Chemical Synthesis and Characterization of Some Conducting Polyaniline Derivatives: Investigation of the Effect of Protonation Medium

AYŞEGÜL GÖK, BEKIR SARI

Department of Chemistry, Faculty of Arts and Science, Gazi University, 06500 Ankara, Turkey

ABSTRACT: Poly(*o*-toluidine) (POT) and poly(2-chloroaniline) (P2ClAn) emeraldine salts were synthesized chemically by using formic (HCOOH), acetic (CH$_3$COOH), propionic (C$_2$H$_5$COOH), and boric (H$_3$BO$_3$) acids. Ultraviolet-visible absorption spectra (UV–Vis) analysis results indicated that POT has the better protonation effects than P2ClAn. Among the POTs synthesized using the four different acids, POT(H$_3$BO$_3$) showed the least protonation effect. The conductivities of prepared polymers were measured by a four-probe technique. The highest conductivities were obtained in POTs synthesized by using formic, acetic, and propionic acids. Magnetic susceptibility measurements of the polymer salts were analyzed by using Gouy scale and it was found that POT(CH$_3$COOH) and POT(C$_2$H$_5$COOH) salts are of bipolaron structure; other polymer salts are of polaron structure. The characterization of the polymers were investigated by Fourier infrared spectroscopy (FTIR), UV–Vis, thermogravimetric analysis, and scanning electron microscopy. It was observed from UV–Vis spectra of the emeraldine salt of POT that wavelengths belonging to $\pi \rightarrow \pi^*$ transitions shifted to shorter wavelengths with increasing pKa values of acids. POT and P2ClAn synthesized in four different protonation media decomposed with three-step and three- or two-step weight loss, respectively. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1993–2000, 2002; DOI 10.1002/app.10487

Key words: conducting polymers; poly(*o*-toluidine); poly(2-chloroaniline)

INTRODUCTION

Conductive polymeric materials containing conjugated π bonds have attracted much interest in scientific and technological areas in recent years. The conducting polymers such as polypyrrole, polythiophene, poly(*p*-phenylene), and polyaniline have commonly been used, in scientific and industrial studies, as rechargeable batteries,[1,2] sensors,[3] and diodes, and in transistor and microelectronic devices,[4] and as modified electrodes.[5] Among the whole conducting polymers, polyaniline has a specific situation owing to its simple synthesis, good environmental stability, and ability to dope with protonic acids.[6–8] Therefore, attempts were made to try to overcome the unsolved problems such as solubility in common organic solvents, processibility at high temperature, and poor mechanical properties.[9–11]

Polyaniline and polyaniline derivatives can be synthesized both chemically and electrochemically by using suitable protonation media.[12–15] Some researchers showed that the protonation media tend rather to acidity of media in X-ray photoelectron spectroscopy (XPS) works done on polyaniline and polyaniline derivatives.[16,17] Moreover, they demonstrated that this protonation level in e^- acceptor groups is lower according to aniline and alkylanilines. Although poly(*o*-toluidine) (POT) and poly(2-chloroaniline) (P2ClAn) have been synthesized by using some acids such as HCl, H$_2$SO$_4$, and HClO$_4$ as protonation media,[18–23] the correlation between properties of these polymers with pKa values of protonation media have not been investigated yet. The synthesis of POT and P2ClAn by using a selected acid such as acetic, propionic, and boric as protonation media and the investigation of the ef-

Table I   The pH, Magnetic Susceptibility, and Conductivity Values of POT and P2ClAn Synthesized by Different Acids

Polymer	Acid	pH of Polymer Solution	Magnetic Susceptibility Measurements (μ_{eff}) (BM)	Conductivity (Scm^{-1})
POT	Formic	1.76	+20	2.31×10^{-4}
	Acetic	2.83	−37	1.82×10^{-4}
	Propionic	3.10	−40	1.52×10^{-4}
	Boric	4.19	+76	2.41×10^{-5}
P2ClAn	Formic	1.74	+645	7.42×10^{-5}
	Acetic	2.71	+105	2.77×10^{-5}
	Propionic	3.02	+188	2.41×10^{-5}
	Boric	4.19	+38	2.94×10^{-5}

μ_{eff}, Effective magnetic moment; BM, Bohr magneton.

fect of these acids on their properties have not been reported so far.

