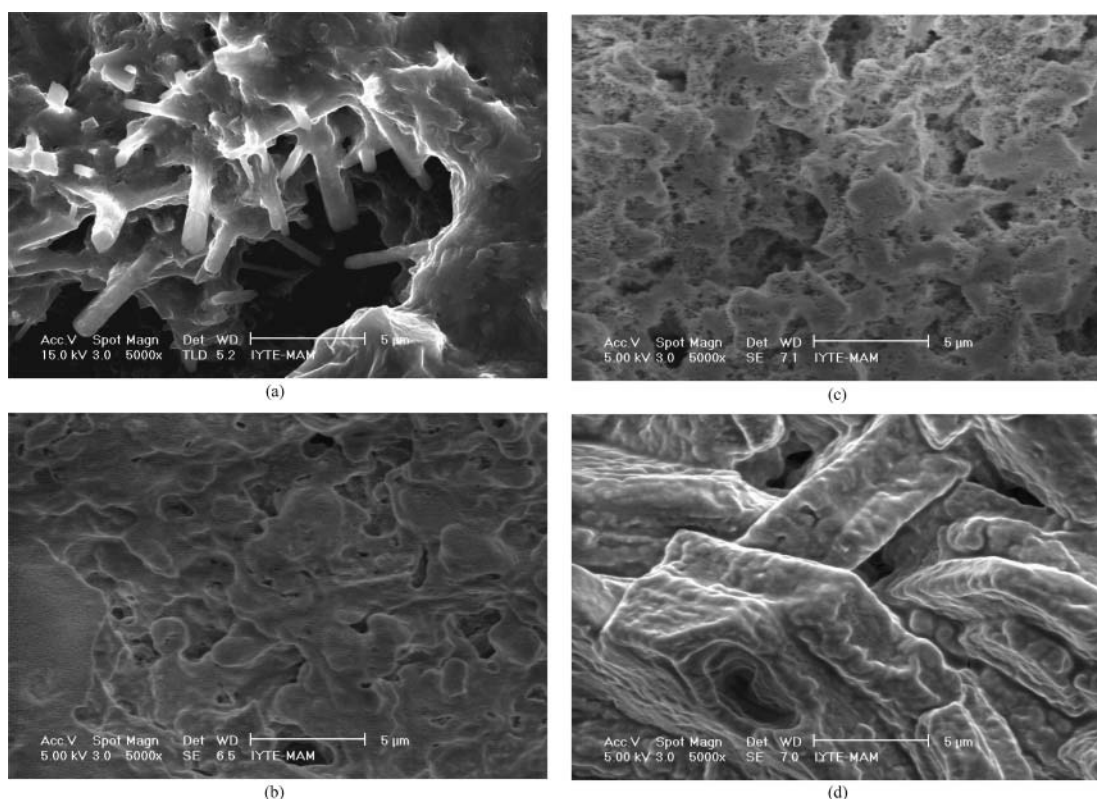
### 3.6 UV-Vis Results

Figure 6 shows the optical spectra of P3DMTPT, P3DMBPT, P3TPT and P3BPT in NMP. In the region of 250–900 nm, all four polymers are soluble in NMP and have absorption maxima in the UV-Vis spectra. P3DMTPT, P3DMBPT and P3TPT show two maxima ( $\pi \rightarrow \pi^*$ ) (17)

indicating longer conjugations, whereas P3BPT has only one. P3DMTPT and P3TPT have inserted a phenyl ring between the two thiophene rings. It could be concluded that the external thiophene rings in trimeric monomer system can increase the planarity of polymer backbone. It seems that the phenyl group at the side chain might not enhance the conjugation length of the resulting polymer compared with other groups. However, the insertion of the phenyl ring into the polythiophene backbone can still play the most important role in the conjugation length. The pendant phenyl groups influence the coplanarity of the polymer backbone due to steric hindrance of the pendant groups.

