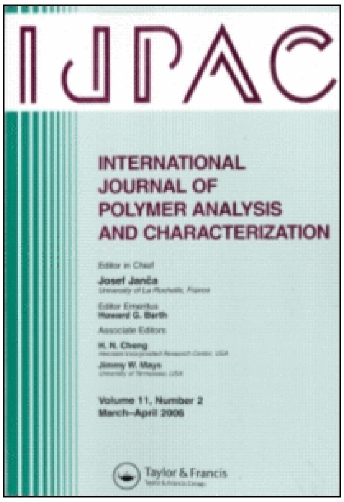


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Synthesis of Poly(*o*-toluidine) in DMF/Water Mixture Using Benzoyl Peroxide

Zerin Mucuk[a]; Meral Karakışla[a]; Mehmet Saçak[a]
[a] Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey

To cite this Article Mucuk, Zerin , Karakışla, Meral and Saçak, Mehmet(2009) 'Synthesis of Poly(*o*-toluidine) in DMF/Water Mixture Using Benzoyl Peroxide', International Journal of Polymer Analysis and Characterization, 14: 5, 403 — 417

To link to this Article: DOI: 10.1080/10236660903031025
URL: http://dx.doi.org/10.1080/10236660903031025

International Journal of Polymer Anal. Charact., 14: 403–417, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/10236660903031025

Synthesis of Poly(*o*-toluidine) in DMF/Water Mixture Using Benzoyl Peroxide

Zerin Mucuk, Meral Karakışla, and Mehmet Saçak
Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey

Abstract: The chemical polymerization of *o*-toluidine was carried out in dimethylformamide/aqueous HCl solution using benzoyl peroxide. The conductivity of poly(*o*-toluidine) (POT) doped with HCl changed from 2.0×10^{-4} to $15.6 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ depending on the polymerization parameters. The solubility of POT in DMSO was found as 0.3 g/100 mL, in which the solubility of HCl-doped polyaniline was 0.042 g/100 mL. Characterization of synthesized POT was performed by conductivity, solubility, FT-IR, UV-vis, and TGA techniques. Thermal-sensing property of POT was also investigated between $-10°$ and $+120°\mathrm{C}$ by heating-cooling cycles.

Keywords: Benzoyl peroxide; Chemical polymerization; Conducting polymer; Temperature sensing

INTRODUCTION

Since the 1970s, many studies have been carried out on the synthesis and characterization of conductive polymers.[1–4] As a member of the family of conductive polymers, polyaniline has received extensive interest due to its controllable electrical conductivity, environmental stability, reversible proton doping, and easy synthesis.

Submitted 16 February 2009; revised 24 April 2009; accepted 11 May 2009.

The authors want to thank Ankara University Research Fund (BAP) for its financial support of this work.

Correspondence: Meral Karakışla, Department of Chemistry, Faculty of Science, Ankara University, 06100 Tandoğan, Ankara, Turkey. E-mail: mkarakisla@yahoo.com.

However, insoluble and infusible properties of polyaniline[5,6] restrict its potential applications in areas such as electromagnetic shielding, antistatic coatings, rechargeable batteries, electrochromic devices, and gas sensors and activators.

The solubility of polyaniline in organic solvents can be increased to a certain extent depending on the type of dopant used.[7,8] Another approach to synthesis of soluble conducting polymers having a chemical structure similar to that of polyaniline is the polymerization of aniline derivatives such as *N*-ethylaniline, *N*-methylaniline, anisidine, and *o*-toluidine.[9–11] Aniline derivatives can be polymerized by chemical or electrochemical methods.[12–14]

The use of benzoyl peroxide as a new oxidant for the synthesis of conductive polymers in the solution[15] and inverse emulsion polymerization[16] of monomers containing amine groups provides some advantages compared with inorganic oxidants. For example, problems such as the formation and removal of by-products that frequently occur with inorganic oxidants are not encountered with benzoyl peroxide. Moreover, the residue and by-products of benzoyl peroxide remaining in the polymerization medium can easily be removed with a suitable organic solvent.

In the present study, the chemical oxidative polymerization of *o*-toluidine by benzoyl peroxide in aqueous organic media was first investigated. The effects of polymerization parameters such as dimethylformamide (DMF)/water volume ratio, oxidant, acid and monomer concentrations, time, and temperature on the yield and conductivity of poly(*o*-toluidine) (POT) were studied. The polymer synthesized was characterized with UV-vis, Fourier transform-infrared (FT-IR), and thermogravimetric analysis (TGA) techniques. Conductivity, solubility, and thermal sensing property of POT were also examined.