In this study, formic (pKa = 3.77), acetic (pKa = 4.75), propionic (pKa = 4.87), and boric (pKa = 9.22) acids having different pKa values were used as both synthesis and protonation media. The effects of these acids on properties of substituted polyanilines having e^- acceptor (2-Cl) and e^- donor (o-CH$_3$) groups were studied. The obtained polymers were characterized by different techniques, and the results were discussed.

EXPERIMENTAL

Monomers were purchased from Aldrich. Dopant salts were supplied from Merck. o-Toluidine and
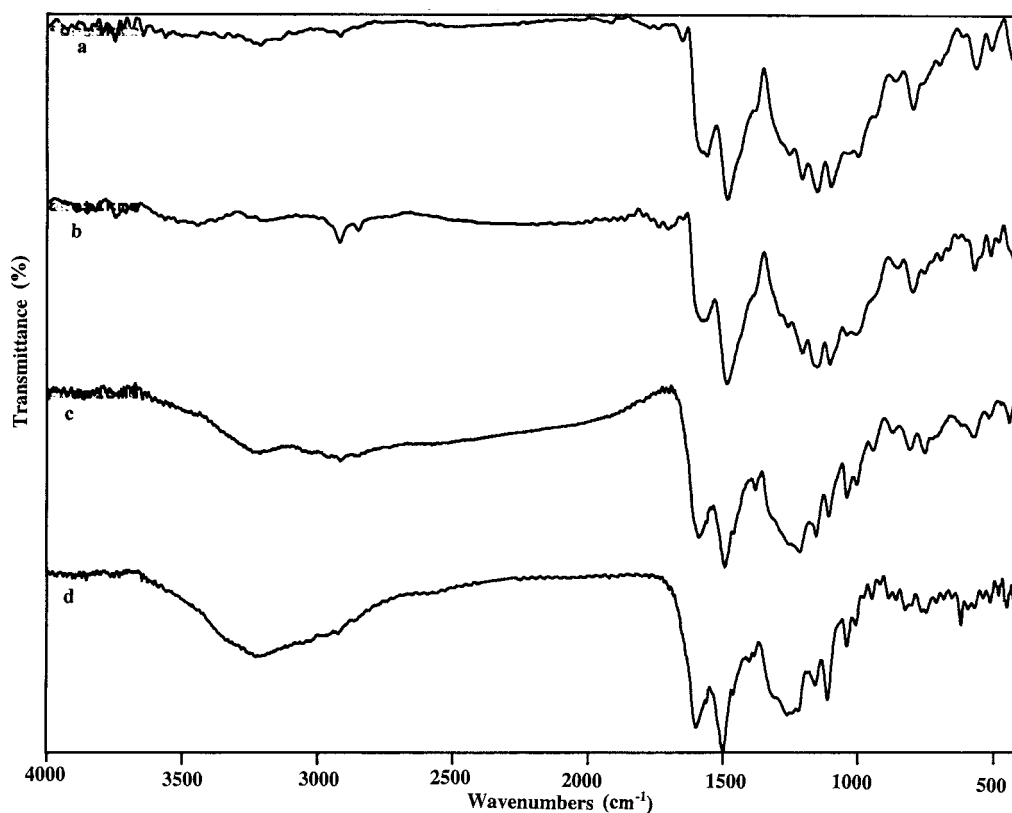

Figure 1   FTIR spectra of POTs synthesized using four different acids: (a) POT(H-COOH); (b) POT(CH$_3$COOH); (c) POT(C$_2$H$_5$COOH); (d) POT(H$_3$BO$_3$).

2-chloroaniline were distilled under vacuum prior to use. The solutions of quarterner ammonium salts were prepared by adding a mixture of 75 mL deionized water and 50 mL acid into a 1.6 mL monomer. A solution in water of ammonium persulfate ($n_{monomer}/n_{salt} = 1.5$) was added drop-wise to the above solution with constant stirring, with the temperature maintained at 2–5°C. The pH of the final solution was measured by using a Jenvey 3010 model pH meter (the pH values are given in Table I). After addition of the oxidant, the mixture was stirred for 4 h. Precipitated polymer was filtered and washed with distilled water until the filtrate was clear. Finally, the polymer was dried in a vacuum oven at 70°C until a constant mass was reached.

