

Microwave-Assisted Simultaneous Synthesis of Conducting and Non-Conducting Polymers from Potassium 2,4,6-Tribromophenolate

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A simultaneous synthesis of white poly(dibromophenylene oxide) (**P**) or yellow radical ion polymer (**RIP**) and black conducting polymer (**CP**) were achieved from potassium 2,4,6-tribromophenolate by microwave energy in a very short time. Polymerizations were carried out (i) under constant microwave energy and constant amount of water with different time intervals ranging from 1 to 7 min or (ii) at constant time intervals and constant amount of water with variation of microwave energy ranging from 70 to 900 watt or (iii) at constant time intervals and constant microwave energy with changing amount of water ranging from 0.5 to 5 mL. The synthesis of **P** and **CP** were achieved in 3 min at 70 watt and in 1 min in the range of 180–900 watt in 0.5 mL water whereas **RIP** was only achieved either at 70 or 350 watt in 17 or 25 min and in 0.5 or 5 mL water. The optimum conditions for synthesis of **P**, **RIP** and **CP** were for (i) 350 watt for 3 min in 5 mL water, for (ii) 350 watt for 25 min in 5 mL water and for (iii) 500 watt for 1 min in 0.5 mL water with maximum values of 39.2, 35.0 and 27.9%, respectively. **RIP** was synthesized only at 70 watt in 17 min and at 350 watt in 3 min, having maximum conversion value of 35.0%. The polymers were characterized *via* elemental analysis, FT-IR, ^1H and ^{13}C NMR, X-ray diffraction spectroscopy, DSC, TGA-FTIR, ESR, SEM conductivity measurement and Light Scattering. Polymerizations of **P** and **RIP** were proceeding though both 1,2- and 1,4-addition at equal rates having a branch structure and their molecular weights were 8.1×10^4 g/mol and 1.2×10^4 g/mol respectively. **P** and **RIP** were rigid polymers having high T_g values. The synthesis of conducting polymer, with the conductivity of 1.34 S cm^{-2} was achieved in the absence of doping process.

KEY WORDS: Microwave Polymerization / Poly(dibromophenylene oxide) / Conducting Polymer /

Microwave power irradiation is known as an incredibly rapid and selective, clean and safe, versatile and energetically-convenient heating method, gaining increasing favor for industrial processing of numerous materials: rubbers, ceramics, textiles, minerals, wood, adhesives, some plastics and thermosetting resins, etc.¹ In the field of polymeric materials, in particular, microwave heating has shown a great potential, still far from being extensively used as it could, for accelerated industrial processing of the entire variety of commercial (both commodity and high-performance) plastics, rubbers, thermosetting resins, and related composites. The microwave polymerization technique provides a new way for production of polymers at high rates and conversions.²

Poly(dihalophenylene oxide)s (**P**) are polyethers having aromatic groups connected by an oxygen linkage at the backbone.³ The polymerizations of halogenated phenols from transition and inner transition metal complexes with various amine ligands have been studied and various decomposition techniques, electroinitiation in solution,⁴ thermal decomposition in solid state,⁵ or in solution⁶ were employed.

An organic polymer that exhibit combination of properties of metal and plastics is termed as conducting polymer (**CP**), more commonly 'synthetic metal.' Interest in conducting polymers is largely due to the wide range of possible applications because of their facile synthesis, good environmental stability and long term stability of electrical conduc-

tivity. An important step in the development of conjugated poly(heterocycles) occurred when polypyrrole, aniline and thiophene were polymerized electrochemically.^{7,8} Since 1977, increasing interest has been devoted to the electrical properties of a new-class organic conducting polymers, which can be either chemically synthesized or electrochemically grafted on electrode.⁹ **CP** represents an important research area with a great potential for commercial and technological applications due to their stability, processability and low cost.

In the previous study of the polymerization of sodium trichlorophenolate, simultaneous synthesis of poly(dichlorophenylene oxide) and **CP** were achieved.¹⁰ As a part of broader study of polymerization of various halophenol, we aimed to improve the very short time polymerization technique for potassium tribromophenolate in the simultaneous synthesis of **P** by using microwave energy and studying the effects of time, amount of water and energy, on percent conversion and structure.

EXPERIMENTAL

Materials

Analytical grade 2, 4, 6-tribromophenol (TBP) (Merck) and reagent grade KOH (Sigma and Aldrich Chemical Co Ltd) were used in the preparation of potassium 2, 4, 6-tribromophenolate. Toluene (Merck) was the solvent and ethyl alcohol

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was the non-solvent for the polymers. Deuterated chloroform was the solvent for ^1H NMR and ^{13}C NMR spectrophotometric measurements.

Polymer Synthesis

Polymerizations were performed over several time intervals (1–7 min), in different ranges of microwave energy (70–700 watt) and in various amounts of water (0.5–5 mL). The decomposition of TBP and KOH in deionized water was performed in a pyrex glass holder, loosely covered with a lid, inserted in a microwave oven, BEKO, working at 2.45 MHz and having a pulse period of 10 s. The resulting solid products were poured into toluene and the insoluble part (CP) was removed by filtration. The polymer (P) or orange colored radical ion polymer (RIP) were precipitated in ethanol containing few drops of concentrated HCl. All the recovered precipitates were dried to a constant weight under vacuum.

