

Synthesis and Properties of Conducting Polypyrrole, Polyalkylanilines, and Composites of Polypyrrole and Poly(2-ethylaniline)

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ABSTRACT: Conducting polymers of alkyilanilines, pyrrole, and their conducting composites were synthesized by oxidation polymerization. The oxidants used were KIO_3 and FeCl_3 for the polyalkylanilines and polypyrrole (PPy), respectively. Among the polyalkylanilines synthesized with KIO_3 salt, the highest conductivity was obtained with poly(2-ethylaniline) (P2EAn) with a value of 4.10×10^{-5} S/cm. The highest yield was obtained with poly(*N*-methylaniline) with a value of 87%. We prepared the conducting composites (PPy/P2EAn and P2EAn/PPy) by changing synthesis order of P2EAn and PPy. The electrically conducting polymers were characterized by IR spectroscopy, ultraviolet-visible spectroscopy, thermogravimetric analysis, and X-

ray diffraction spectroscopy. From the results, we determined that the properties of the composites were dependent on the synthesis order of the polymers. The thermal degradation temperature of PPy was observed to be higher than that of the other polymers and composites. We determined from X-ray results that the structures of the homopolymers and composites had amorphous regions (88–95%) and crystal regions (5–12%). From the Gouy balance magnetic measurements, we found that the polymers and composites were bipolaron conducting mechanisms. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 241–249, 2006

Key words: composites; conducting polymers; polypyrroles

INTRODUCTION

Electroconductive polymers have attracted a great deal of attention, mainly due to their potential applications in a variety of new technologies, such as electronic devices,¹ electrochromic displays,² rechargeable batteries,³ polymer-modified electrodes,⁴ biosensors,⁵ and anticorrosion primer layers.⁶ Among these conducting polymers, polyaniline (PAn), polythiophene, and polypyrrole (PPy) can be easily prepared by an oxidative polymerization.^{7–9} If one considers the much higher cost of thiophene versus pyrrole and aniline, PPy and PAn should be the most attractive conducting materials within the brilliant industrial foreground.

The poor mechanical properties of PPy, including its brittleness and low level of processability, constitute major obstacles to its extensive application.¹⁰ PPy is both insoluble and infusible, and its film is hard and usually brittle. The improvement of the processability becomes very important and necessary. In addition, π -conjugated polymers containing flexible aliphatic side groups have been a major subject of recent inter-

est.^{11–14} For example, polyalkylanilines have much better solubility than PPy and PAn,¹⁵ although their electrical conductivity is not as good as that of PPy and PAn.^{16,17} Attempts have been made to solubilize PPy by the copolymerization of pyrrole with other monomers or by the introduction of a single long alkyl and sometimes ester groups onto the 3 and 4 positions of PPy.¹⁸ There are some reports concerning the copolymerization of pyrrole with aniline.^{19–21}

The goal of this study was to develop conducting polymer composites with controlled conductivities and enhanced physical, thermal, crystal, and solubility properties. This was done by the incorporation and chemical oxidation of pyrrole and ethylaniline. After the polyalkylanilines were synthesized with a KIO_3 oxidant, composites of PPy with the most conductive polyalkylaniline [poly(2-ethylaniline) (P2EAn)] were prepared. The synthesis orders of P2EAn and PPy and the weight percentages of the host polymer in the composite were changed. The properties of the composites and the homopolymers were investigated with different methods.

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EXPERIMENTAL

Pyrrole, 2-methylaniline, 2-ethylaniline, *N*-methylaniline, and *N*-ethylaniline were distilled twice in vacuo. FeCl_3 , KIO_3 , and HCl were obtained from Merck (Ger-

many). All other chemicals [*N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), chloroform (CHCl₃), dimethyl sulfoxide (DMSO), and H₂SO₄] were analytical grade and were used as procured.

Synthesis of PPy

Pyrrole (0.01 mol) monomer was dissolved in water (100 mL), and a FeCl₃ (0.02 mol)/H₂O solution was slowly added into the monomer solution under vigorous magnetic stirring. The reaction temperature was maintained at 25°C. After 24 h, the precipitates were filtered and sequentially washed with water, HCl, methanol, and diethyl ether to remove all residues until the filtrate became colorless; they were then dried in a vacuum oven at 70°C for 24 h. The polymerization yield was determined by the weight ratio of dry polymer to the initially charged monomer.

Synthesis of polyalkylanilines

The alkyylaniline (2-methylaniline, 2-ethylaniline, *N*-methylaniline, or *N*-ethylaniline; 0.01 mol) was added under mechanical stirring to a 100-mL solution of 1.5M HCl. Separately, 0.02 mol of KIO₃ was dissolved in 100 mL of water. Then, the KIO₃ solution was added to the alkyylaniline solution at 5°C. It was mechanically stirred for 1 day, and then it was filtered and washed with HCl, water, and ether. After drying at 70°C, the yield was quantitative.

Synthesis of the PPy/P2EAn composite

For synthesis of the PPy/P2EAn composite, a certain amount of PPy powder was dispersed in 2-ethylaniline (2EAn) with a HCl solution with stirring at 5°C. Then, the KIO₃ solution was added to the medium, and the solution was stirred for 24 h. The composite was collected and washed with 1.5M HCl, water, and ether. The quantity of P2EAn in the composite was calculated from the total mass of the composite. We synthesized the PPy/P2EAn composites, including P2EAn at different percentages, by varying the amount of 2EAn monomer at a constant $n_{2EAn}/n_{oxidant}$ ratio.