The obtained polymers were analyzed with the following explained techniques. The absorption spectra of these polymers preparing solutions at (0.5 mg/10 mL) concentration in *N,N*-dimethylformamide were recorded by using Unicam UV-2 model ultraviolet-visible absorption spectra (UV–Vis) spectrophotometer and Epson FX-870 model printer. TGA thermograms of the samples were obtained by Rigika thermal analyzer Var 2.22E2 model thermogravimetric instrument at a heating rate of 10°C min^{-1} under a nitrogen (N_2) atmosphere and at a temperature range of 0–1000°C. FTIR spectra of the polymers were taken in KBr disks and were recorded on Mattoson-1000 model spectrometer. Conductivities of the synthesized polymers were measured by us-ing a four-probe technique. Magnetic susceptibility measurements were carried out by using a Sherwood Scientific model MKI Gouy scale. Finely powdered polymers were placed into a glass tube at a height of not less than 2.5 cm. Then, the glass tube was placed into the hole of the Gouy balance, which was on a wooden bench, to obtain a constant value.

RESULTS AND DISCUSSION

The conductivity values of synthesized polymers are given Table I. The conductivities of POTs synthesized by using different acids (except boric acids) are higher than conductivities of P2ClAn. It may be that POT has an electron-donating group (—CH_3) which increases the formation of the imine units.[24] This also causes the increase of the protonation effect and conductivity. Magnetic susceptibility data of the polymers are also shown in Table I. As seen in Table I, magnetic susceptibility values of POT(CH_3COOH) and POT(C_2H_5-COOH) are negative, whereas the other polymers are positive. Negative magnetic susceptibility values reveal diamagnetism and positive values demonstrate paramagnetism.[25] These analyses indicate that the conducting mechanism of POT(CH_3COOH) and POT(C_2H_5COOH) are bipolaron by nature (Structure I), whereas the other polymer salts are polaron by nature (Structure II)[26]:
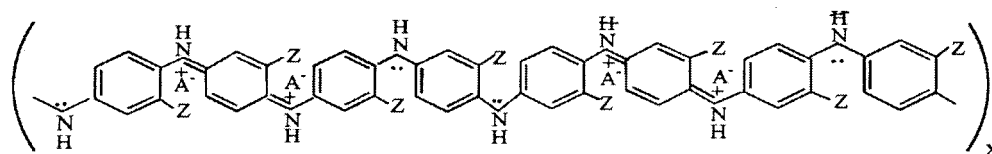
I. Bipolaron Structure
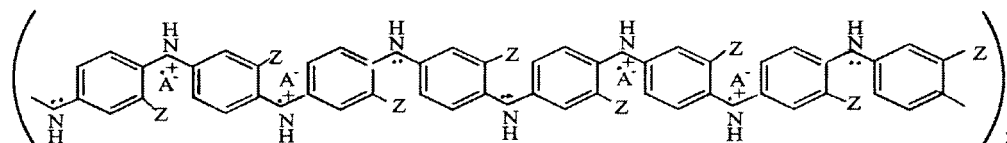
II. Polaron Structure
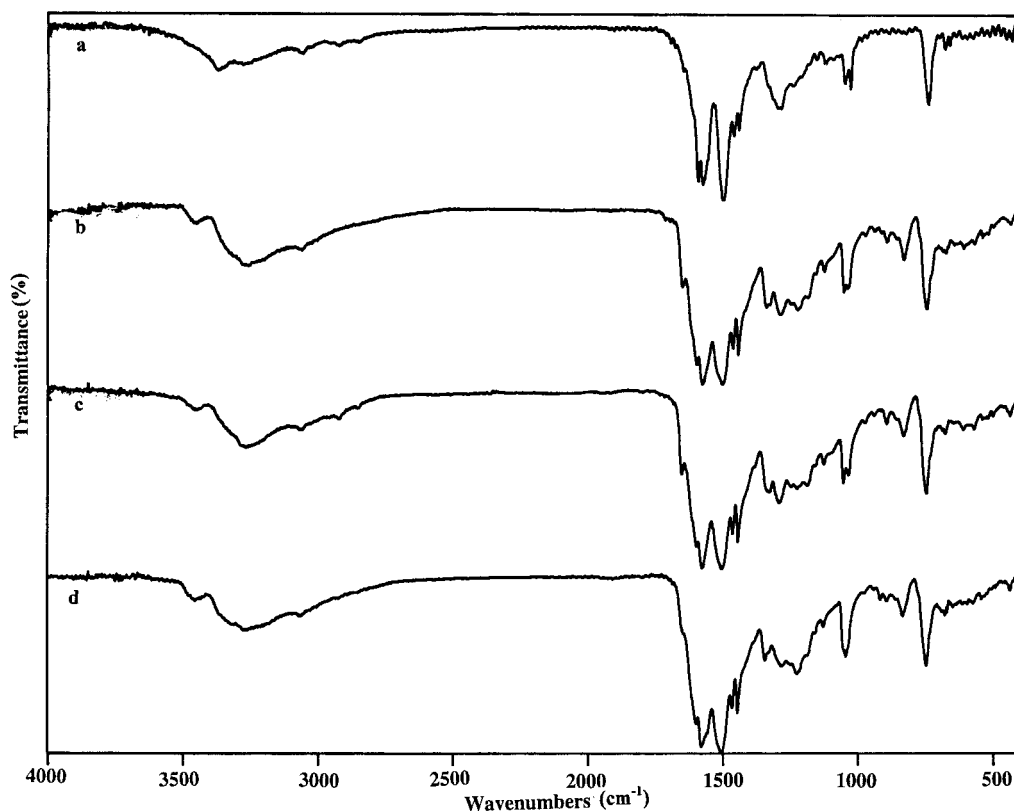
Z:-CH_3 ; -Cl   A: dopant anion