Polymer Characterization

Infrared spectra of the samples were obtained on a Bruker IFS 66/S FT-IR spectrometer in the 4000–400 cm^{-1} region by dispersing the sample in KBr pellets.

^1H NMR and decoupled ^{13}C NMR spectra of poly(dibromophenylene oxide) were recorded on a Bruker NMR spectrometer (DPX-400) in deuterated chloroform and TMS as an internal reference. Carbon–Hydrogen analysis of samples were carried out with a Leco 932 CHNSO elemental analyzer.

Glass transition temperatures (T_g) were measured by Du Pont Thermal Analyst 2000 DSC 910S Differential Scanning Calorimeter with a scanning rate of 10 $^\circ\text{C}/\text{min}$ for 10 mg sample under nitrogen atmosphere. As the temperature increased (30 $^\circ\text{C}$ to 850 $^\circ\text{C}$), the weight losses of the polymers were recorded with a heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere by Perkin Elmer Pyris TGA. Powder diffraction X-ray spectra of both unwashed and washed conducting polymer were measured by using a computer controlled automatic Hünner-Guinner powder diffractometer with $\text{CuK}\alpha$ radiation, having a voltage of 30 kV and a current of 7 mA. ESR spectra of the products were recorded by Bruker Xepre ELEXSY-580 spectrometer in quartz cell at room temperature where diphenylpicrylhydrazyl was the reference. Molecular weight, radius of gyration, and virial coefficient of P were determined at 37 $^\circ\text{C}$ by using Multi-angle laser scattering spectrometer (Malvern 5000). The ALV/CG-3 Goniometer system is designed to perform dynamic and static light scattering simultaneously. Conductivity of unwashed and washed CP was measured by four-probe technique.

RESULTS AND DISCUSSION

The effect of polymerization time, energy and amount of water on the % conversions¹⁸ are listed in Tables I, II, III, IV and V. The synthesis of P and CP were achieved in 3 min at 70 watt whereas in 1 min in the range of 100–900 watt. In addition, RIP synthesis was only achieved in between 17 to 25 min in 5 mL water at 70 watt and at the end of 3 min in

Table I. The effect of polymerization time and amount of water (w) on the % P, CP and RIP at 70 watt energy

Synthesized Polymers	Applied Time and Amount of Water					
	3 min 0.5 mL w	3 min 5 mL w	5 min 0.5 mL w	5 min 5 mL w	17 min 5 mL w	25 min 5 mL w
% P	18.1	20.7	29.5	30.2	—	—
% CP	10.8	9.3	11.0	10.9	—	—
% RIP	—	—	—	—	29.6	29.6

Table II. The effect of polymerization time and amount of water (w) on the % P, CP and RIP at 180 watt energy

Synthesized Polymers	Applied Time and Amount of Water					
	1.5 min 0.5 mL w	1.5 min 5 mL w	3 min 0.5 mL w	3 min 5 mL w	5 min 0.5 mL w	5 min 5 mL w
% P	20.5	23.7	23.5	24.0	26.7	29.5
% CP	12.8	13.1	11.3	11.9	11.0	10.9

Table III. The effect of polymerization time and amount of water (w) on the % P, CP and RIP at 350 watt energy

Synthesized Polymers	Applied Time and Amount of Water					
	1 min 0.5 mL w	1 min 5 mL w	1.5 min 0.5 mL w	1.5 min 5 mL w	3 min 0.5 mL w	3 min 5 mL w
% P	31.5	39.2	32.7	32.9	—	—
% CP	25.6	25.0	23.1	24.3	22.6	21.3
% RIP	—	—	—	—	31.9	35.0

Table IV. The effect of polymerization time and amount of water (w) on the % P, CP and RIP at 500 watt energy

Synthesized Polymers	Applied Time and Amount of Water					
	1 min 0.5 mL w	1 min 5 mL w	1.5 min 0.5 mL w	1.5 min 5 mL w	3 min 0.5 mL w	3 min 5 mL w
% P	30.0	33.9	30.6	30.8	—	—
% CP	27.9	26.0	25.8	18.4	—	—

Table V. The effect of polymerization time and amount of water (w) on the % P, CP and RIP at 900 watt energy

Synthesized Polymers	Applied Time and Amount of Water					
	1 min 0.5 mL w	1 min 5 mL w	1.5 min 0.5 mL w	1.5 min 5 mL w	3 min 0.5 mL w	3 min 5 mL w
% P	29.9	30.2	31.5	31.8	—	—
% CP	19.5	19.1	18.3	15.4	—	—

Table VI. Elemental analysis results of P, RIP and CP (TBP and KOH) (experimental errors ± 0.5)

	% C		% H	
	Calc.	Found	Calc.	Found
P*	29.12	29.51	1.111	0.986
RIP**	29.20	29.26	1.273	1.204
CP***	—	68.36	—	1.216

*: Synthesized at 350 watt, 1 min and 5 mL water. **: Synthesized at 350 watt, 3 min and 5 mL water. ***: Synthesized at 350 watt, 3 min and 0.5 mL water.