Synthesis of the P2EAn/PPy composite

A certain amount of P2EAn was dispersed in an aqueous solution of PPy at 25°C. FeCl₃ dissolved in water was added to the dispersed solution under vigorous magnetic stirring. After 24 h, the composite was filtered and washed with water, HCl, methanol, and ether. P2EAn/PPy composites were synthesized in which the percentage of PPy varied but the ratios were kept constant.

TABLE I
Yield, Conductivity, and Magnetic Susceptibility Values of the Homopolymers and Composites

Polymer	Salt	Yield (%)	Conductivity (Scm)	Magnetic susceptibility [μ_e^* (BM)]
PPy	FeCl ₃	79	0.22	-20
POT	KIO ₃	28	2.60×10^{-5}	-23
P2EAn	KIO ₃	16	4.10×10^{-5}	-42
PNMAAn	KIO ₃	87	3.10×10^{-5}	-41
PNEAn	KIO ₃	46	3.20×10^{-5}	-47
PPy/P2EAn	—	18	1.50×10^{-2}	-15
PPy/P2EAn	—	30	0.70×10^{-2}	-24
PPy/P2EAn	—	50	1.29×10^{-3}	-31
PPy/P2EAn	—	69	8.13×10^{-5}	-30
PPy/P2EAn	—	85	2.94×10^{-5}	-51
P2EAn/PPy	—	16	0.37	-25
P2EAn/PPy	—	46	0.58	-29
P2EAn/PPy	—	75	0.82	-32
P2EAn/PPy	—	81	1.46	-27
P2EAn/PPy	—	85	1.50	-31

μ_e^* , effective magnetic moment; BM, Bohr magneton.

Characterization

Fourier transform infrared (FTIR) spectra were recorded with a Mattson model 1000 spectrophotometer (Unicam, UK) by the KBr pellet technique. To record the ultraviolet–visible (UV–vis) absorption spectra, a Unicam UV-2 model spectrophotometer was used. Solutions of the polymers in DMF were used to record the spectrum. The electrical conductivities [direct current (dc)] were measured by the four-probe technique with a Nippon NP-900 multimeter (Osaka, Japan). A general V2.2A DuPont model 9900 thermogravimetric analyzer (Raleigh, NC, USA) was used to measure the weight loss of the polymers with the sample size at a heating rate of 10°C/min under a nitrogen atmosphere. The powder diffraction patterns of the synthesized samples were recorded with a Philips manual spectrogoniometer (LabX, Midland, Canada) with Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation over the range $5^\circ < 2\theta < 50^\circ$. The degrees of crystallinity of the new products were determined by the area ratio method.²² Magnetic susceptibility measurements were carried out with a Sherwood Scientific model MKI Gouy scale with a procedure reported elsewhere.²³ The intrinsic viscosities of the polymers were measured in H₂SO₄ at 25°C with an Ubbelohde-type viscometer (Cannon Instrument Company, USA).

RESULTS AND DISCUSSION

Conductivity

Table I shows the yield percentage, conductivity, and magnetic susceptibility values of the PPy and polyalkylanilines. The highest yield among the polyalkylanilines were obtained for poly(*N*-methylaniline)

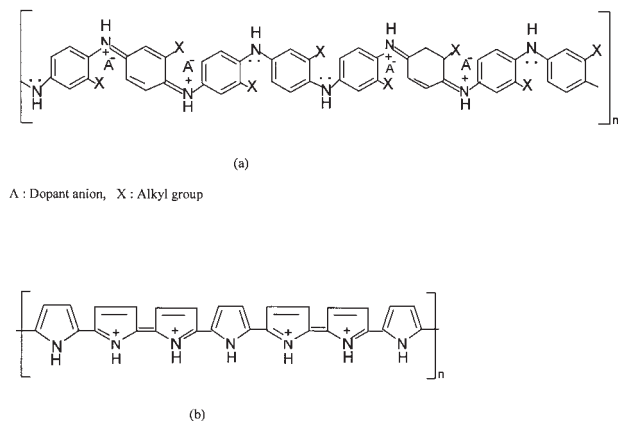


Figure 1 Bipolaron structure of (a) polyalkylanilines and (b) PPy.

(PNMA) at 87%. The conductivity of PPy (0.22 S/cm) was higher than those of the polyalkylanilines. Among the polyalkylanilines, P2EAn had the highest conductivity value (4.10×10^{-5} S/cm). The conductivities of the polyalkylanilines were low compared to those reported for the PAN's.²⁴ The low value of conducting could have been due to the substitute groups on the ring.²⁵ The magnetic susceptibility data of the polymers also are given in Table I. We determined that the magnetic susceptibility values of the homopolymers had diamagnetic properties; that is, their conducting mechanisms were of a bipolaron nature [Fig. 1(a,b)].²⁶

We synthesized the conductive composites of PPy/P2EAn and P2EAn/PPy by changing the synthesis order of the host polymer. We preferred to prepare the P2EAn composite with PPy with the highest conductivity value.

