

Spectroelectrochemical Investigations of Aniline–Thiophene Copolymers in Acetonitrile

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ABSTRACT: The copolymerization of aniline and thiophene with varying concentration ratios was studied in acetonitrile/tetrabutylammonium tetrafluoroborate. *In situ* UV-vis and *in situ* surface resonance Raman spectroscopic studies revealed that polythiophene and polyaniline units of different lengths enter into the electropolymerization products. The copolymers deposited were either polyaniline-

based or polythiophene-based polymeric structures depending on the initial concentration of the monomers used. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3417–3423, 2003

Key words: copolymerization; conducting polymers; UV-vis spectroscopy; Raman spectroscopy; electrochemistry

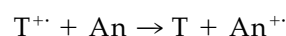
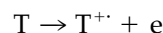
INTRODUCTION

Polyaniline has been studied extensively in the last few years due to its good environmental stability and facile synthesis. Such properties make this polymer suitable for a variety of technological applications.^{1–4} Polythiophene also has promising industrial applications because of its thermochromism, electrochromism, solvatochromism, luminescence, and photoconductivity. A disadvantage of polythiophene in technological applications is its overoxidation, which causes irreversible degradation.⁵

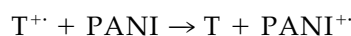
Recently, attempts have been made to copolymerize different kinds of heterocyclic compounds such as pyrrole–thiophene and pyrrole–terthienyl to improve the processability of the resulting conducting structure. Electrochemical properties of these resulting copolymers have been studied.^{6,7} There are few studies about the synthesis of copolymers of aniline and thiophene or their derivatives with physical properties that are different from those of homopolymers prepared by electrochemical^{8–10} and chemical^{11–13} methods. Hu et al. carried out electrochemical preparation of bithiophene and aniline copolymers in an aqueous/organic mixed medium.⁸ In another study concerning the electrochemical copolymerization of thiophene and aniline, polythiophene was coated with polyaniline, which produced a composite. In coating polyani-

line with polythiophene, on the other hand, the system produced was claimed to be a copolymer.⁹ Electrocopolymerization of aniline and thiophene has been found to be difficult because of a large difference in their oxidation potentials. This problem can be solved by controlling the concentration of monomers and adjusting the polymerization potential according to the concentration of the monomers. Bithiophene can also be used for copolymerization instead of thiophene, but thiophene is more conventional.

In previous studies from our laboratory, the electrochemical preparation and properties of polyaniline and polythiophene in acetonitrile were extensively elucidated.^{10,14,15} In one of these studies, the effect of thiophene on the electro-preparation and properties of polyaniline was investigated on a Pt electrode in acetonitrile.¹⁰ The presence of thiophene in aniline solutions in acetonitrile accelerates the formation and caused an improvement in the conductivity of polyaniline films. A catalytic mechanism related to the role of thiophene cation radicals which involves chemical and electrochemical oxidation steps was proposed. An electrolytically produced thiophene cation radical chemically oxidizes aniline and also polyaniline chains, forming the polypernigriline form during deposition:



and



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TABLE I
Solution Conditions for Deposited
Homopolymers and Copolymers

Polymer	Solution
Polyaniline	175 mM aniline, 75 mM HBF ₄
Polythiophene	100 mM thiophene, 10 mM HBF ₄
Copolymer A	175 mM aniline, 75 mM HBF ₄ , 150 mM thiophene
Copolymer B	175 mM aniline, 75 mM HBF ₄ , 175 mM thiophene
Copolymer C	175 mM aniline, 75 mM HBF ₄ , 200 mM thiophene

In acidic solutions containing higher thiophene-to-aniline concentration ratios, thiophene entered into the structure of the polymer forming a copolymer. The properties of this copolymer were elucidated using cyclic voltammetry, GCMS, elemental analysis, and DSC methods.