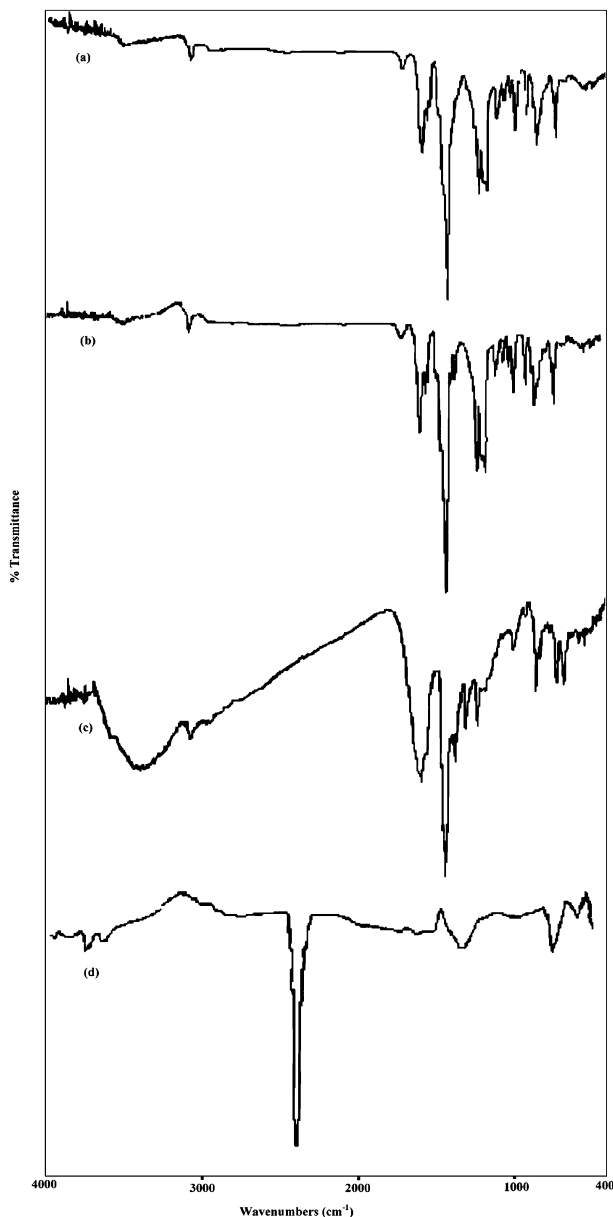


Figure 1. FT-IR spectra of (a) **P**, (b) **RIP**, (c) **CP** and (d) evolved gases during polymerization.

between 0.5 to 5 mL water at 350 watt. In the range of 100–900 watt, generally %conversion slightly increased for **P** whereas decreased for **CP** as the time increased. On the other hand, %conversion slightly increased for **P** while decreased for **CP** as the amount of water was increased (0.5–5.0 mL). Hence, the optimum condition for **P** and **CP** was 350 watt for 1 min in 5 mL water and 500 watt for 1 min in 0.5 mL water, having maximum values 39.2 and 27.9% respectively.

Elemental analysis results of all polymers correlate perfectly with the written stoichiometries as tabulated in Table VI.

FT-IR spectrum of **P** and **RIP** exhibit the characteristic absorptions at 850 cm^{-1} (out of plane C-H bending), $955\text{--}1040\text{ cm}^{-1}$ (C-O-C stretching), $1140\text{--}1210\text{ cm}^{-1}$ (C-O stretching), 1440 and 1580 cm^{-1} (C=C ring stretching), 3079 cm^{-1}

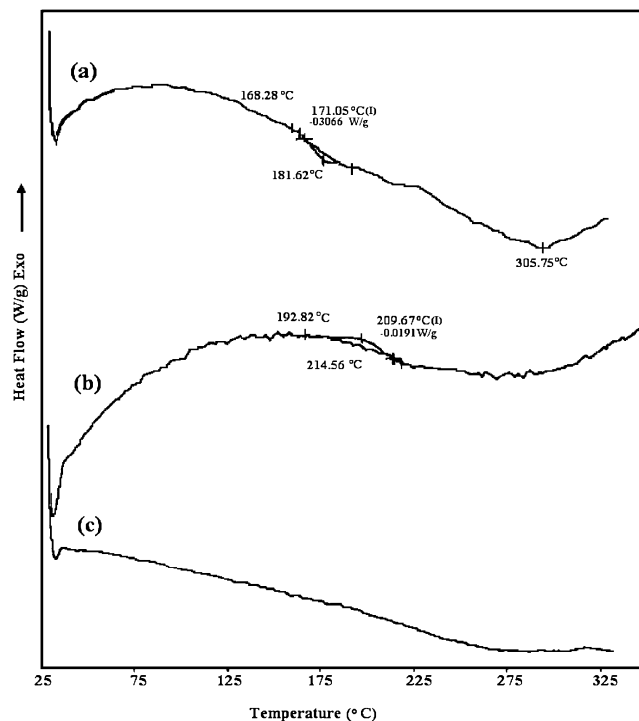


Figure 2. DSC thermograms of (a) **P**, (b) **RIP** and (c) **CP**.