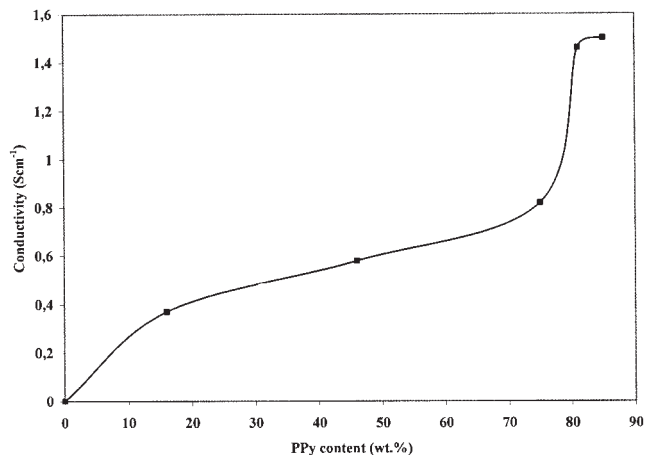


Figure 3 Dependence of the dc conductivity of the P2EAn/PPy composite on the PPy content at room temperature.

Figure 2 displays the dependence of the dc conductivity on the P2EAn content in the composite. The surface conductivity measured at a room temperature (300 K) varied from 1.50×10^{-2} to 2.94×10^{-5} S/cm when the P2EAn percentage varied from 18 to 85 wt %. With high amounts of P2EAn, the conductivity of the PPy/P2EAn composite also decreased with increasing P2EAn. A sharp change in the conductivity was observed at 20 wt % P2EAn for the PPy/P2EAn composites, as shown in Figure 2. This point probably corresponded to the percolation threshold, and the conductivity value at this point was determined to be 0.9×10^{-2} S/cm. As the P2EAn content increased above 20 wt %, the conductivities of the composites showed little change. The decrease in the conductivity with increasing P2EAn was due to the increasing pre-

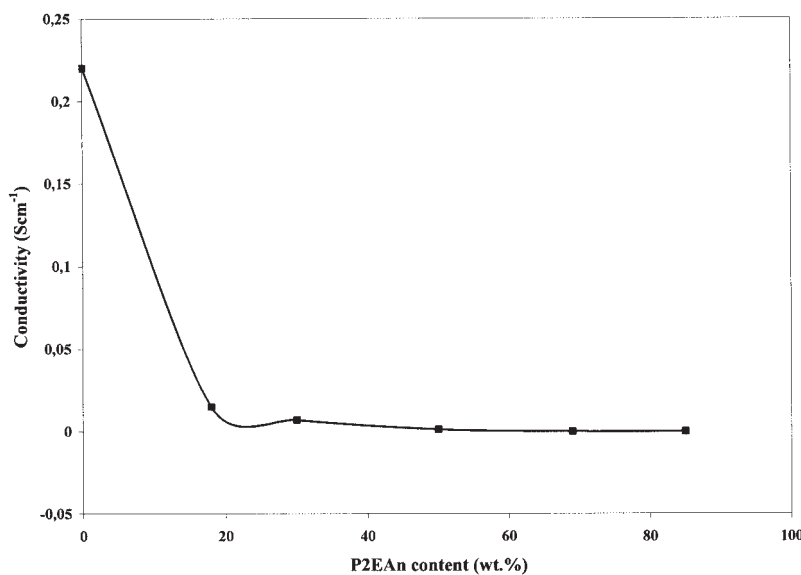


Figure 2 Dependence of the dc conductivity of the PPy/P2EAn composites on the P2EAn content at room temperature.