Figure 2 FTIR spectra of P2ClAns synthesized using four different acids: (a) P2ClAn(HCOOH); (b) P2ClAn(CH₃COOH); (c) P2ClAn(C₂H₅COOH); (d) P2ClAn(H₃BO₃).

FTIR spectra of POT and P2ClAn synthesized using four different acids are identified in Figures 1 and 2, respectively. From FTIR bands (Fig. 1) was found that polymerization occurs with head-to-tail coupling. The 1160–1200 cm^{-1} bands belong to the —N=Q=N or B—NH—B (where B denotes benzenoid and Q denotes quinoid ring) vibration bands of POT. The observed bands at 1260–1300 and 1000–1050 cm^{-1} belong to C—N stretching vibrations and C—H vibration bands, respectively. The C=C stretching vibrations in benzenoid and quinoid rings are observed at 1500 and 1590 cm^{-1}. At 800–810 cm^{-1}, the peak corresponds to C—H bending vibration of p-phenyl rings and the peak at 850–900 cm^{-1} appears to be due to the methyl group attached to the phenyl ring. The bands corresponding to the 3050–3300 cm^{-1} region that are seen for aromatic N—H bands have broad rather in structures synthesized using boric and propionic acids. This situation may be caused by differentiation of the acids used. Although the bands belonging to aliphatic C—H vibrations were observed around 2900 cm^{-1}, they have not been determined in the spectra of some polymers because of the enlarged bands in this region. In FTIR spectra of P2ClAn (Fig. 2), although vibration frequency of bands have the same value as POT, the bands corresponding to p-phenyl rings at 800 cm^{-1} are sharper.