(aromatic C-H stretching) and 3500 cm^{-1} (the phenolic end group) (Figure 1a and 1b), respectively. FT-IR spectrum of **CP** exhibits the peaks at $1460\text{--}1600\text{ cm}^{-1}$ (C=C stretching of both benzenoid and quinoid structures), 1710 cm^{-1} (C=O stretching), $1110\text{--}1280\text{ cm}^{-1}$ (C-O stretching), 3050 cm^{-1} (aromatic C-H stretching) and $730\text{--}760\text{ cm}^{-1}$ (C-Br stretching) (Figure 1c). The FT-IR spectrum of the evolved gas collected in a glass cell during polymerization, exhibits the peak at 2450 cm^{-1} (CO_2) (Figure 1d).

The glass transition temperature of the **P** and **RIP** were observed at 171.05 and $209.67\text{ }^\circ\text{C}$ respectively in the DSC thermogram, indicating high rigidity of polymers. However, the glass transition temperature was not observed for **CP** (Figure 2).

In the TGA thermogram, the **P** and **RIP** were stable up to nearly $360\text{ }^\circ\text{C}$ and then approximately 98% of sample was lost when the temperature reached to $800\text{ }^\circ\text{C}$ (Figure 3a and 3b). Weight loss was not observed up to $190\text{ }^\circ\text{C}$ and decomposition occurs in four stages with the small weight loss around $190\text{ }^\circ\text{C}$ and $380\text{ }^\circ\text{C}$, main degradation around $480\text{ }^\circ\text{C}$ and $620\text{ }^\circ\text{C}$. The characteristic peaks of aromatic group (2974 , 2880 , 1380 cm^{-1}) were observed in the first and the second stages of degradation with a weight loss of 2% and 8% respectively. The main degradations around $480\text{ }^\circ\text{C}$ showed bands of CO_2 (2358 and 2309 cm^{-1}), CO ($2100\text{--}2200\text{ cm}^{-1}$), HBr ($2300\text{--}2700\text{ cm}^{-1}$), vinyl bromide (1460 and 2950 cm^{-1}). The fourth emission around $620\text{ }^\circ\text{C}$ showed bands of CO_2 , CO and HBr . However, thermal stability of **CP** was higher than other polymers. Significant the weight loss started from $500\text{ }^\circ\text{C}$ having residues less than 65% beyond $800\text{ }^\circ\text{C}$ (Figure 3c). The

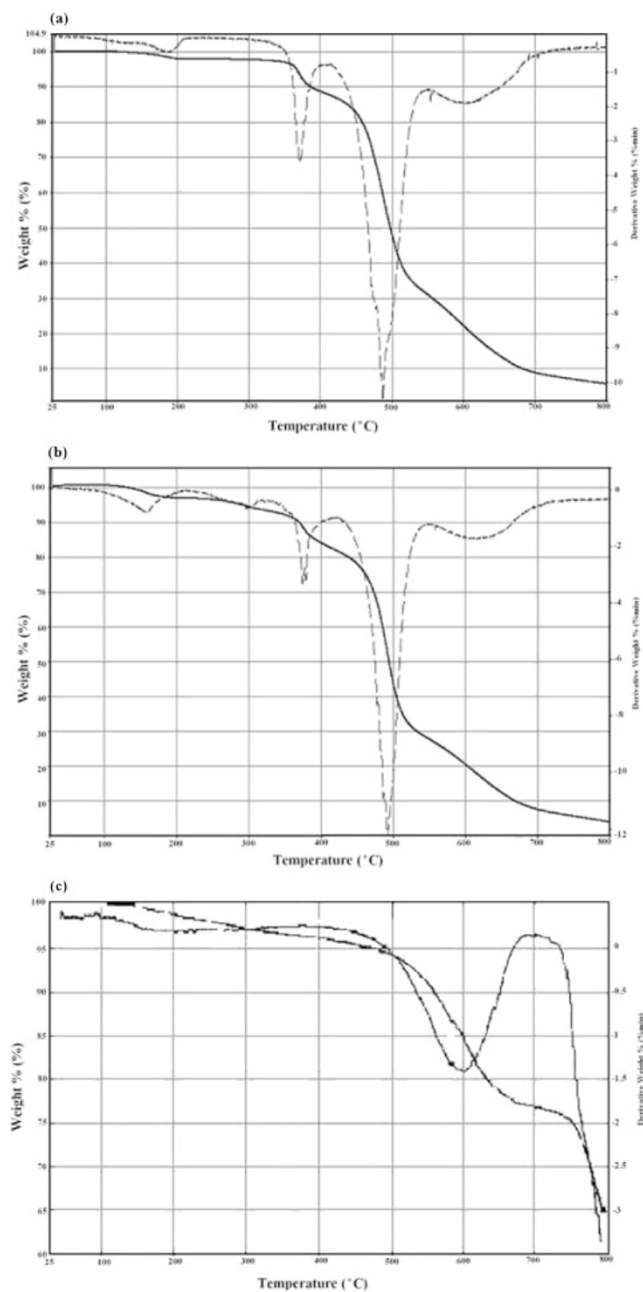


Figure 3. TGA thermograms of (a) P, (b) RIP and (c) CP.