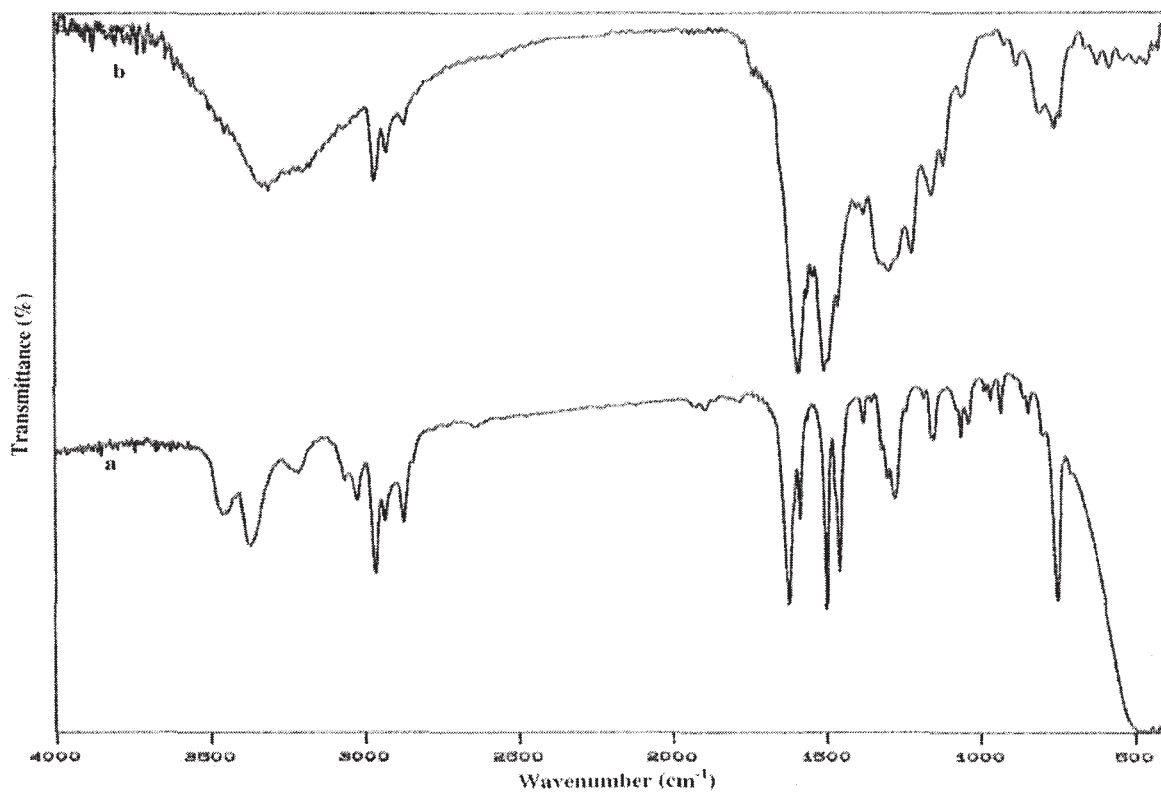


Figure 4 FTIR spectra of (a) the monomer and (b) P2EAn.

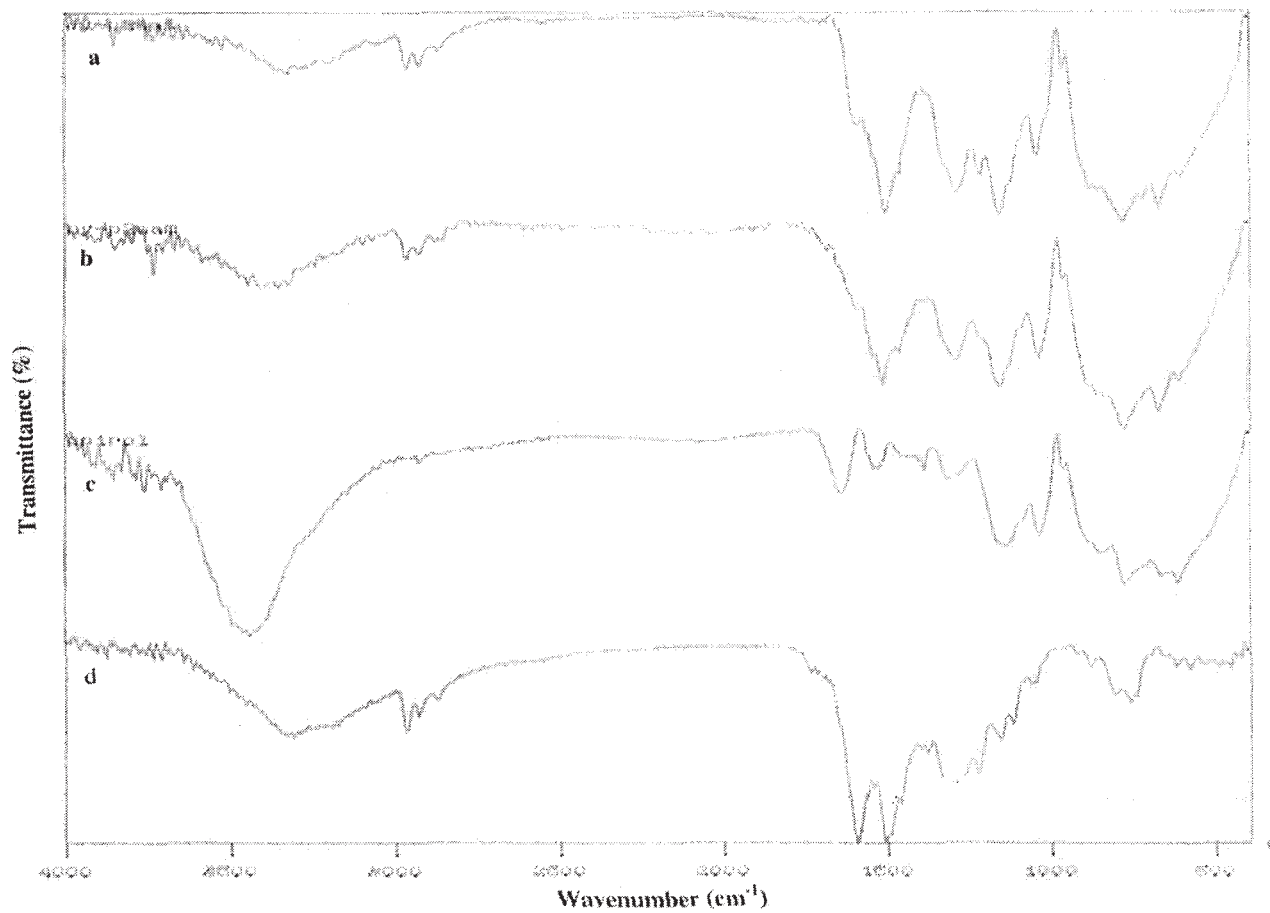


Figure 5 FTIR spectra of the (a) PPy/P2EAn composite, (b) 1:1 PPy/P2EAn mechanical mixture, (c) PPy, and (d) P2EAn.