Figures 3 and 4 show to the optic absorption spectra of POT and P2ClAn synthesized by using four different acids, respectively. When the optic spectra of synthesized polymers are investigated, it is seen that POT gives more regular emeraldine salt structures than P2ClAn because of bands observed at 316–320 and 552–594 nm.[27] The band belonging to emeraldine salts at 594 nm of POT(HCOOH) has shifted to 590 nm in POT(CH₃COOH). As seen from Figure 3, the band at 577 nm of POT(C₂H₅COOH) has shifted to 552 nm in POT(H₃BO₃). However, this shift to blue at the bands is attributed to different molecular orientations and to the decrease of conjugation in the polymer chain also. The bands in UV–Vis spectra of POT synthesized by using different acids are in shorter wavelengths than POTs synthesized in HCl medium. In addition, the band belonging to emeraldine salts seen at long wavelengths of P2ClAn synthesized in HCl medium[28] had not been observed in P2ClAn salts synthesized
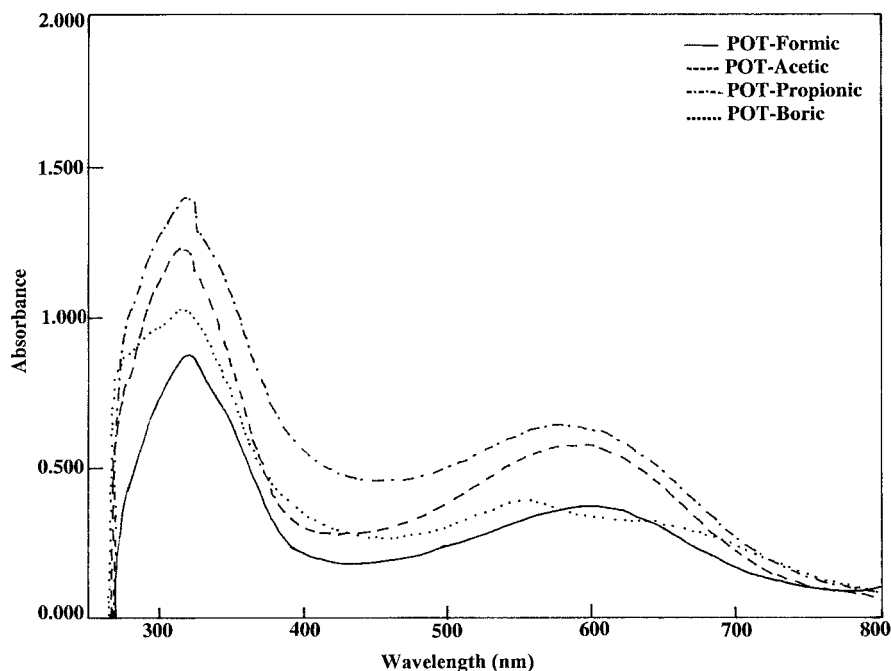
Figure 3 Optical absorption spectra of chemically synthesized POTs.

in this study. When the UV–Vis spectra of polyanilines synthesized using inorganic and organic acids were compared with POT and P2ClAn, similar states were observed.[29] Consequently, acids used as synthesis and dopant media decreased conjugation in POT and P2ClAn. The bands belonging to emeraldine salts seen at 594–552 nm in the spectrum of

POT have not been observed in the UV–Vis spectra of P2ClAn. The absorption bands of $\pi \rightarrow \pi^*$ transitions disappeared in P2ClAn synthesized using boric acid.