main decomposition occurs in two stages with maximum rate of degradation around 600 °C and 800 °C. Small degradation (5%) observed up to 500 °C. In the first emission around 600 °C, characteristic bands of CO₂ (2358 and 2309 cm⁻¹), CO (2100–2200 cm⁻¹) were observed. In the second main weight loss which is beyond 700 °C, characteristic peaks of HBr (2300–2700 cm⁻¹) were observed in addition to CO₂ and CO peaks.

The ¹H NMR spectrum of **P** and **RIP** were characterized by the peak around 7.0 ppm due to protons of 2,6-dibromo-1,4-phenylene oxide (1,4-addition) and the small peak at 7.3 ppm due to protons of 2,4-dibromo-1,6-phenylene oxide unit (1,2

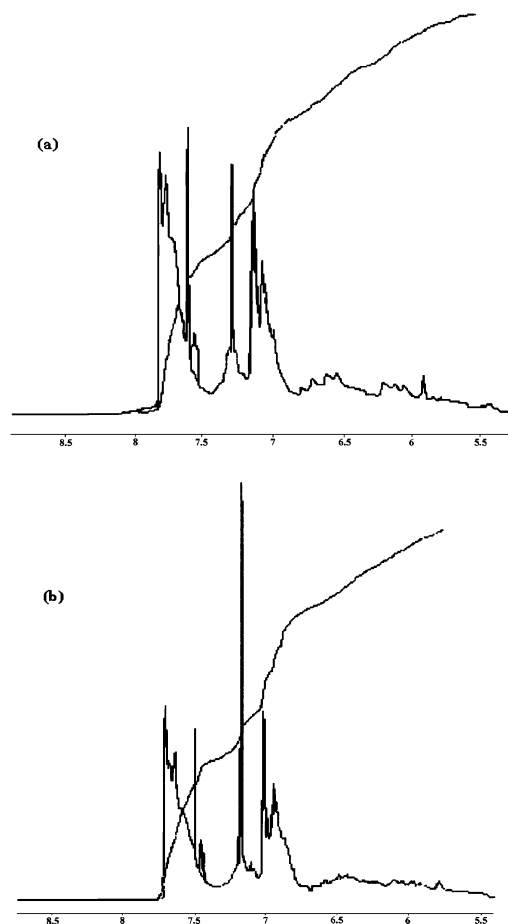


Figure 4. ¹H NMR spectrum of (a) P and (b) RIP.

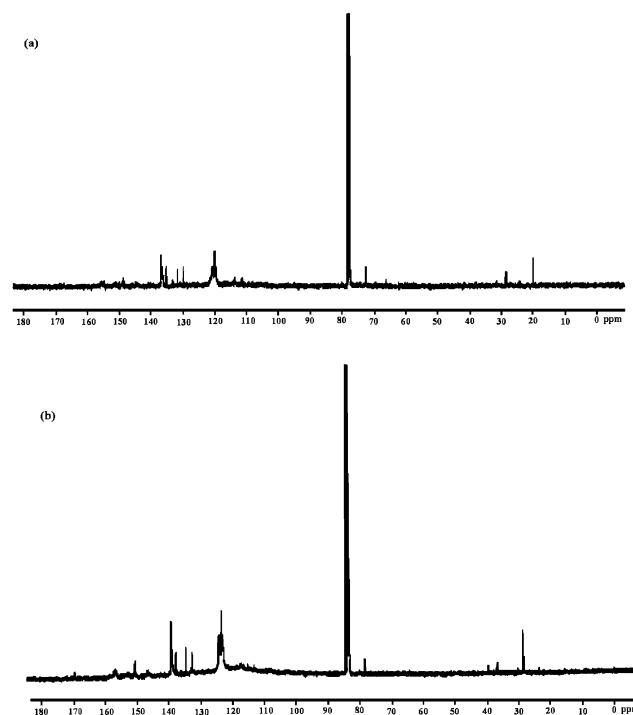


Figure 5. Proton-decoupled ¹³C NMR spectrum of (a) P and (b) RIP.