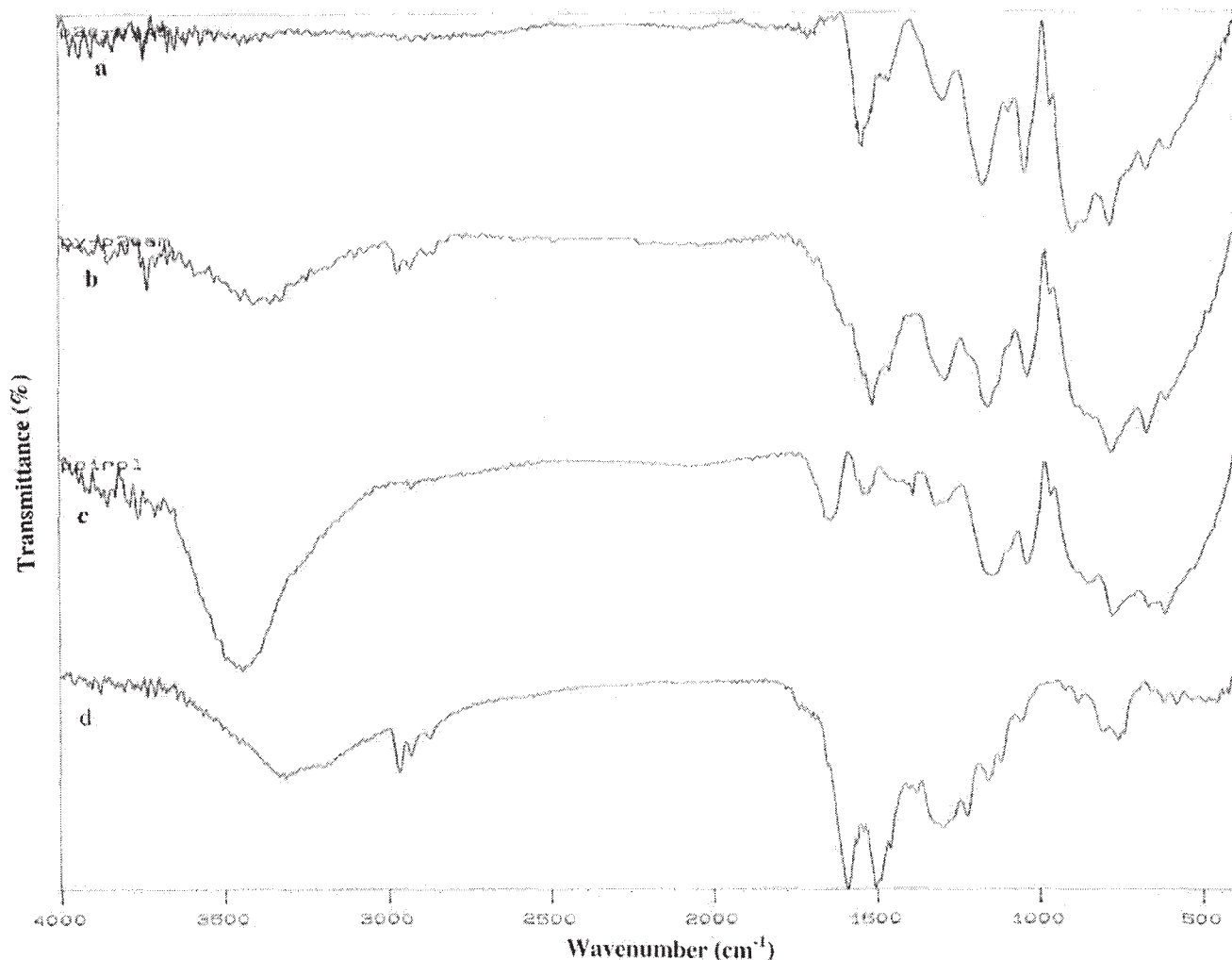


Figure 6 FTIR spectra of the (a) P2EAn/PPy composite, (b) 1:1 PPy/P2EAn mechanical mixture, (c) PPy, and (d) P2EAn.

vention of the formation of PPy channels for electron transport.

The effect of the amount of PPy on the conductivity of the composite polymer is shown in Figure 3. The room-temperature dc electrical conductivity of the P2EAn/PPy composite including 16 wt % PPy was substantially higher than that of the pure polymer (P2EAn) prepared under identical conditions and kept increasing with increasing PPy fraction. In the range 75–85% PPy, the conductivity increased quickly with PPy content. The percolation threshold and conductivity values were about 80% and 1.42 S/cm. The conductivities of all P2EAn/PPy composites were higher than those of both P2EAn and the PPy homopolymer. When the PPy content was varied from 0 to 85%, the electrical conductivity was enhanced from 4.10×10^{-5} to 1.50 S/cm, as shown in Figure 3. The percolation threshold in both composites was observed in the vicinity of about 80 wt % PPy. These results were consistent with a three-dimensional network of conducting polymer aggregates in an host matrix.