In a recent study,[27] although the bands belonging to emeraldine salt are not observed in UV–Vis spectra of polyaniline synthesized in acetic acid
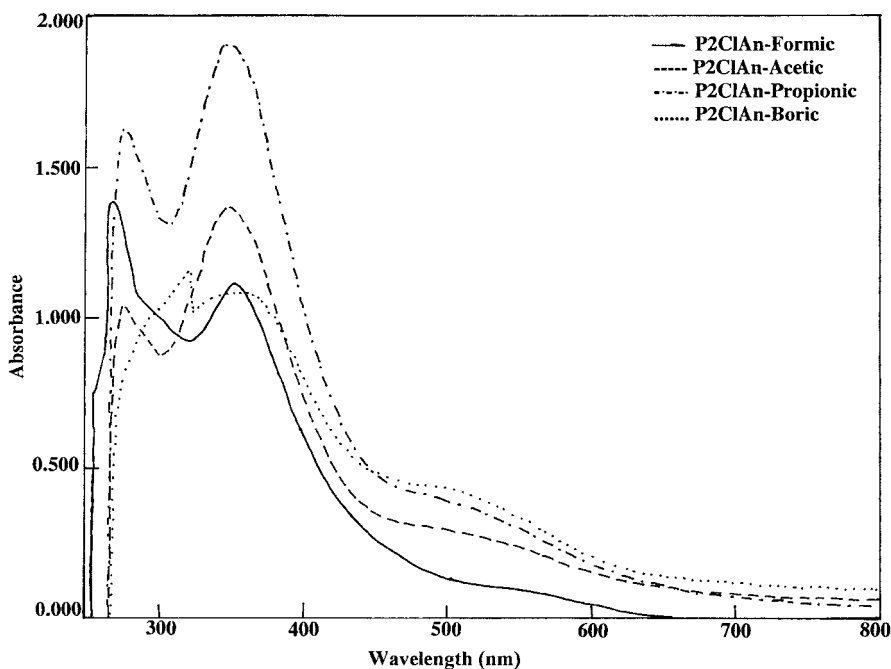

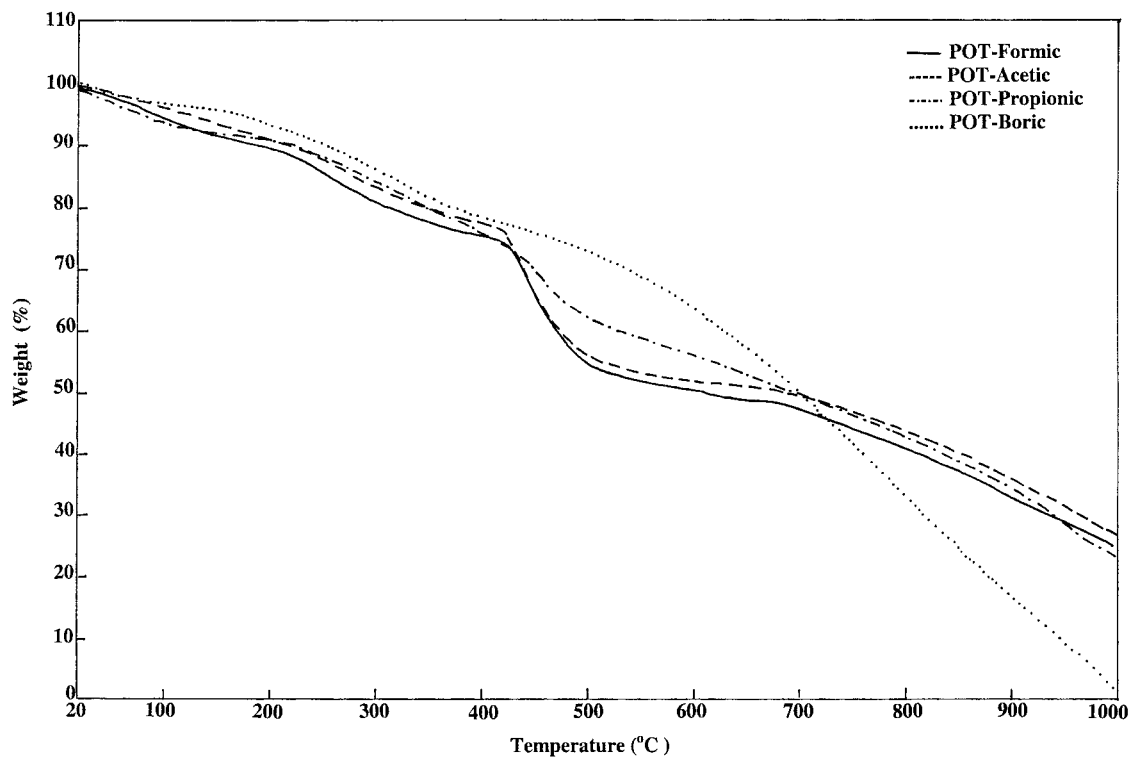**Figure 4** Optical absorption spectra of chemically synthesized P2ClAns.