### 3.7 Electrorheological Measurements

Change of shear stress of suspensions with shear rate at constant conditions ( $c = 5\ wt\%$ ,  $T = 25^\circ C$ ) is shown in Figure 7. As seen from Figure 7, shear stress of suspensions increases with increasing shear rate and shows a Newtonian flow behavior in the absence of an electric field ( $E = 0\ kV/mm$ ). However, Bingham plastic behavior was observed under the influence external electric field strength ( $E = 2\ kV/mm$ ). This is caused by the role of induced polarization forces, which is a typical rheological characteristic of ER fluids under the influence of external electric field strength (27). This means that flows have occurred

**Fig. 5.** SEM images of poly(3-substituted) thiophenes (a) P3DMTPT, (b) P3DMBPT, (c) P3TPT, (d) P3BPT.

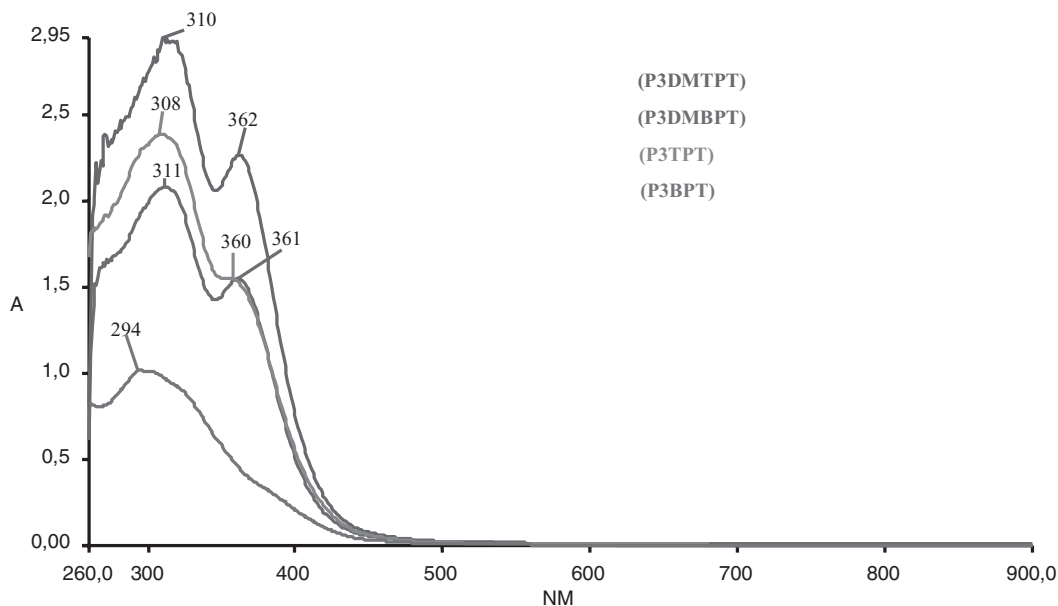


Fig. 6. UV-Vis spectra of poly(3-substituted) thiophenes into NMP.

only after exceeding a minimum yield stress ( $\tau_y$ ). The yield stress from Figure 7 is determined as 176 Pa. The yield stresses of polymer/silicone oil suspensions were  $\tau_y = 176$  Pa, for P3TPT,  $\tau_y = 198$  Pa, for P3BPT,  $\tau_y = 237$  Pa, for P3DMTPT and  $\tau_y = 316$  Pa, for P3DMBPT. Yield stress of polythiophene/silicone oil suspension was measured 308 Pa reported by Eyrik et al. (28).

The viscosity of suspensions decreases with increasing shear rate. This is a typical shear thinning non-Newtonian viscoelastic behavior of polypropylene/SO suspensions. Py particles are affected by the hydrodynamic interactions and the viscous forces (F), which have the following magnitude (29).

$$F = 6\pi\eta_s r^2 \dot{\gamma}$$

Where,  $\eta_s$  is the viscosity of the suspension and  $\dot{\gamma}$  is the average shear rate. Although the viscous forces are proportional to the shear rate at higher shear rates, the viscosities of suspensions are less dependent on E. This

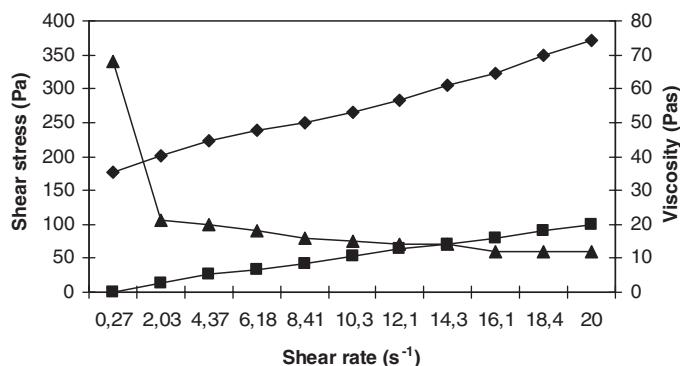


Fig. 7. Change shear stress and viscosity with shear rate.

suggests that at higher shear rates, the viscous forces are dominant to the polarization forces, and the suspensions structures do not vary appreciably with E. Similar behaviors were reported for the studies of polyaniline/SO [30] and poly(naphthalene quinone)/SO [31] and saponite/SO (32) suspensions.