FTIR spectroscopy

FTIR measurements were performed with the KBr pellet method in the range 4000–500 cm^{-1} . Figure 4(a,b) shows the FTIR spectra of the monomer (2EAn) and P2EAn. A single band centered at 3400 cm^{-1} [Fig. 4(b)] due to the characteristic N—H stretching vibration suggested the presence of —NH— groups in 2EAn units. The C=C stretching of the benzene ring appeared at 1490 cm^{-1} , and the C=C stretching of the quinone ring appeared at 1560 cm^{-1} . The peak at about 1300 cm^{-1} was induced by the C—N stretching.²⁷ The peaks at 696, 751, and 831 cm^{-1} corresponded to the ortho and para disubstitutions in the ethylaniline rings. Similar bands were obtained for poly(*o*-toluidine) (POT), PNMA, poly(*N*-ethylaniline) (PNEAn)²⁸

Figures 5 and 6 show a comparison of the FTIR spectra of PPy/P2EAn and the P2EAn/PPy composites with P2EAn, PPy, and the 1:1 P2EAn/PPy mechanical mixture. In the FTIR spectrum [Fig. 5(c)] of PPy, the peak at 1529 cm^{-1} came from the C=C

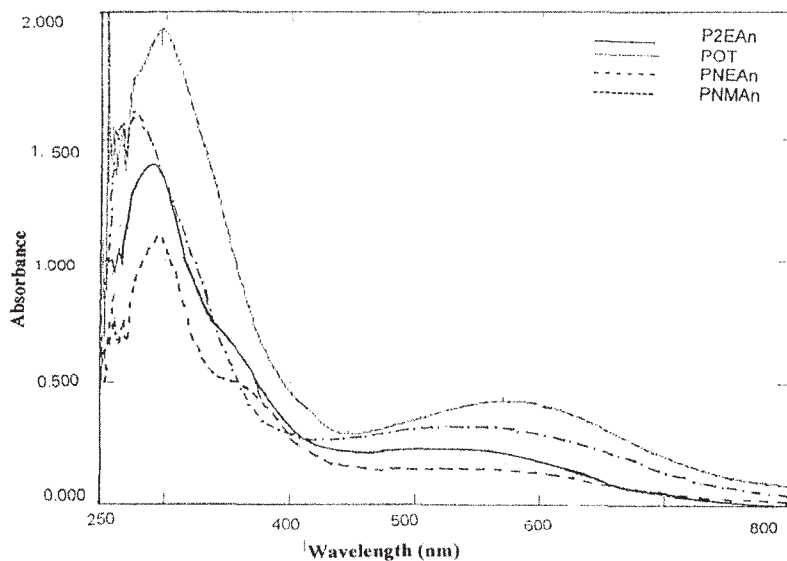


Figure 7 UV-vis spectra of polyalkylanilines in DMSO.

stretching of the pyrrole ring, the peak at 1144 cm^{-1} was caused by C—H in-plane deformation of the PPy unit, and the peaks around $922\text{--}784\text{ cm}^{-1}$ were due to the C—H out-of-plane deformation of the pyrrole unit.²⁹

The FTIR spectrum of the composites [Fig. 5 and 6(a)] in the region below 1800 cm^{-1} was similar to that of PPy; however, the bands of PPy and P2EAn were present. Thus, the composite was composed of PPy and P2EAn. A similar phenomenon was also observed for PPy-*o*-anisidine and PPy-PAN-polycarbonate systems.^{30,31} The 1:1 PPy/P2EAn mechanical mixture showed the bands of both PPy and P2EAn.

UV-vis spectra

The UV-vis spectra of the polyalkylanilines and PPy/P2EAn composites were taken in DMF, CHCl_3 , DMSO, and NMP. The UV-vis spectra of the P2EAn/PPy composites and PPy could not be taken due to insolubility in common solvents. Figure 7 shows the UV-vis spectra of the polyalkylanilines in DMSO. Their first absorptions appeared at 294, 275, 295, and 297 nm for P2EAn, POT, PNEAn, and PNMAAn, respectively. The second absorptions were located at

529, 527, 538, and 570 nm for P2EAn, POT, PNEAn, and PNMAAn, respectively. The first and second bands at 275–297 and 527–570 nm corresponded to $\pi\rightarrow\pi^*$ transition and $n\rightarrow\pi^*$ transition, respectively.^{32,33} Table II shows the absorption bands of the polyalkylanilines in all solvents. The values of these bands varied with changing solvents and substitute groups. The N-substituted polyalkylanilines showed transitions at longer wavelengths compared to the ring-substituted polyalkylanilines.