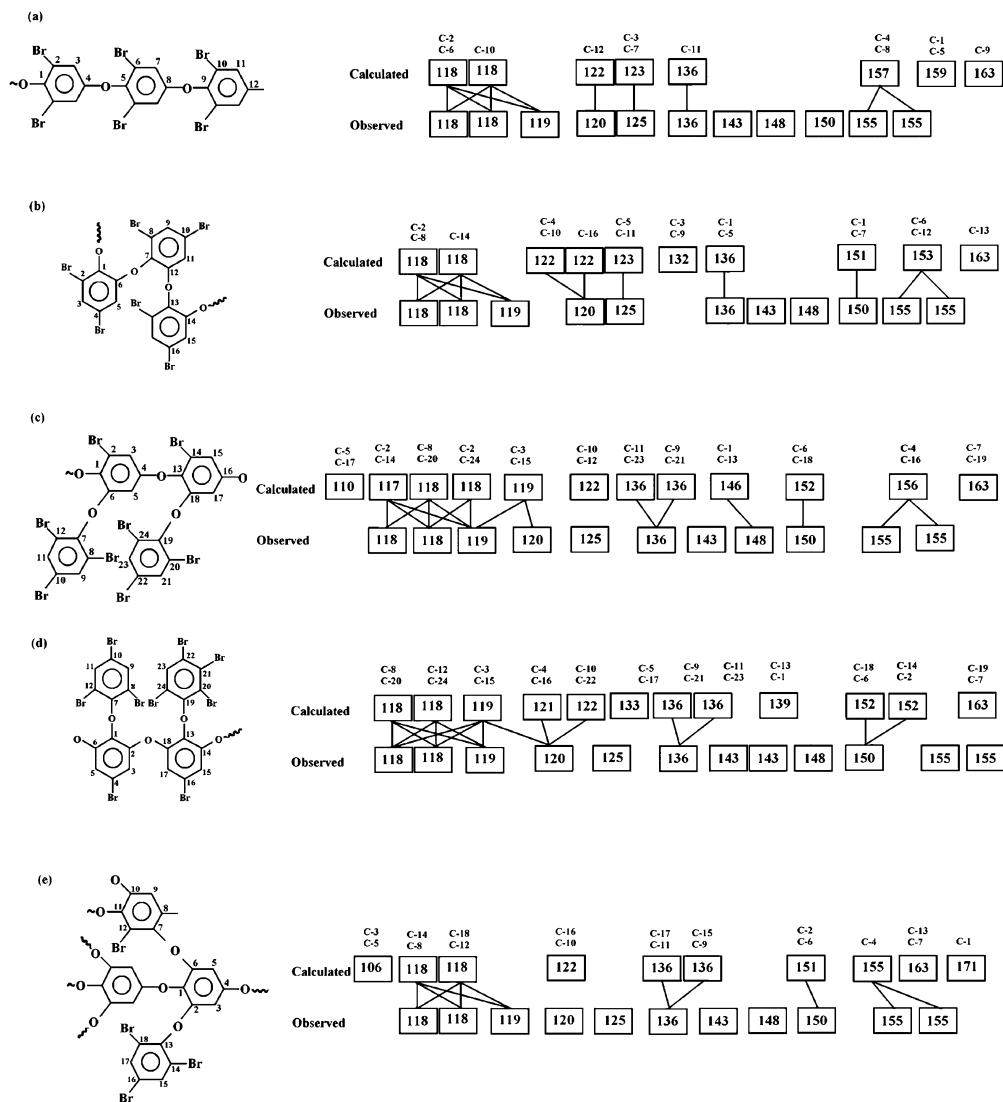


Figure 6. ^{13}C NMR proton shift data of P.

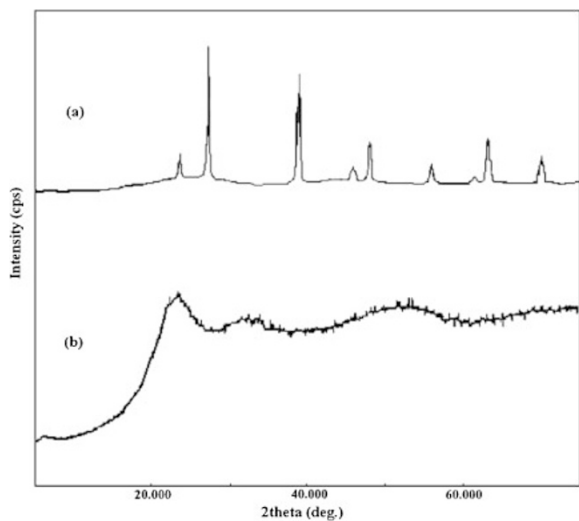


Figure 7. X-Ray powder diffraction spectra of (a) unwashed CP and (b) washed CP.