MATERIALS AND METHODS

Materials

o-Toluidine (Merck) was distilled under vacuum and benzoyl peroxide (Bz_2O_2) (Merck, Germany) was recrystallized from methanol-chloroform mixture. Solvents, acids, and other chemicals were supplied from Merck and employed without further purification.

Chemical Polymerization of *o*-toluidine

Chemical polymerization was carried out in a polymerization tube 3 cm in diameter and 15 cm long immersed in a temperature-adjustable water bath. A 17 mL amount of the aqueous acid solution containing an appropriate concentration of *o*-toluidine was first put into the tube and then the total volume of the mixture was made up to 20 mL by adding 3 mL of Bz_2O_2 solution prepared in a suitable organic solvent.

At the end of the polymerization, the mixture was cooled, and POT precipitated in the medium with a green color was separated by a centrifuge, washed with acetone, and then diluted by an acid solution in order to remove the residual Bz_2O_2 and unreacted aniline. Finally, the polymer was dried under vacuum for 12 h at 50°C.

The percentage yield of POT (POT yield, %) was determined gravimetrically.

The polymerization of *o*-toludine in acids such as HNO_3, $HClO_4$, HCl, H_2SO_4, H_3PO_4, HCOOH, HOOCCOOH, and CH_3COOH was carried out according to the above-mentioned procedures.

Solubility Test

First, 1 g POT was added to 10 mL solvent and filtered after having been vigorously mixed for 24 h at 25°C. The filtrate was then dried at 50°C under vacuum until the constant weight and the solubility value were calculated as gram of POT in 100 mL solvent.

Characterization Techniques

The conductivities of the polymer samples, which were prepared as pellets with diameters of 1.3 cm and thickness of 1 mm under 80 kN/m^2 pressure, were calculated from their resistivity values measured by the two-probe method using a Keithley 6517A electrometer.

The change in the electrical resistivity of the POT pellet with temperature was also monitored. The pellet was mounted to two copper wires with a conductive adhesive and then placed in a glass chamber whose temperature was controlled by a Huber model TC50E cryostat and oil bath. The resistivity was recorded during the heating period from $-10°$ to $+120°C$ and recooling to $-10°C$ at a heating rate of 2°C min^{-1}. This heating-cooling process was repeated three times.

The FT-IR spectra of the polymer samples were taken by a Mattson 1000 spectrometer. The UV-vis spectra of the solutions of undoped and doped POT in dimethyl sulfoxide (DMSO) were recorded with a Shimadzu 1700 UV-vis spectrophotometer.

The thermogravimetric analysis was carried out with a Shimadzu DTA-60H, DSC-60 model thermal analyzer at a flow rate of 10 mL min^{-1} and a heating rate of 10°C min^{-1} under N_2 atmosphere.

RESULTS AND DISCUSSION

Solvent Type and DMF/Water Volume Ratio

In the graft copolymerization studies carried out by Bz_2O_2, it is known that the solvents used to dissolve Bz_2O_2 affect the graft yield.[17,18] Therefore, Bz_2O_2 dissolved in different organic solvents was added to the polymerization tube containing acidic water and monomer to start the polymerization, where the organic solvent/water mixture ratio was kept at a value of 20/80 (v/v). The data for the yield and conductivity of POT given in Table I were obtained.

From Table I, it can be seen that POT with high yield and conductivity was obtained with the DMF/water mixture. Since the solvents could influence the polymerization process by interfering with some reactions, changing the mobility of reactants, etc., the explanation of their role in polymerization is difficult.[18]

In order to elucidate the effect of the amount of DMF on the yield and conductivity of POT, a set of experiments was also performed with different DMF/water ratios (Figure 1).

As can be seen from Figure 1, the maximum POT yield of 17.5% was obtained at a DMF/water ratio of 30/70 (v/v). This ratio was chosen for further runs. The decrease in the POT yield at a high amount of DMF can be attributed to increasing solubility of POT in the medium.

Dopant Type

The polymerization of *o*-toluidine was carried out in the presence of different dopants, and experimental results are indicated in Table II.

Table I. Change of yield and conductivity of POT with various solvent/water mixtures at a ratio of 20/80 (v/v)

Solvent type	POT yield (%)	Conductivity (10^4S cm^{-1})
Methanole/water	2.8	0.86
Ethanole/water	3.4	0.67
Propanole/water	2.2	0.57
Acetone/water	6.0	0.56
Acetonitrile/water	2.4	0.12
DMF/water	7.2	6.10
DMSO/water	3.9	0.78

[HCl], 1.0 mol L^{-1}; [Bz_2O_2], 7.5×10^{-3} mol L^{-1}; [*o*-toluidine], 0.1 mol L^{-1}; temperature, 40°C; polymerization time, 2 h.