Figure 5   TGA thermograms of POTs obtained using different protonation media.
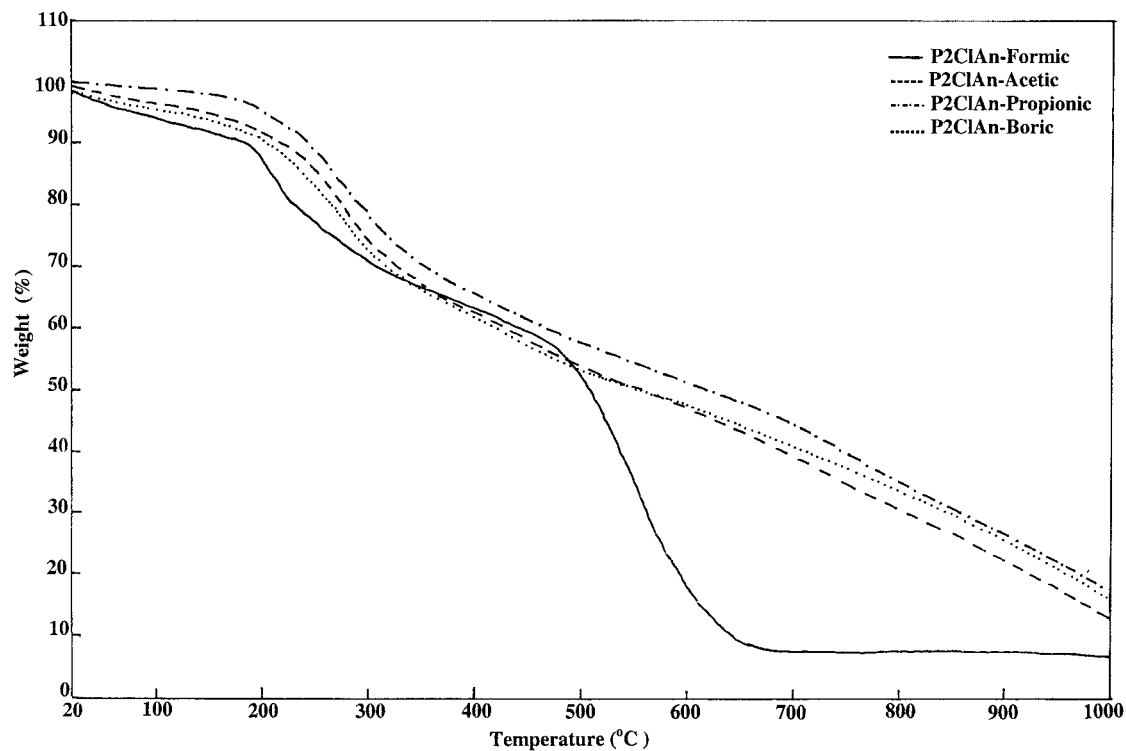

Figure 6   TGA thermograms of P2ClAns obtained using different protonation media.

Table II Results of TGA Analysis of Polymers

Polymer	Decomposition Temperature (°C)		
	T_i	T_m	T_f
POT(HCOOH)	227	277	329
	425	454	481
POT(CH$_3$COOH)	259	277	300
	432	459	514
POT(C$_2$H$_5$COOH)	246	343	439
	439	466	500
POT(H$_3$BO$_3$)	200	287	368
	368	443	552
P2ClAn(HCOOH)	200	246	314
	487	557	621
P2ClAn(CH$_3$COOH)	200	259	305
P2ClAn(C$_2$H$_5$COOH)	196	273	327
P2ClAn(H$_3$BO$_3$)	207	264	311
	311	399	480

T_i, Initial degradation temperature; T_m, maximum degradation temperature; T_f, final degradation temperature.