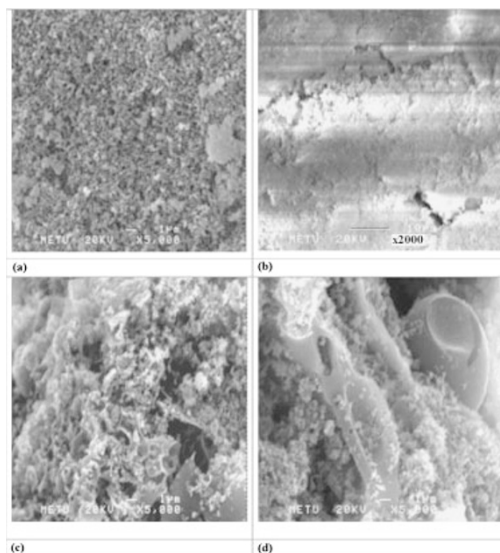


Figure 8. SEM micrographs of (a) P, (b) RIP, (c) and (d) CP.

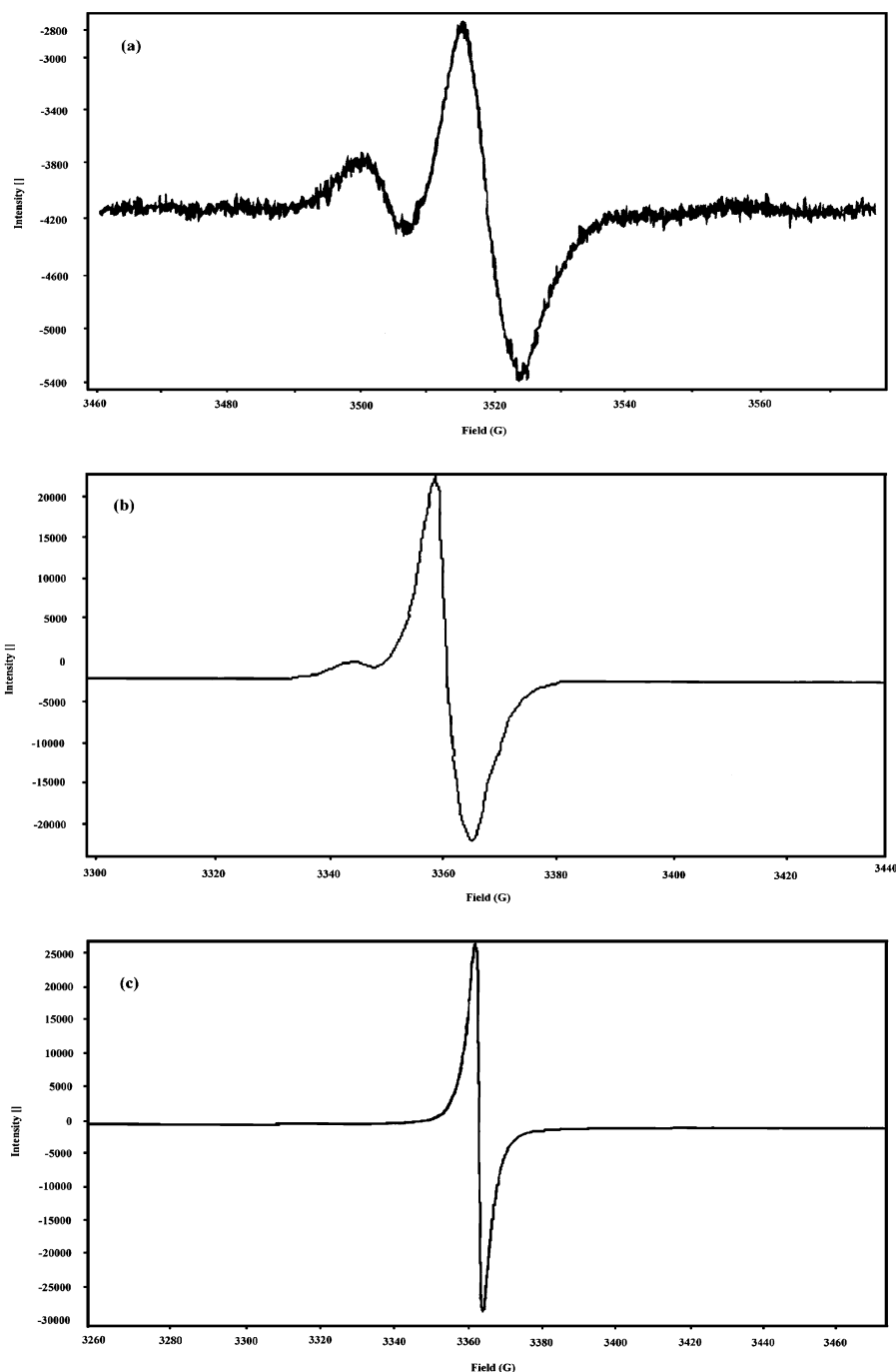


Figure 9. ESR Spectrum of (a) **P**, (b) **RIP** and (c) **CP** at room temperature.

addition) and the boarder peaks at higher field due to the presence of 1,2 and 1,4-addition on the same monomeric unit (Figure 4a and 4b).⁴⁻⁷ ^{13}C NMR decoupled spectra of **P** and **RIP** were displayed in Figure 5. The theoretical ^{13}C NMR chemical shift data for five possible addition products were calculated by using appropriate Tables.¹¹ ^{13}C NMR shift data showed that **P** and **RIP** correlated well with the branched structure indicating 1,2- and 1,4-addition at almost equal rate (Figure 6).