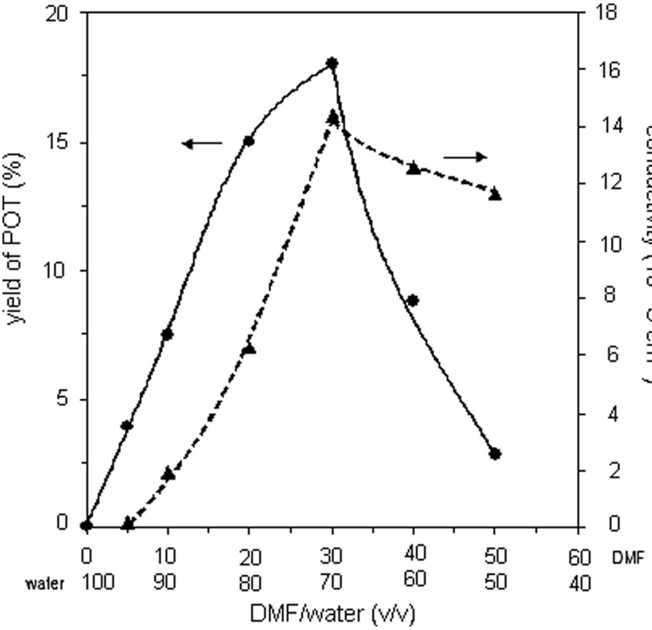


Figure 1. Effect of DMF/water (v/v) ratio on yield and conductivity of POT. [Bz_2O_2], 7.5×10^{-3} mol L^{-1}; [*o*-toluidine], 0.1 mol L^{-1}; [HCl], 1.0 mol L^{-1}; temperature, 40°C; polymerization time, 2 h.

Among the eight different acids employed as dopants, POT was obtained as a green powder only with HCl and HOOCCOOH, and no polymer formation was observed with HCOOH and CH_3COOH. The products obtained with HNO_3, $HClO_4$, H_3PO_4, and H_2SO_4 were brownish oily substances.

Table II. Change of yield and conductivity of POT with dopant type

Dopant type	POT yield (%)	Conductivity (S cm^{-1})
HCl	17.5	15.6×10^{-4}
HOOCCOOH	0.8	0.02×10^{-4}
HNO_3	oily product	—
$HClO_4$	oily product	—
H_3PO_4	oily product	—
H_2SO_4	oily product	—
HCOOH	nil	—
CH_3COOH	nil	—

[acid], 0.5 mol L^{-1}; [Bz_2O_2], 7.5×10^{-3} mol L^{-1}; [*o*-toluidine], 0.1 mol L^{-1}; DMF/water ratio, 30/70 (v/v); temperature, 40°C; polymerization time, 2 h.

Our result shows that HCl is a favorable dopant within the dopants examined for the synthesis of POT with high yield and conductivity by Bz_2O_2. Rao et al.[19] also reported that the conductivity of polyaniline prepared by the polymerization of aniline in an organic peroxide system by the inverted emulsion process is higher with HCl.

The effect of HCl concentration on the yield and conductivity of POT was investigated with another set of experiments, and the data are given in Figure 2. With an increase in the dopant concentration from 0.25 to 2.0 mol L^{-1}, there is a rapid increase up to 1.0 mol L^{-1} HCl in the conductivity of the POT. However, when the concentration is raised above this value, the conductivity of POT decreases. A similar effect of acid concentration on the yield and conductivity of polyaniline obtained in different aqueous acid media such as H_2SO_4, HNO_3, H_3PO_4, and CH_3COOH has been reported.[19,20]

One of the reasons for the decrease in POT yield at high acid concentration is the degradation of the POT formed in the medium.[19] Another reason is that during the polymerization of *o*-toluidine, the propagation reactions take place by the combination of the monomer cation radicals, and this process requires the removal of an H^+ ion from the dimeric structure formed. At high HCl concentrations, the removal of an