medium, this band has been observed in UV–Vis spectra of POT synthesized using this acid. Therefore, POT synthesized by this acid have protonated easier than polyaniline. This result agrees with Mattoso et al.'s results.[30] This research group had shown that ease of protonation
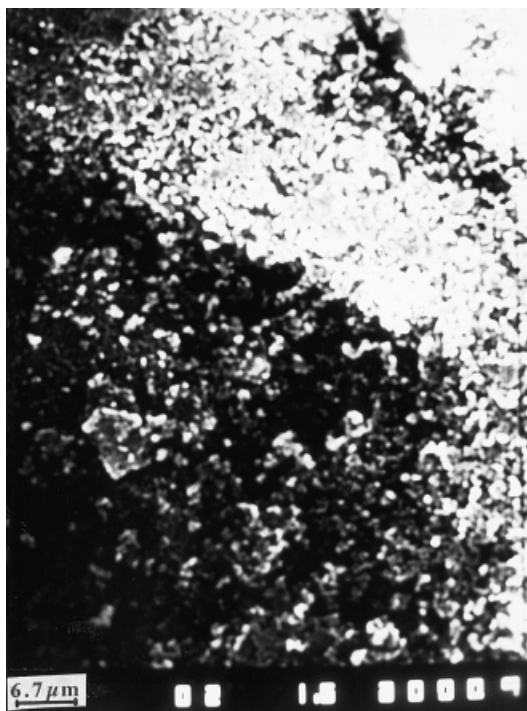

Figure 8 Scanning electron micrographs of P2Cl-An(H$_3$BO$_3$); magnification, ×800; bar = 12.57 μm.

is in the sequence OC$_2$H$_5$ > OCH$_3$ > CH$_3$ > H. Protonation is the first step of the oxidative polymerization of these anilines.

The presence of different phases in POT and P2ClAn can be as explained on the basis of the protonation strength of the solutions, also with effect e^- donor and e^- acceptor groups attached to the ring in these polymers. The number of protons of P2ClAn synthesized by using four different acids is not sufficient for the complete protonation of pernigraniline base. Consequently, it has been shown that the acids used as synthesis and dopant media in this study protonated better to POT than P2ClAn, from UV–Vis analysis and conductivity measurements.

The thermogravimetric analysis curves of POT and P2ClAn are given in Figures 5 and 6, respectively. The decomposition temperatures (T_i, T_m, T_f) obtained from thermograms are tabulated in Table II. According to initial decomposition temperature (T_i) among the polymers, POT(CH$_3$-COOH) has the highest decomposition temperature, 259°C. As seen in Table II, POTs synthesized in four different protonation media and P2ClAn's synthesized using formic and boric acids show three-step weight loss, whereas P2ClAn salts with acetic and propionic acids indicate decomposition with two-step weight loss. The first weight loss step (20–130°C) indicates adsorbed

Figure 7 Scanning electron micrographs of POT-(H$_3$BO$_3$); magnification, ×1500; bar = 6.7 μm.

moisture, free acids, and volatile molecules in polymer matrix.[7,31,32] The second weight-loss step occurs between 200 and 439°C and may be attributed to the loss of acid dopant bound to the polyaniline chain. The third decomposition step occurs between 313 and 620°C. In this final step, the skeletal polyaniline chain structure decomposes after the elimination of the dopant from the polymer structure.[33]

In decompositions occurring at two-step, the first weight loss step is due to the expulsion of water molecules from the polymer structure. The second degradation between 195 and 327°C was composed of polymer salt.

When SEM micrographs of POT and P2ClAn synthesized using different acids are investigated, it was seen that morphological structures of polymers are different from each other. Among these polymers, POT and P2ClAn synthesized using boric acid show smoother morphological structure than others. The film of POT(H_3BO_3) demonstrates a granular morphological structure, whereas P2ClAn(H_3BO_3) yields a riblike and fibrillar morphological structure (Figs. 7 and 8). As a result, it was revealed that different monomer and acid yield conductive polymers with different morphological structure.

CONCLUSION

In this study, the effect of acids having different pKa values on properties of POT and P2ClAn was discussed. The acids, such as formic, acetic, propionic, and boric, were used both as synthesis media and as dopant anions. It was elucidated that POT and P2ClAn have different properties. We demonstrated that these acids have better protonated POT than P2Cl and POT thermally has more stability than P2ClAn. The smooth morphological structures were obtained in POT and P2ClAn synthesized using boric acid. POT especially can be widely used for its attractive protonation effect; this improvement may find application in various areas.

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