

# Effect of Synthesis Temperature and Doping Level on Conductivity and Structure of Poly(3-methyl thiophene)

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## Abstract

Poly(3-methyl thiophene) was synthesized by oxidative chemical polymerization technique using ferric chloride as the dopant in an inert atmosphere. Samples of different doping levels were prepared and analyzed by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy, and direct current (DC) conductivity measurement at room temperature (300 K). Synthesis of the polymer was confirmed by FTIR studies. FTIR spectra showed a shift in the heterocyclic bands in the region of 700–1200 cm<sup>-1</sup> with a decrease in synthesis temperature. It was evident from the scanning electron micrographs that the surface structure of the polymer became denser with an increase in doping level. The measured DC conductivity increased initially up to the doping level of 0.8 M and then this increase tended to slow down. Samples having a doping level of 0.4 M were synthesized at 300, 280, and 270 K while maintaining the other synthesis parameters. The conductivity and yield were found to increase as the temperature of the polymerization decreased.

**Index Entries:** Oxidative chemical polymerization; poly(3-methyl thiophene); surface structure; direct current conductivity.

## Introduction

There has been tremendous advancement in the development of organic conducting polymeric materials during the last decade. As a result, these polymers have become valuable components of various branches of

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science and technology and offer tremendous commercial opportunities. It is evident from the vast literature available on these materials (1–27) that their structural versatility is attracting researchers for their multiple applications such as conducting electrode materials (12), rechargeable batteries and capacitors (12), organic light-emitting diodes (12), transparent conducting coatings (18), electrically conducting textiles (19), membranes for gas separation (20), DNA sensors (21), and chemical and biological sensors (22). Among the numerous conducting polymers, polythiophenes and their alkyl derivatives are gaining more attention because of their environmental stability (13,16). The most important factor, which determines the properties of conjugated polymers, is their regioregularity, which plays an important role in determining the properties of poly(3-alkylthiophenes). Several methods have been reported for the preparation of regioregular head-to-tail polythiophenes; the simplest is the polymerization of the monomer with ferric chloride (25,26). Also, the quality of the polymer is greatly influenced by the concentrations of monomer and dopant, impurities, synthesis temperature, electrodes, and so on (27). By changing the reaction conditions, polymers with different structural, mechanical, and electrical properties can be obtained (1,2,12–16,18–24). Polythiophenes can be prepared both by electrochemical polymerization and by chemical oxidative polymerization method. Although electrochemical polymerization is suitable for the preparation of polythiophene and poly(3-methyl thiophene) (P3MT), the polymers are not processible when these are formed. In addition, the yield of the polymers is low and the polymers often do not have a well-defined structure (13). On the other hand, chemical oxidative polymerization is found suitable for the polymerization of polythiophene and P3MT with iron (III) chloride ( $\text{FeCl}_3$ ) because it produces the processible polymers in high yield (13). We have synthesized P3MT having different doping levels of  $\text{FeCl}_3$  by chemical oxidative polymerization.

In the present article, we have emphasized the temperature of polymerization of P3MT and have attempted to find out the effect of doping level and synthesis temperature on the conductivity and structure of the polymer.

## Materials and Methods

P3MT was synthesized using the Sugimoto et al. (26) method by oxidative coupling of the monomer 3-methyl thiophene with  $\text{FeCl}_3$  in chloroform ( $\text{CHCl}_3$ ) according to the polymerization reaction shown in Fig. 1. In this polymerization reaction, head-to-tail (HT) (i.e.,  $\alpha$ - $\alpha'$ ) coupling is favored, and this method usually yields 70–80% of HT-HT coupling (28). The monomer 3-methyl thiophene (Fluka-Chemie) was doubly distilled before use. The requisite moles of  $\text{FeCl}_3$  were mixed in 100 mL of  $\text{CHCl}_3$  under constant stirring in an inert atmosphere with the help of a stirrer coupled with a speed control motor. After adequate stirring, 0.1 M 3-methyl