Figure 8 shows the change in the electric field viscosity with electric field strength at constant conditions:  $\dot{\gamma} = 0.2 \text{ S}^{-1}$ ,  $c = 5 \text{ wt}\%$  and  $T = 25^\circ\text{C}$ . As seen from the plot, electric field viscosity ( $\eta_E$ ) increases with increasing electric field strength and reaches  $\eta_E = 82$  Pas.

Electric field viscosity of polymers/silicone oil suspensions were changed as follows:  $\eta_E = 82$  Pas, for P3TPT  $\eta_E = 118$  Pas, for P3BPT  $\eta_E = 147$  Pas, for P3DMTPT,  $\eta_E = 212$  Pas, for P3DMBPT. Yield stress and electric field viscosity values of polymer were compatible conductivities of polymers.

Under applied electric field strength, the magnitude of the polarization forces between particles increases, and in turn, the particles rapidly aggregate into the chain length

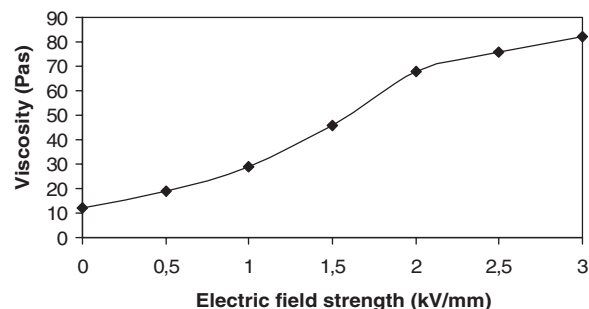


Fig. 8. Change with electric field strength.

(formed by the polarized particles) perpendicular to the electrodes, hence resulting in the improvement of the viscosity. A similar trend was observed by Dürschmidt and Hoffmann (33) in ER studies of saponite suspensions prepared in SO, by Unal et al. (34) in ER studies of poly(Li-2-hydroxy ethyl methacrylate) suspensions prepared in SO and Lengalova et al. (35) in polyaniline suspensions.

#### 4 Conclusions

We have successfully synthesized and characterized a series of (3-substitute) thiophenes and poly(3-substitute) thiophenes. (3-Substitute) thiophenes are soluble in common organic solvents, such as chloroform, THF, whereas poly(3-substitute) thiophenes are soluble in N-methyl pyrrolidine, NMP. However, poly(3-substitute) thiophenes were prepared via chemical oxidative polymerization of (3-substitute) thiophenes in  $\text{CHCl}_3$  using anhydrous  $\text{FeCl}_3$  as the oxidant. We presented a joint theoretical and experimental investigation of new poly(3-substitute) thiophenes. The theoretical calculations indicated that substitution of backbone ring with side phenyl group affects the backbone planarity and, thus results in the variation of electronic properties, structural, thermal and morphological properties. All of the samples were successfully characterized with FTIR, SEM, TGA, UV-Vis and electrical conductivity measurements. FTIR and UV-Vis results showed that polymerization of monomers were achieved successfully. From the SEM analysis, it was observed that each polymer has a different morphological structure. Spectroscopic, morphological, thermal and conductivity properties of the prepared polymers were affected by the type of functional group of thiophene. P3DMTPT has a higher initial thermal degradation temperature ( $354^\circ\text{C}$ ) than that of others. Electrorheological measurements were then conducted on the synthesized polymers as a potential application of these materials. It has been shown that ER activity of suspension increases with increasing electric field strength, concentration and decreasing shear rate. The electric field viscosity of suspension has decreased sharply with increasing shear rate, thus showing a typical shear thinning non-Newtonian visco-elastic behavior. The diode applications of the newly synthesized polymers are in progress and will be published separately.

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