In another study about this copolymer, the conductance properties were extensively elucidated.¹⁶ *In situ* conductivity characteristics of aniline–thiophene copolymers were found to be different from those of the homopolymers. Polyaniline-based (Cop A, see Table I) and polythiophene-based (Cop B, Cop C; see Table I) copolymers, which are interrupted by either thiophene or aniline units, were prepared. The conductivity curve of the polyaniline-based copolymer (Cop A) was similar to that of polyaniline, except that its conductivity value was almost constant to 1.0 V versus Ag/AgCl and 2.5 orders of magnitude lower than that of pure polyaniline. The *in situ* conductivity behavior of the polythiophene-based copolymer (Cop B, Cop C) resembles that of polythiophene, the important difference being that no degradation of these copolymers took place between 1.4 and 1.9 V versus Ag/AgCl due to the presence of aniline units within the polythiophene chains. This way, the range of stability of these copolymers was considerably extended compared to polythiophene for which a complete loss of conductivity occurs during potential excursions to 1.9 V versus Ag/AgCl. The reversible doping/undoping behavior of polyaniline up to this potential limit was also observed in this copolymer, albeit with much lower overall conductivities. In other words, copolymers of aniline and thiophene combine the advantages of both homopolymers as far as the range of stability and reversible doping/undoping behavior is concerned.

This article deals with the results obtained by *in situ* UV-vis and *in situ* surface resonance Raman (SRR) spectroscopic investigations of aniline–thiophene copolymers (Cop A, Cop B, Cop C) deposited at constant potential (1.7 V versus Ag/AgCl) on Au and ITO electrodes in acetonitrile. The spectroscopic properties of these copolymers were compared with those of the homopolymers.

EXPERIMENTAL

Acetonitrile (LiChrosolv; Merck, Germany) was purged with nitrogen prior to use. Aniline (Merck) was distilled at reduced pressure and stored under a nitrogen atmosphere at -10°C in the dark. Thiophene (Aldrich) and a diethylether complex of tetrafluoroboric acid (HBF₄; Aldrich) were kept at -10°C in the dark under a nitrogen atmosphere and used directly. Electrolyte solutions were prepared from tetrabutylammonium tetrafluoroborate (TBABF₄; Aldrich) without purification. *In situ* UV-vis and *in situ* SRR studies were carried out in electrolyte solutions containing 2 mM HBF₄ and 15 mM HBF₄, respectively.

Electrochemical experiments were carried out under a nitrogen atmosphere in a three-electrode-type cell with separate compartments for the reference electrode [Ag, AgCl (sat) in acetonitrile] and the counter-electrode (Pt wire). For *in situ* UV-vis measurements, the polymers were deposited at a constant electrode potential (1.7 V versus Ag/AgCl) on ITO electrodes, which were washed with acetonitrile and dried prior to use. A platinum wire was used as a counterelectrode and the reference electrode was connected via a salt bridge. UV-vis spectra were recorded with a Shimadzu UV-2101PC spectrometer.

SRR spectra were measured on an ISA 64000 spectrometer equipped with a liquid nitrogen-cooled CCD camera detector at a resolution of 2 cm^{-1} . Samples were illuminated with laser light provided by Coherent Innova 70 systems. The polymer was deposited on a working electrode made from $2 \times 4\text{ mm}$ Au embedded in epoxy resin and polished with Al₂O₃ ($0.05\text{ }\mu\text{m}$ grain size) before each new deposition.

RESULTS AND DISCUSSION

The potential scan up to the potential values of thiophene oxidation should result in coating polyaniline film with polythiophene film due to the large difference in the electrooxidation potentials of aniline and thiophene in 0.1M TBABF₄/acetonitrile (0.90 and 2.0 V versus Ag/AgCl, respectively).^{14,15} To avoid this, aniline–thiophene copolymers were deposited at an experimentally predetermined constant potential (1.7 V versus Ag/AgCl) instead of potential scanned electrolysis. Polyaniline, polythiophene, copolymer A, copolymer B, and copolymer C were deposited on an Au electrode, from solutions whose detailed compositions are given in Table I.