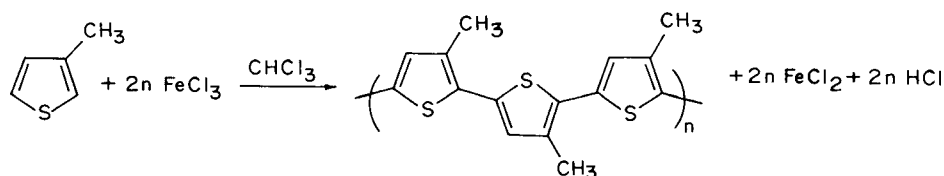


Fig. 1. Polymerization reaction for the synthesis of P3MT showing  $\alpha$ - $\alpha'$  (HT-HT) coupling.

thiophene was transferred to the solution ( $\text{FeCl}_3 + \text{CHCl}_3$ ) and stirred continuously for 2 h at room temperature (300 K). Because of polymerization, the solution yielded a greenish black precipitate. Methanol was added in a copious amount in the precipitate, and the precipitate was collected using vacuum filtration technique. The precipitate was washed with methanol of high-performance liquid chromatography grade until the filtrate became colorless and was dried under dynamic vacuum. The synthesis of the polymer was confirmed by Fourier transform infrared (FTIR) spectra recorded on a Bio-Rad 175C spectrophotometer. To observe the effect of dopant concentration, P3MT samples were prepared at 300 K by using the following concentrations of ferric chloride: 0.1, 0.2, 0.4, 0.8, 1.0, 1.5, 2.0, and 4.0 M. To observe the effect of synthesis temperature of the polymer on conductivity and surface morphology, P3MT at a dopant concentration of 0.4 M was also prepared at 280 and 270 K while keeping the other synthesis parameters the same. The yield was found to increase as the temperature of synthesis was decreased. The dried powder was ground properly and pressed at a pressure of  $\sim 5 \times 10^8$  Pa in a hydraulic press to form pellets of 6 mm diameter. Scanning electron micrographs (SEMs) of the samples were taken using scanning electron microscope Model Jeol JSM 200 to study the surface morphology using the fractal surface of different samples. Gold electrodes were vacuum evaporated on both sides of the samples, making an Au-Polymer-Au structure for the measurement of direct current (DC) conductivity. The DC conductivity was measured at room temperature (300 K) with four-probe, as well as two-probe, techniques using Keithley's 220 constant current source, 617 electrometer, and 2000 DMM.

## Results and Discussion

Figure 2 shows the FTIR spectra of the P3MT samples prepared at 300, 280, and 270 K. Table 1 summarizes the comparison of the prominent vibrational bands. The absorption bands associated with  $\text{C}=\text{C}/\text{C}-\text{C}$  stretching vibrations occur near  $1540$  and  $1658 \text{ cm}^{-1}$ , which may be considered to arise predominantly from both endocyclic and exocyclic double bonds in the oxidized species of polyheterocyclics (29). Their shift to higher energies with a decrease in synthesis temperature indicates that the better oxidation of the monomers occurs at lower temperatures. Neugebauer et al. (30) have studied electrochemically polymerized 0.4 M P3MT and observed the