The powder diffraction X-ray spectra of unwashed **CP** contains three strongest line of d-spacing of KBr (by product of the polymer synthesis) (Figure 7a) and washed **CP**, having a broad line, indicating an amorphous polymer (Figure 7b).

The molecular weight of the **P** and **RIP** were determined as 8.1×10^4 g/mol and 3.3×10^4 g/mol respectively by the light scattering. Radius of gyration and second virial coefficient of the **P** and **RIP** were determined as 2.78×10^1 nm and 6.13×10^{-8} mol.dm³/g² and 7.53×10^1 nm and 2.91×10^{-7}

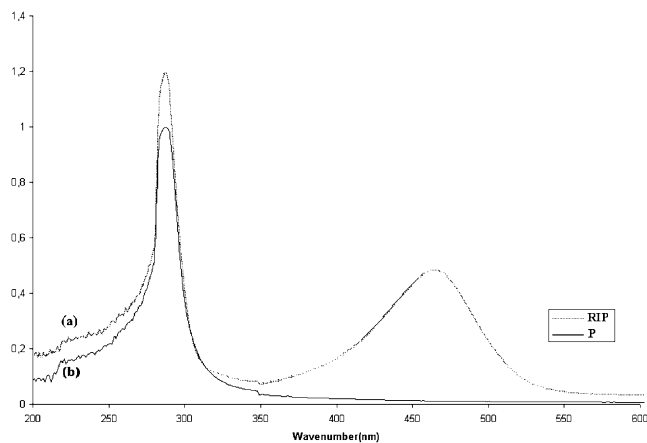


Figure 10. UV-vis Spectrum of (a) **P** and (b) **RIP** at room temperature.

mol.dm³/g² respectively indicating that toluene was a theta solvent.

The surface morphology analyses of all type of polymers were done by scanning electron microscope. In Figure 8a, **P** had fine granular structure, significantly different from the **CP** having sponge like structures (Figure 8c and 8d) and tubular structures when magnified 5000 times and orange colored coarse surface of **RIP** was detected when magnified 2000 times (Figure 8b). The X-ray microanalysis system detected the existence of O, Br and C on all of **P**, **CP** and **RIP** whereas K detected on the unwashed **CP**.

ESR spectrum of microwave initiated **P**, **RIP** and **CP** products were revealed the signals with g values of 2.00550, 2.00549 and 2.00294 respectively (Figure 9) which were very close to g values of free electron.

The UV-visible absorption spectra of synthesized polymers dissolved in toluene were shown in Figure 10. The spectrum of monomer (TBP) and **P** show single absorption maxima around 270 nm which can be correlated to absorption of benzene ring K-band (Figure 10a and 10b). However, in the spectrum of **RIP**, evolution of new broad band located around 470 nm were observed, which was related to the π - π^* transition and the formation of polarons (Figure 10c and 10d).

The electrical conductivities of washed **CP**, unwashed **CP** and **RIP** were measured as 0.2, 1.34 and 2×10^{-5} S cm⁻¹ respectively whereas **P** was an insulator. Conductivity of washed **CP** was higher than unwashed **CP**. Conductivity values of **CP** which was synthesized at different reaction conditions (microwave-energy, time and water content) were very close to each other.

CONCLUSION

Microwave-assisted polymerization was achieved very

rapidly (1 to 5 min) compared to previously used methods (3 to 48 hours).⁴⁻⁷ In addition, induction period for the polymerization was very short (less than 3 min at 70 watt and 1 min at higher watts) when compared to the syntheses in solution or in solid state. The synthesis of poly(dibromophenylene oxide) and conducting polymer and/or radical ion were achieved simultaneously from potassium 2,4,6-tribromophenolate by microwave energy. The optimum conditions for **P** and **CP** were 350 watt and 500 watt for 1 min, having maximum conversion values of 39.2 and 27.9%, respectively. **RIP** was synthesized only at 70 watt in 17 min and at 350 watt in 3 min, having maximum conversion value of 35.0%. The percent conversions of TBP are higher than TCP (microwave-assisted synthesis of polymers from sodium trichlorophenolate)¹⁸ for **P** whereas lower for **CP**. **P** and **RIP** proceed through 1,2- and 1,4-addition at almost equal rate leading to a branched polymer. Molecular weight of the **P** and **RIP** were 8.1×10^4 g/mol and 1.2×10^4 g/mol respectively, higher than TCP. The direct synthesis of highly conducting polymer, with the higher conductivity value of 1.34 S cm⁻² compared to **CP** of TCP was achieved in the absence of applied doping process in a very short time. ESR spectrum of microwave initiated **P**, **RIP** and **CP** products were revealed the signals very close to g values of free electron. Analysis of the surface morphologies of all type polymers indicated fine granular, sponge like and coarse surface structures for **P**, **CP** and **RIP** respectively. High T_g value of **P** and **RIP** indicates high rigidity.

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