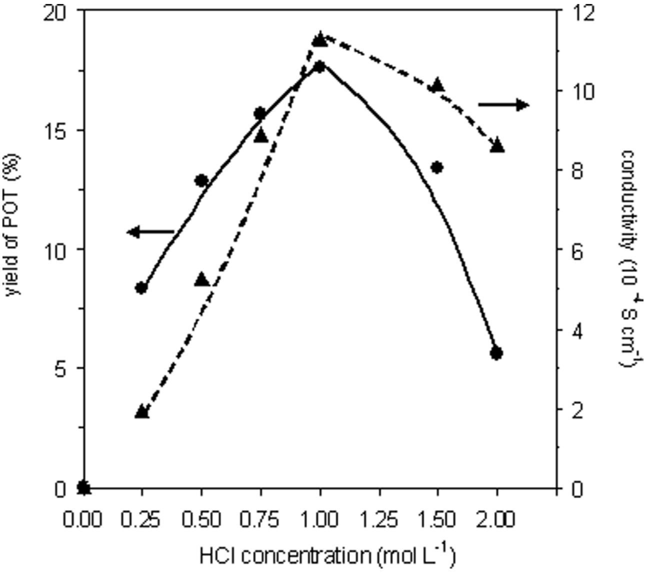


Figure 2. Change of yield and conductivity of POT with HCl concentration. DMF/water ratio, 30/70 (v/v); $[Bz_2O_2]$, 7.5×10^{-3} mol L^{-1}; [*o*-toluidine], 0.1 mol L^{-1}; temperature, 40°C; polymerization time, 2 h (●, yield; ▲, conductivity).

H^+ ion is not possible and the product remaining at oligomer level due to the restricted chain growing[21] is soluble.

The decrease in the conductivity of POT is related to the degree of its crystallinity, which affects the conductivity of the conducting polymers.[20] At the high acid concentrations, POT chains contract and their conformations convert to a compact coil form, which is not favorable for electrical conductivity because of the screening effect of H^+ and the anions of the excess acid.

Monomer and Oxidant Concentration

The maximum yield (17.5%) and the highest conductivity (15.6×10^{-4} $S\,cm^{-1}$) of POT were obtained with *o*-toluidine concentration of $0.1\,mol\,L^{-1}$ (Figure 3). At concentrations above this, the yield and conductivity decrease due to the formation of a large number of monomeric active sites, which could produce soluble oligomeric species in the polymerization medium.[22] Decrease in the electrical conductivity of POT at high monomer concentration is a result of the short chain conjugation of the precipitated polymer.

Yield and conductivity of POT-doped HCl were observed to depend on the concentration of Bz_2O_2 (Figure 4). The POT yield reaches its

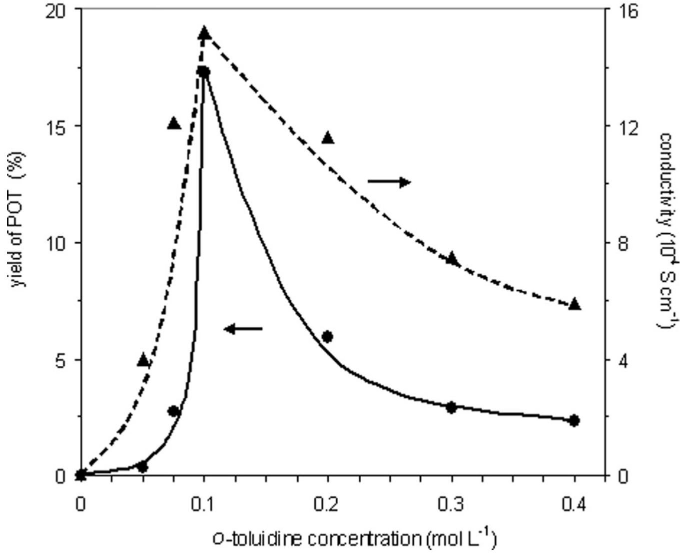


Figure 3. Change of yield and conductivity of POT with *o*-toluidine concentration. DMF/water ratio, 30/70 (v/v); [Bz_2O_2], $7.5 \times 10^{-3}\,mol\,L^{-1}$; [HCl], $1.0\,mol\,L^{-1}$; temperature, 40°C; polymerization time, 2 h (●, yield; ▲, conductivity).