Figure 8 shows the UV-vis spectra of two composite solutions with PPy/P2EAn ratios of 82:18 and 70:30 in DMSO. With increasing P2EAn content from 18 to 30%, the wavelengths of both bands (301 and 559) shifted to longer values (308 and 580), respectively.³⁴ Moreover, the PPy/P2EAn (82:18) composite exhibited the transitions at much longer wavelengths than pure P2EAn. These results suggest that the conjugation length of the composite increased with the addition of PPy to P2EAn. Furthermore, whereas pure PPy was not soluble,³⁵ the PPy/P2EAn composite was soluble. Therefore, the oxidative polymer from PPy with P2EAn was confirmed to be a composite of two polymers rather than a mixture of two homopolymers. In addition, we tried to take the UV-vis spectra of the

TABLE II
Maximum Wavelengths of the Polyalkylanilines into Different Solvents

Polymer	DMF		CHCl_3		DMSO		NMP	
	λ_1 (nm)	λ_2 (nm)	λ_1 (nm)	λ_2 (nm)	λ_1 (nm)	λ_2 (nm)	λ_1 (nm)	λ_2 (nm)
POT	293	556	279	502	275	527	290	609
P2EAn	295	533	280	506	294	529	265	541
PNMAAn	293	573	291	494	297	570	312	609
PNEAn	294	544	290	—	295	538	260	546

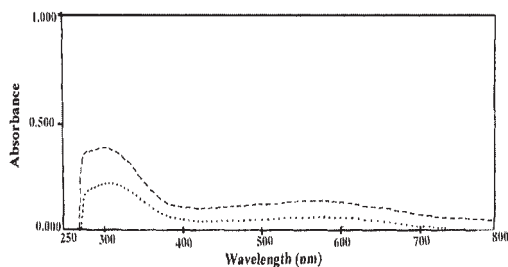


Figure 8 UV-vis spectra of the (---) 18% and (···) 30% PPy/P2EAn composites in DMSO.

PPy/P2EAn composite in others solvents. However, the composites did not dissolve in these solvents (NMP, CHCl_3 , and DMF).

Thermal stability

Thermogravimetric analysis (TGA) curves of the polyalkylanilines are shown in Figure 9. The TGA results of P2EAn, POT, and PNMAN showed a two-step weight loss, whereas those of PNEAn showed a one-step weight loss. The polymers exhibited a 3–5% weight-loss process at 40–50°C due to moisture evaporation.³⁶ The weight loss in the first step corresponded to the loss of dopant. The second weight loss was due to the degradation of the polymer.^{37,38}

Figure 10 shows the thermograms of pure PPy, PPy/P2EAn, P2EAn/PPy composites, and the 1:1 PPy/P2EAn mechanical mixture. The low weight loss observed at approximately 100°C in the thermogram of PPy (Fig. 10) was related to the removal of water from the structure. Table III summarizes the results of the TGA studies of the polyalkylanilines, PPy, and the composites. Pure PPy showed a weight loss starting at 200°C. From Figure 9 and Table III, we can also deduce that PNMAN was thermally more stable than

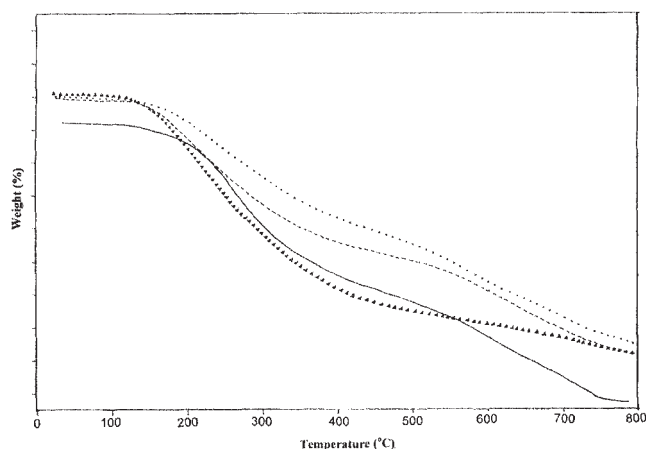


Figure 9 TGA curves of the polyalkylanilines: (···) POT, (---) P2EAn, (—) PNMAN, and (▲) PNEAn.

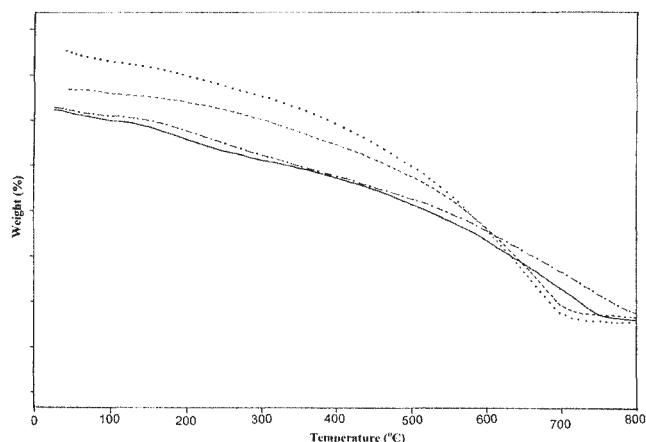


Figure 10 TGA curves of (---) PPy, (·-·-·) the PPy/P2EAn composite, (···) P2EAn/PPy, and (—) the PPy/P2EAn mechanical mixture.

PNEAn, as suggested by the initial degradation temperature (T_i) and the temperature of half decomposition [$T_{d(1/2)}$]. The mechanical mixture of P2EAn and PPy yielded somewhat different patterns due to the presence of PPy. These data showed that the thermal stability of the P2EAn/PPy composite was higher than that of PPy/P2EAn and P2EAn. However, its thermal properties were between those of pure P2EAn and PPy, which it contained in its structure. Similar results were also observed for a poly(2-chloroaniline/polyfuran) (P2ClAn/PFu) composite.³⁹ The thermal stability of P2EAn was enhanced from 160 to 172°C in the preparation of the P2EAn/PPy composite.