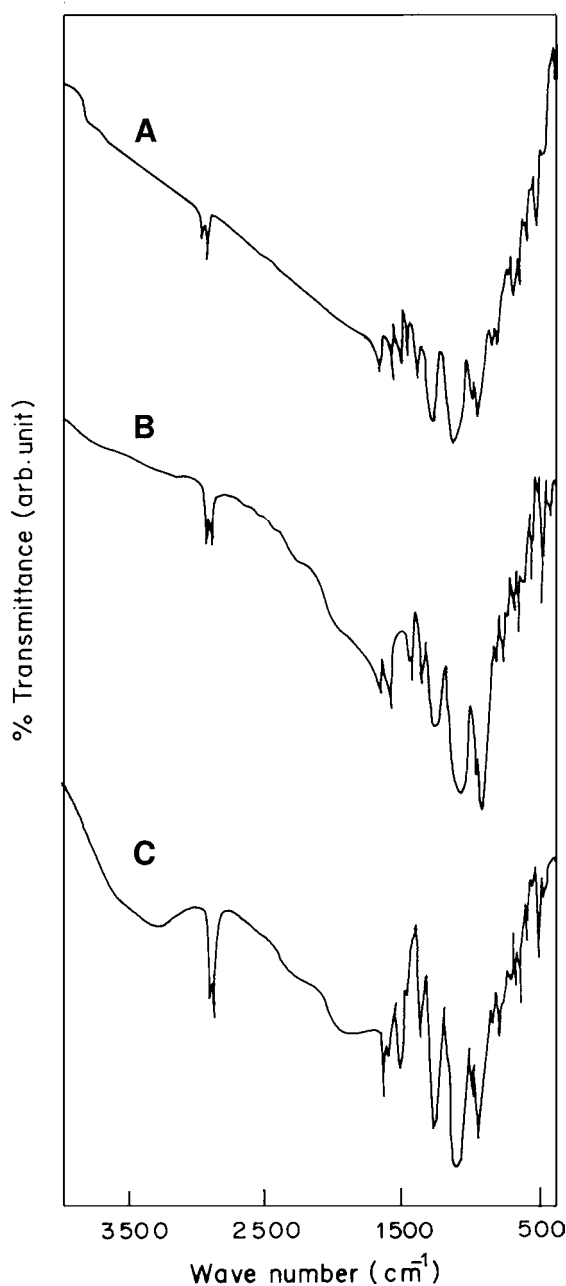


Fig. 2. FTIR spectra of P3MT synthesized at (A) 300, (B) 280, and (C) 270 K.

prominent vibrational bands in the range of 1688–612 and 3059–2860  $\text{cm}^{-1}$ . Moreover, an increase in the intensity and shift of  $\text{C}_\beta\text{-H}$  vibrational bands (2963–2900  $\text{cm}^{-1}$ ) has been observed for the samples prepared at lower temperatures (Fig. 2). In general, a shift in the heterocyclic bands in the region of 700–1200  $\text{cm}^{-1}$  with a decrease in synthesis temperature was observed in

Table 1  
Comparison of FTIR Spectra of Samples Synthesized at Different Temperatures

Band assignment	Synthesis temperature		
	300 K	280 K	270 K
	Wave number (cm <sup>-1</sup> )	Wave number (cm <sup>-1</sup> )	Wave number (cm <sup>-1</sup> )
C-H wagging	711	710	707
C-H ring bending	822	819	815
C-Cl terminal	973	971	969
C-H (deformation)	1005	1004	984
C-H (ring breathing)	1147	1127	1107
C-H in-plane bending	1295	1292	1286
Methyl deformation	1397	1392	1387
C=C/C-C stretching	1540	1523	1507
C=C/C-C stretching	1658	1653	1634
C <sub>β</sub> -H	2963	2930	2900