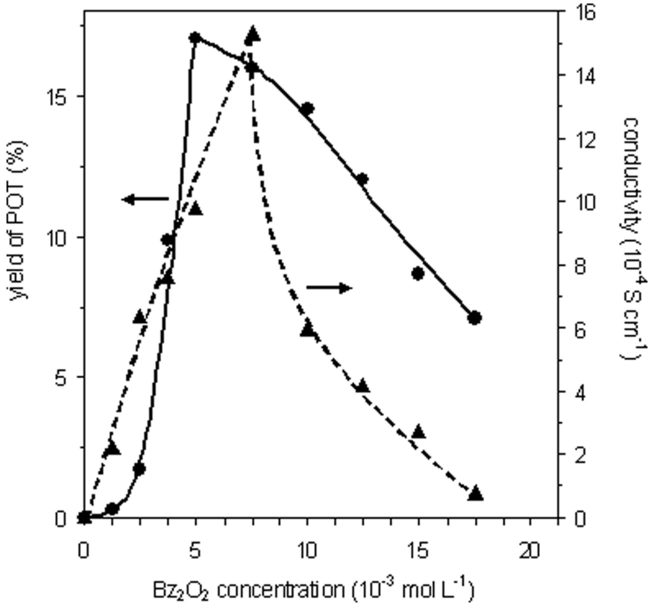


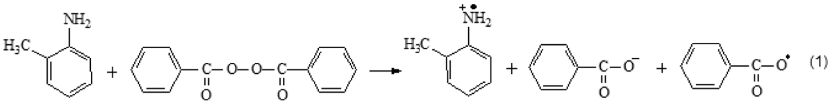
Figure 4. Change of yield and conductivity of POT with Bz_2O_2 concentration. DMF/water ratio, 30/70 (v/v); [*o*-toluidine], 0.1 mol L^{-1}; [HCl], 1.0 mol L^{-1}; temperature, 40°C; polymerization time, 2 h (●, yield; ▲, conductivity).

maximum value at Bz_2O_2 concentration of 5×10^{-3} mol L^{-1} and shows a rapid decrease at higher concentrations than that. Similarly, the conductivity of POT increases up to 7.5×10^{-3} mol L^{-1} of Bz_2O_2 concentration and decreases thereafter.

The decrease in the yield and conductivity of POT at higher Bz_2O_2 concentrations may be assigned to over-oxidation of radical cations and POT.[23,24] The over-oxidation of radical cations, which are responsible for growth of the polymer chains, interrupts the polymerization and causes the decrease in yield. On the other hand, the over-oxidation of POT to its nonconducting form decreases the conductivity of POT.[19]

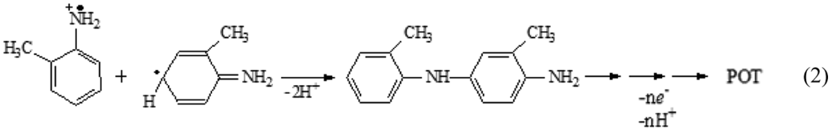
MECHANISM

When the general reactions of amines with peroxides are taken into account,[25–27] it can be concluded that the possible reaction between aniline and Bz_2O_2[15] is valid for *o*-toluidine as well. Thus, the mechanism in Reaction 1 was suggested for the formation of the radical cation of *o*-toluidine.



Reaction 1. Formation of the radical cation of *o*-toluidine.

As was observed with the aromatic amines having electron donor groups, the methyl group on the ring of *o*-toluidine has the effect of increasing the rate of reactions given above.[28] The polymerization of *o*-toluidine takes place through an oxidative mechanism, and the radical cation of *o*-toluidine that occurred according to reaction 1 could react with other types of radical cations to form POT as shown in Reaction 2.



Reaction 2. Formation of POT.

During polymerization, the color of the mixture first turned slowly to pink, then blue and green before the precipitation of POT. This color change is a result of the formation of radical cations of *o*-toluidine in the medium.[23]

Solubility

The solubility of POT was tested in various solvents, and POT showed the highest solubility in DMSO with a value of 0.3 g/100 mL. The solubility of POT doped with HCl in DMF and *N*-methyl pyrrolidone was found to be 0.08 and 0.16 g/100 mL, respectively. POT was not dissolved in other organic solvents such as acetonitrile, methanol, and ethanol.

For comparison, the solubility of HCl-doped polyaniline was also examined in DMF, *N*-methyl pyrrolidone, and DMSO and was found to be 0.03, 0.11, and 0.042 g in 100 mL of solvent, respectively. These results show that the solubility of HCl-doped POT in the solvents used was higher than that of polyaniline.

Temperature-Sensing Property

The temperature-sensing property of POT was evaluated by the monitoring of electrical resistivity of POT during the heating-cooling cycles repeated three times in the temperature range of −10° to +120°C (Figure 5).

At all heating steps, resistivity values reached a maximum (i.e., the lowest conductivity) at +30°C. At further heating, resistivity showed a decrease in a narrow temperature range, increased up to +80°C, and finally decreased up to +120°C. The high resistance values observed at about 30°C and 80°C can be attributed to the weak electrical charge hopping process between polymer chains. The change in the polymer chain conformations at these temperatures may also negatively affect the conductivity.[29,30]

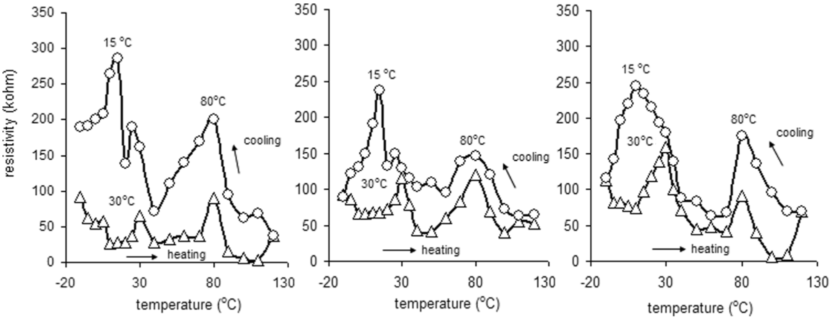
In cooling cycles starting at +120°C, there was an increase in the resistivity values at +80°C and +15°C. The resistivity value of POT at +80°C was lower than that observed at +15°C.