Wide-angle X-ray diffraction (WAXD) analysis

Figure 11(1–5) shows the WAXD patterns obtained for PPy, P2EAn/PPy, P2EAn, the 1:1 PPy/P2EAn mixture, and PPy/P2EAn powders in the reflection mode.

TABLE III
TGA Results for the Polymers

Polymer	T_i (°C)	T_m (°C)	T_f (°C)	$T_{d(1/2)}$ (°C)
POT	158	258	366	480
P2EAn	538	630	716	350
	160	248	346	
	542	632	726	
PNMAN	182	262	326	472
	542	640	738	
PNEAn	148	262	380	292
PPy	200	454	706	560
P2EAn/PPy	172	446	704	546
PPy/P2EAn	158	364	570	558
P2EAn:PPy (1:1 mixture)	142	300	456	516
	456	600	744	

T_m , maximum degradation temperature; T_f , finally degradation temperature.

The WAXD diagrams in Figure 11 exhibit broad diffraction peaks, suggesting that all of the polymers were amorphous. This is easily understood because PPy and P2EAn have been proposed to be amorphous polymers.⁴⁰ Two broad peaks, centered at about $2\theta = 14$ and 29° are shown in Figure 11^{2,4,5} [scan d; attributed to PPy; Fig. 11(1)].⁴¹ However, the scans of pure P2EAn, PPy, and the composites were nearly similar. A broad peak at $2\theta = 14^\circ$ was observed for P2EAn [Fig. 11(2)]. Moon et al.⁴² suggested scattering perpendicular to the chain direction. The position of this peak for P2EAn was shifted to a lower degree than for PAn. This indicated that the interchain distance of P2EAn was larger than that of PAn.⁴³

Table IV shows the degrees of crystallinity of the polymers as calculated from X-ray patterns. P2EAn had a higher crystallinity than PPy. This may be explained from by intramolecular and intermolecular interactions and H bonding.⁴⁴

The crystallinity of PPy/P2EAn was the highest among all of the polymers. However, P2EAn/PPy and the 1:1 PPy/P2EAn mixture had about the same values, which were between the crystallinities of PPy and P2EAn. The crystallinities of PPy and P2EAn were enhanced by the preparation of the PPy/P2EAn composite.

The solubility tests of polymers were carried out in some organic solvents. The solubilities of the polyalkylanilines doped and synthesized here were improved in some organic solvents compared to PAn and its derivatives.⁴⁵ They were more soluble in polar solvents such as DMSO, NMP, DMF, and also H_2SO_4 . Furthermore, whereas PPy was not soluble in common solvents, the PPy/P2EAn composite was more soluble than pure PPy in these solvents. The intrinsic viscosity values of the polyalkylanilines were measured in H_2SO_4 at $25^\circ C$. The data show that the intrinsic viscosities (0.19 and 0.24 g/dL) of POT and P2EAn were higher than those of PNMan and PNEAn.

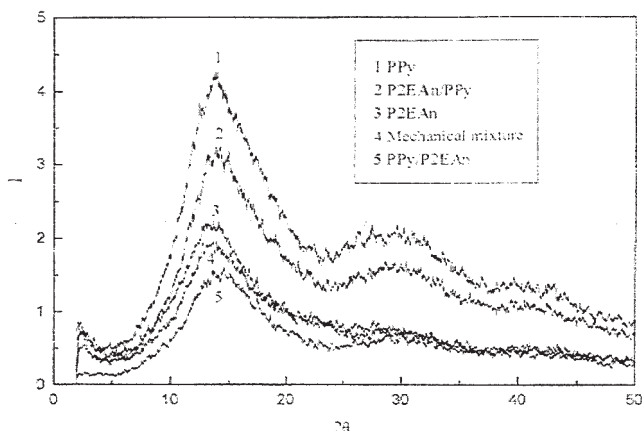


Figure 11 WAXD scans: (1) PPy, (2) P2EAn/PPy, (3) P2EAn, (4) PPy/P2EAn mechanical mixture, and (5) PPy/P2EAn.

TABLE IV
Degrees of Crystallinity of the Polymers

Polymer	Crystallinity (%)
PPy	5.0
P2EAn	11.0
PPy/P2EAn	12.0
P2EAn/PPy	5.0
PPy:P2EAn (1:1 mixture)	5.0

CONCLUSIONS

Polyalkyl-substituted anilines, PPy, and their composites have been successfully and directly synthesized by oxidative polymerization. The conductivity values and electronic and thermal properties of the composites obtained by different techniques changed according to the host variation and the guest polymer order. The conductivities of the P2EAn/PPy composites were higher than that of both homopolymers and the PPy/P2EAn composite. The PPy/P2EAn composites had better solubility than P2EAn/PPy in the solvents. The thermal stability of P2EAn was enhanced in the P2EAn/PPy composite. The Gouy balance measurements suggested that the electrical conduction mechanism of the homopolymers and composites was bipolaron hopping. These improvements in the conductivities and thermal stabilities of the homopolymers through the preparation of novel composites made them suitable for various technological applications.

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