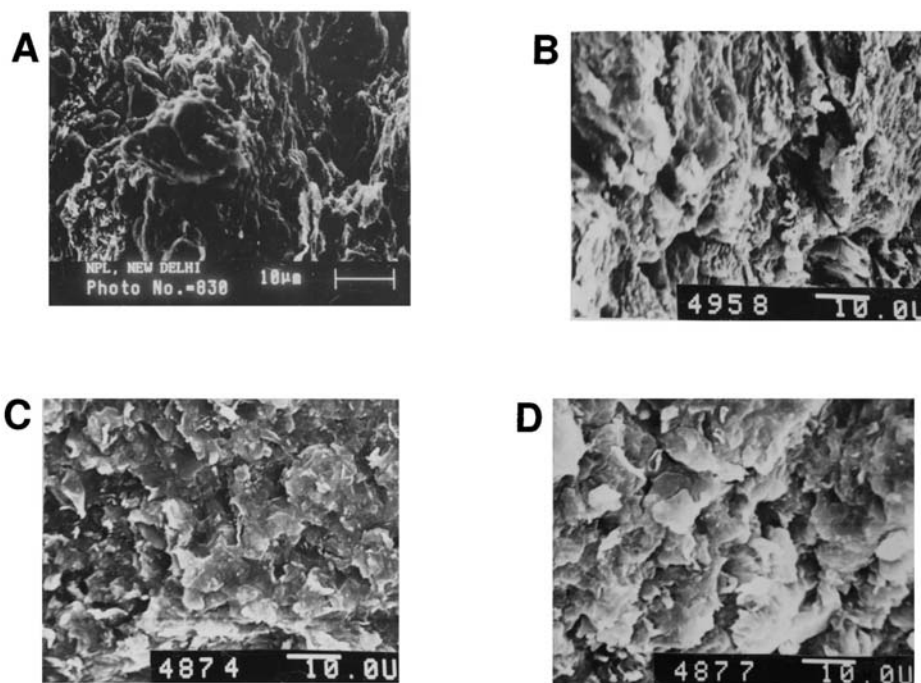


Fig. 3. SEMs of the surface structure of P3MT as a function of doping level at (A) 0.1, (B) 0.2, (C) 0.8, and (D) 1.0 M.

the present investigation and may be owing to the lower energies resulting from the coupling of skeletal backbone vibrations with  $\pi$ -electron localization along the chain (16,29–32). Some changes in the surface morphology of the polymers were observed in the initial doping levels up to 0.8 M (Fig. 3).

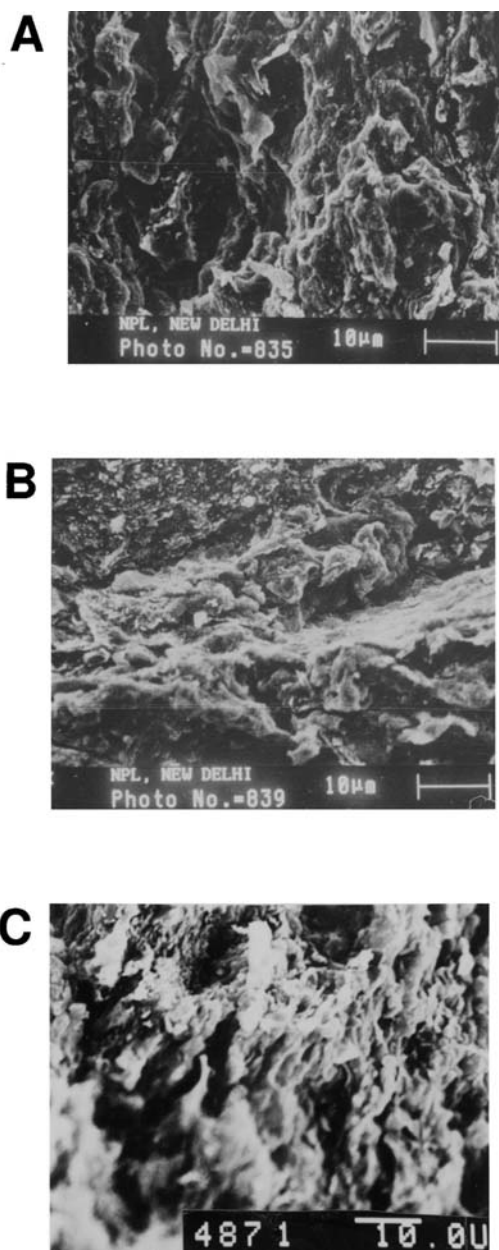


Fig. 4. SEMs of the surface structure of P3MT synthesized at (A) 300, (B) 280, and (C) 270 K.

This indicates that the surface structure changes with the doping level, which may in turn cause a change in the electrical conductivity (33). The SEMs showing the surface morphology of the samples prepared at 300, 280, and 270 K are given in Fig. 4. It can be seen from these micrographs that the surface of the sample prepared at 270 K contains fewer voids and pores.