UV-Vis Spectra

Figure 6 shows UV-vis spectra of HCl-doped POT and its undoped form prepared by stirring in NaOH for 24 h.

The band at 420 nm observed in conductive POT in Figure 6(a) belongs to localized polaron bands for the protonated structure of POT. The band at 780 nm is the characteristic for emeraldine salt structure and the same band for the conducting PAn is encountered at 800 nm.[26] This blueshift of 20 nm can be explained by the fact that the bulky methyl substituents on benzene rings of POT force the polymer chain to be less planar and decrease the delocalization capability of electrons.[23,27]

In the spectrum of undoped POT (Figure 6(b)), the characteristic conduction bands at 780 nm completely disappeared and a new band at 570 nm representing the form of nonconducting POT appeared.



(a) (b) (c)

Figure 5. Change of electrical resistivity of HCl-doped POT with the heating-cooling process performed three times between −10° and +120°C: (a) first cycle, (b) second cycle, (c) third cycle.

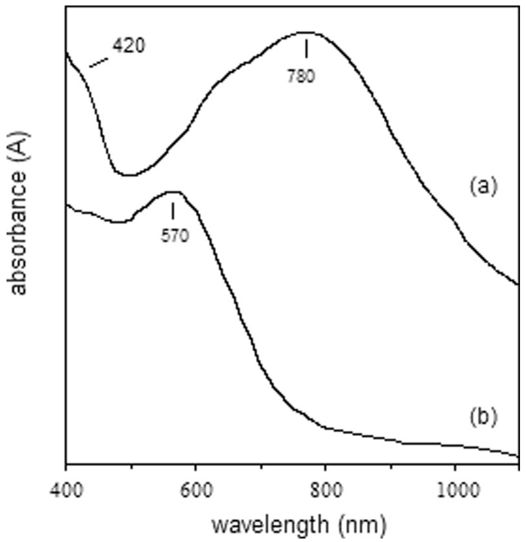


Figure 6. UV-vis spectra of (a) HCl-doped, (b) undoped POTs in DMSO.

FT-IR Spectra

On the spectra given in Figure 7, the peaks observed at 2922 cm^{-1}, 1591 cm^{-1}, and 1469 cm^{-1} correspond to C-H stretching of methyl substituent, C-N stretching of quinoid, and benzenoid rings of POT, respectively.

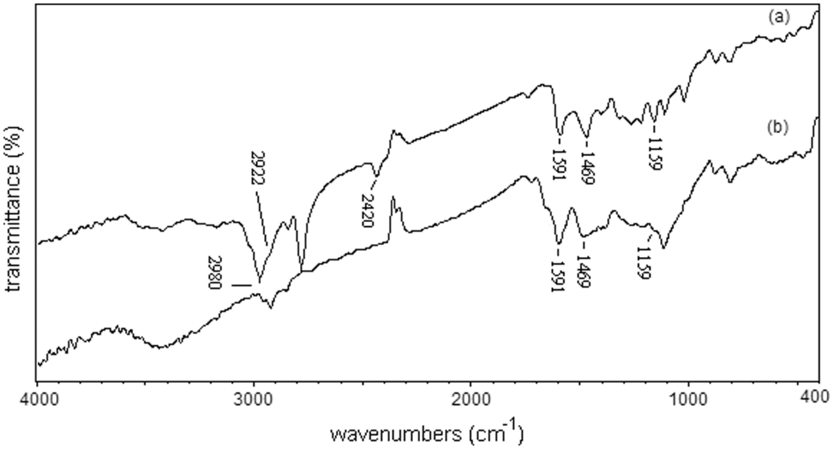


Figure 7. FT-IR spectra of (a) HCl-doped, (b) undoped POT.

The band at 1159 cm^{-1} in conductive POT (Figure 7(a)) exhibits the degree of electron delocalization, thus the electrical conductivity[28] and its intensity decreases with the removal of dopant, as observed in the spectrum of undoped POT (Figure 7(b)).