To establish the differences between the various oxidation states of copolymer B, polythiophene, and polyaniline, UV-vis spectra of freshly prepared, reduced (at 0.5 V versus Ag/AgCl), and oxidized (at 1.5 V versus Ag/AgCl) samples were recorded in a blank solution containing 2 mM HBF₄ [Fig. 1(a–c)]. It can be seen that the copolymer spectrum is clearly not a

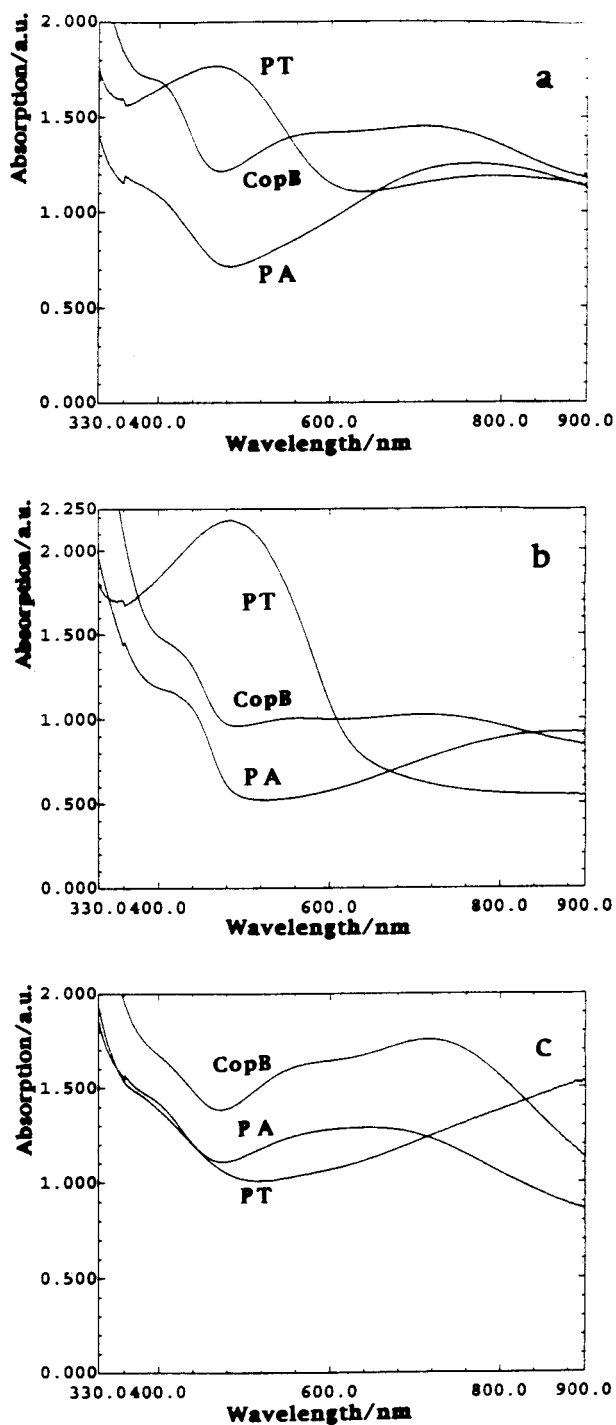


Figure 1 UV-vis spectra of (a) freshly prepared, (b) after reduction at 0.5 V versus Ag/AgCl in a blank solution containing 2 mM HBF_4 and (c) after oxidation at 1.5 V in same blank solution of polyaniline, copolymer B, and polythiophene.

simple mixture of the spectra of fresh, reduced, and oxidized homopolymer films. Fresh polyaniline, polythiophene, and copolymer B, all prepared at 1.7 V versus Ag/AgCl, were then put in the same blank solution and electrolyzed at progressively increasing

applied potentials to 1.9 V versus Ag/AgCl, and *in situ* UV-vis spectra were recorded [Fig. 2(a-c)].

During the partial oxidation of polyleucoemeraldine to polyemeraldine (at 0.5 V versus Ag/AgCl), new strong absorption bands at 441 nm (polaron state) and 889 nm (bipolaron state) were observed, similar to those reported in the literature^{17,18} [Fig. 2(a)]. The absorption band at 889 nm increases in intensity with an increased degree of oxidation to polypernigriline