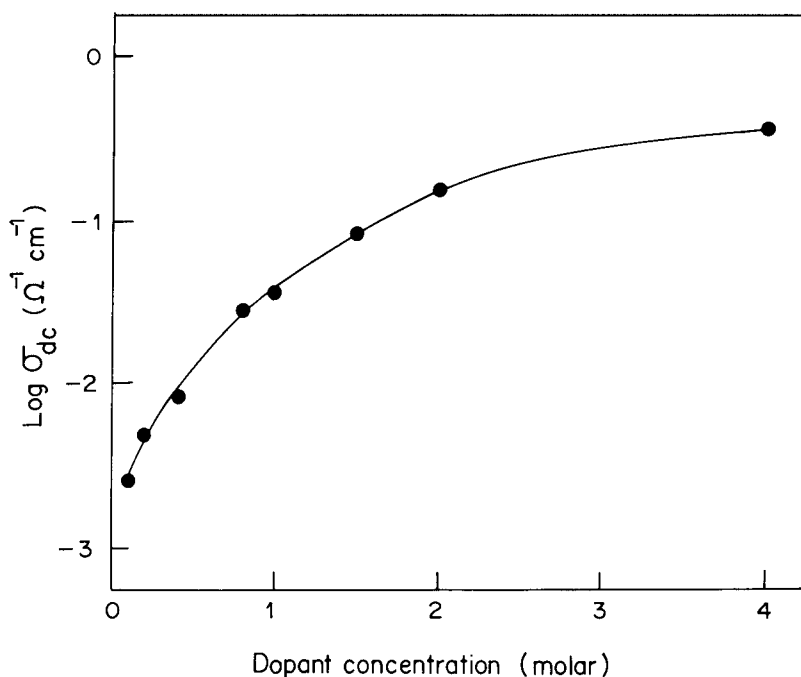


Fig. 5. Variation in DC conductivity of P3MT as a function of dopant concentration at 300 K.

This signifies that because of better  $\alpha$ - $\alpha'$  coupling, the polymer growth is more uniform at lower temperatures, which may be the reason for the higher conductivity values at lower temperatures.

Figure 5 shows the variation in DC conductivity of the P3MT samples as a function of dopant concentration at room temperature (300 K). The maximum conductivity of  $3.5 \times 10^{-1} \Omega^{-1} \text{ cm}^{-1}$  was achieved for the samples having a dopant concentration of 4.0 M. The conductivity dependence on dopant concentration (Fig. 5) indicates that the macroscopic conductivity determined on pressed pellets of P3MT initially increases up to a certain doping level (0.8 M), and thereafter the increase slows down because of the presence of impurities and structural defects, which in turn limit the doping level, resulting in trapping of the charge carriers (31,34). Although the macroscopic conductivity measured on the pellets increased with the doping level, the overall observed values are much less than what could be expected. This discrepancy could be attributed to the morphology of the polymer (32,35). The morphology of the original polymer is more regular and homogeneous at a microscopic level; however, a large structural inhomogeneity can be expected when the polymer is pressed into a pellet form. As a consequence, although the molecular properties of the polymer (i.e., its intrachain conductivity) are still retained, the poorer interfibril contacts may be limiting the overall macroscopic conductivity (35). To analyze the effect of synthesis temperature on the conductivity and morphol-

ogy of the polymer, the samples having a dopant concentration of 0.4 M were synthesized at two more temperatures: 280 and 270 K. The conductivities of the samples prepared at 300, 280, and 270 K were  $7.94 \times 10^{-3}$ ,  $3.43 \times 10^{-2}$ , and  $8.67 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ , respectively. This implies that owing to the better  $\alpha$ - $\alpha'$  coupling, giving highly conjugated chain (23,36), the samples synthesized at lower temperatures have higher conductivity values.

## Conclusion

P3MT samples synthesized at lower temperatures had fewer voids and pores in the surface structure and better  $\alpha$ - $\alpha'$  coupling, and, therefore, the samples had higher conductivity values. The conductivity dependence on dopant concentration indicated that the macroscopic conductivity determined on pressed pellets of P3MT samples initially increased up to a certain doping level (0.8 M), and thereafter the increase slowed down. In addition, after a doping level of 0.8 M, no significant changes in the surface structure were seen.

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