The band that belongs to the $-NH_3^+$ antisymmetrical and $-NH_3$ symmetrical stretchings at the terminal parts of the polymer chains was observed at about 2980 cm^{-1} for the POT doped with HCl in Figure 7(a). The band at 2420 cm^{-1}, which disappeared in the spectrum of undoped POT, comes from the N-H stretching of $Q{=}N^+H\text{-}B$ in conductive POT chains.[29]

Thermogravimetric Analysis

The thermograms of HCl-doped and undoped POTs are given in Figure 8. The weight loss observed between 165° and 250°C in the thermogram of the HCl-doped POT in Figure 8(a) corresponds to the removal of the dopant from the polymer structure.[30] The fact that there is no significant weight loss in this temperature range in the thermogram of undoped POT (Figure 8(b)) also supports this explanation.

The second weight loss of 20% between 432° and 500°C corresponds to the degradation of POT chains.[30] The total weight loss of HCl-doped POT at 600°C is higher than that of its undoped form.

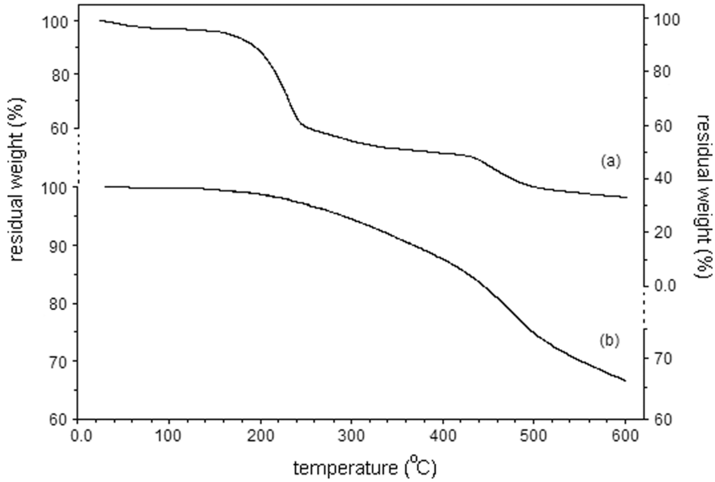


Figure 8. Thermograms of (a) HCl-doped, (b) undoped POT.

CONCLUSIONS

Our results showed that *o*-toluidine could be polymerized using Bz_2O_2 as an oxidant in DMF/water mixture. While oily products were obtained in the polymerizations carried out in HNO_3, $HClO_4$, H_3PO_4, and H_2SO_4 media, POT having the highest conductivity and yield was obtained as a dark green powder form in aqueous HCl solution. Resistivity-temperature relation of POT recorded during the heating-cooling cycles in the temperature range of $-10°$ to $+120°C$ showed that POT can be used as a thermal-sensing material in narrow temperature ranges. It was found that the solubility of POT in various solvents such as DMF, *N*-methyl pyrrolidone, and DMSO was higher than that of polyaniline. Thermal analysis results showed that total weight loss of doped POT at 600°C was higher than that of its undoped form.

REFERENCES

[1] Kulkarni, M. V., A. K. Viswanath, R. Marimuthu, and U. P. Mulik. (2004). Investigation of the effect protonic acid media on the optical and thermal properties of chemically synthesized poly(o-toluidine). *J. Mater. Sci. Mater. Electron.* **15** (12), 781–785.

[2] Macit, H., Ş. Şen, and M. Saçak. (2005). Electrochemical synthesis and characterization of polycarbazole. *J. Appl. Polym. Sci.* **96**, 894–898.

[3] Blinova, N. V., J. Stejskal, M. Trchova, J. Prokes, and M. Omastova. (2007). Polyaniline and polypyrrole: A comparative study of the preparation. *Eur. Polym. J.* **43**, 2331–2341.

[4] Diaz, A. F., K. K. Kanazawa, and G. P. Gardini. (1979). Electrochemical polymerization of pyrrole. *J. Chem. Soc. Chem. Commun.* (14), 635–636.

[5] Pan, W., S. L. Yang, G. Li, and J. M. Jiang. (2005). Electrical and structural analysis of conductive polyaniline/polyacrylonitrile composites. *Eur. Polym. J.* **41**, 2127–2133.

[6] Wang, S., F. Wang, and X. Ge. (1986). Polymerization of substituted aniline and characterization of polymer. *Synth. Met.* **16**, 99–104.

[7] Erdem, E., M. Saçak, and M. Karakışla. (1996). Synthesis and properties of oxalic acid-doped polyaniline. *Polym. Int.* **39**, 153–159.

[8] Tetsuo, H., S. Yuki, T. Toshihiro, and K. Noriyuki. (2006). Synthesis and characterization of polyanilines doped with several carboxylic acids and with a carboxylic acid equivalent. *Polym. Int.* **55**, 243–247.

[9] Mav, I., and M. Zigon. (2001). Chemical copolymerization of aniline derivatives: Preparation of fully substituted PANI. *Synth. Met.* **119**, 145–146.

[10] Wazzan, A. A., M. N. Ismail, and M. A. Abd El Ghaffar. (2005). Evaluation of some polyaromatic amines as antirads and antifatigue agents in SBR vulcanizates. *Int. J. Polym. Anal. Charact.* **10**, 57– 69.

[11] Kulkarni, M. V., and A. V. Kasi. (2004). Comparative studies of chemically synthesized polyaniline and poly(*o*-toluidine) doped with p-toluene sulphonic acid. *Eur. Polym. J.* **40**, 379–384.

[12] Kulkarni, M. V., and A. V. Kasi. (2005). Studies on chemically synthesized organic acid doped poly(*o*-toluidine). *Mater. Chem. Phys.* **89**, 1–5.

[13] Bedekar, A. G., S. F. Patil, and R. C. Patil. (1996). Comparative studies of electrochemically deposited poly(*o*-toluidine) and poly(*m*-toluidine) films. *Polym. Int*. **40**, 201–205.

[14] Hosseini, S., M. Dabiri, and M. Ashrafi. (2006). Chemical and electrochemical synthesis of conducting graft copolymer of acrylonitrile with aniline. *Polym. Int*. **55**, 1081–1089.

[15] Karakışla, M., and M. Saçak. (2002). The chemical synthesis of conductive polyanline by using benzoyl peroxide. *J. Macromol. Sci. Part A Pure Appl. Chem.* **A39**, 1349–1359.

[16] Palaniappan, S. (2004). Benzoyl peroxide oxidation route to polyaniline salts—Part I. *Polym. Adv. Technol.* **15**, 111–117.

[17] Ongun, N., M. Karakışla, L. Aksu, and M. Saçak. (2004). Graft polymerization of methacrylamide onto poly(ethylene terephthalate) fibers with benzoyl peroxide as initiator and their characterization. *Macromol. Chem. Phys.* **205**, 1995–2001.

[18] Saçak, M., N. Baştuğ, and M. Talu. (1993). Azobisisobutyronitrile-initiated graft-copolymerization of methyl-methacrylate onto poly(ethylene-terephthalate) fibers. *J. Appl. Polym. Sci.* **50**, 1123–1129.

[19] Rao, P. S., D. N. Sathyanarayana, and S. Palaniappan. (2002). Polymerization of aniline in an organic peroxide system by the inverted emulsion process. *Macromolecules*. **35**, 4988–4996.

[20] Ayad, M. M., and M. A. Sheneshin. (2004). Effect of acids on in situ polyaniline film formation. *Polym. Int.* **53**, 1180–1184.

[21] Yasuda, A., and T. Shimidzu. (1993). Chemical oxidative polymerization of aniline with ferric chloride. *Polym. J.* **25**, 329–338.

[22] Cao, Y., A. Andreatta, A. J. Heeger, and P. Smith. (1989). Influence of chemical polymerization conditions on the properties of polyaniline. *Polymer*. **30**, 2305–2311.

[23] Dan, A., and P. K. Sengupta. (2004). Synthesis and characterization of polyaniline prepared in formic acid medium. *J. Appl. Polym. Sci.* **91**, 991–999.

[24] Cortes, M. T., and E. V. Sierra. (2006). Effect of synthesis parameters in polyaniline: influence on yield and thermal behavior. *Polym. Bull.* **56**, 37–45.

[25] Imoto, M., and S. Choe, S. (1955). Vinyl polymerization. V. Decomposition of sym-substituted benzoyl peroxides in presence of dimethylanilide. *J. Polym. Sci.* **15** 485–501.

[26] Horner, L., and K. Scherf. (1951). Über den einfluß der substituenten auf die chemische reaktivität. I. Der zerfall von dibenzoylperoxyd durch substituierte tertiäre amine. *Justus Liebigs Ann. Chem.* **573**, 35–55.

[27] Bartlett, B., D. Paul, and K. Nozaki. (1947). *J. Polym. Sci.* **5**, 2299.

[28] Lal, J., and R. Green. (1955). Effect of amine accelerators on the polymerization of methyl methacrylate with benzoyl peroxide. *J. Polym. Sci.* **17**, 403–409.

[29] Zuo, F., M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein. (1987). Transport studies of protonated emeraldine polymer: A granular polymeric metal system. *Phys. Rev. B*. **36**, 3475–3476.

[30] Kobayashi, A., H. Ishikawa, K. Amano, M. Satoh, and E. Hasegawa. (1993). Electrical conductivity of annealed polyaniline. *J. Appl. Phys.* **74**, 296–299.