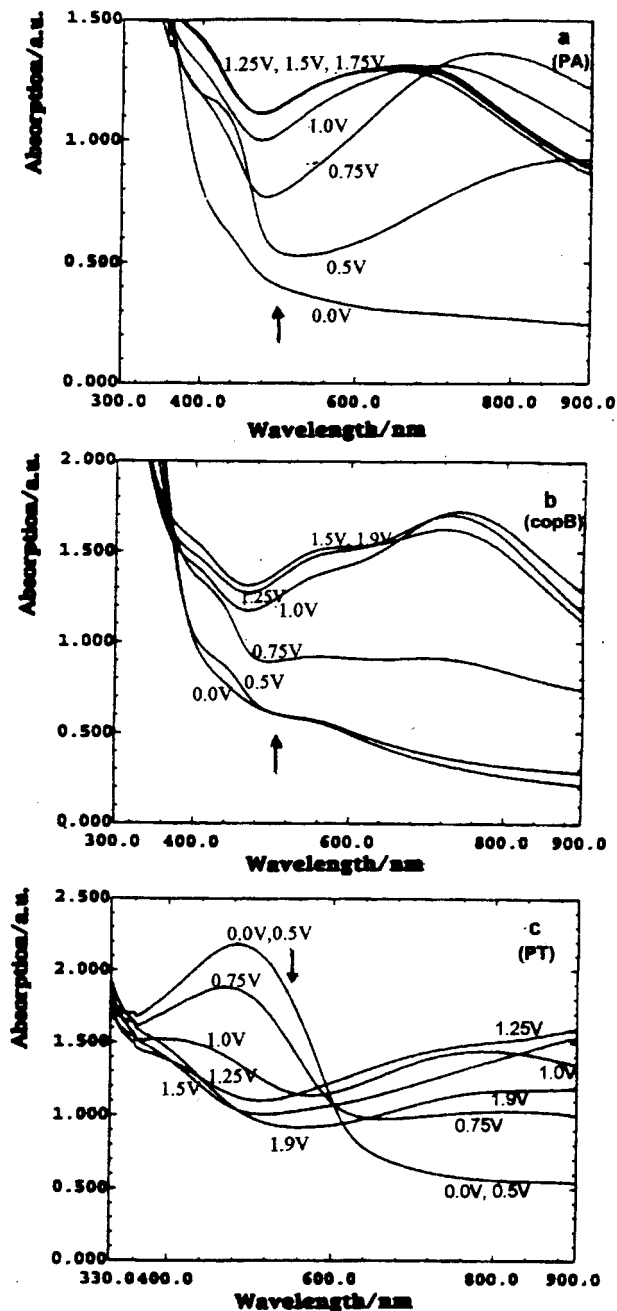


Figure 2 UV-vis spectra of (a) polyaniline, (b) copolymer B, and (c) polythiophene while keeping the applied potentials at a constant value (at 0.0, 0.5, 0.75, 1.0, 1.25, 1.5, and 1.9 V versus Ag/AgCl) in a blank solution containing 2 mM HBF_4 .

in the polymer structure (at 1.0 and 1.25 V versus Ag/AgCl). Thus, this peak is inherently associated with the presence of the quinoid structures in polyemeraldine. Further oxidation of polypyrroline at more positive applied potentials results in a blue shift of this quinoid peak.

In the reduced state of polythiophene (at 0.0 V versus Ag/AgCl), a strong absorption at 483 nm was observed, which was assigned to a transition from the valence to the conduction band (interband transition) in the literature^{19,20} [Fig. 2(c)]. During stepwise oxidation of this film, the intensity of this interband transition decreased and a new broad absorption band related to bipolaron states appeared around 760 nm. Due to the low degree of conjugation observed for polythiophene and the low doping levels, the intensity of the absorbance around 760 nm starts to decrease upon further electrooxidation, indicating degradation, again consistent with the literature findings.^{19,20}

In the reduced state of the aniline–thiophene copolymer (copolymer B), two weak absorption bands at 441 and 555 nm were observed [Fig. 2(b)]. During the stepwise oxidation of this film, the absorption band around 441 nm shows features similar to observed for the polyaniline film. On the other hand, an absorption band at 740 nm starts to appear and increases its intensity with stepwise oxidation, but does not show a blue shift like that observed in polyaniline. The intensity of a new absorption band at 555 nm, which was only observed in the UV-vis spectra of copolymer B, increases in intensity during the stepwise oxidation but without any blue shift. Wang and MacDiarmid synthesized tetraniline by the chemical method²¹ and characterized it using UV-vis spectroscopy. According to these UV-vis studies, only one transition was observed at 333 nm in dimethyl sulfoxide due to the π – π^* transition centered on the benzenoid ring. When tetraniline was slowly oxidized by the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the UV-vis spectra showed that a new chromophore characteristic of the quinoid group began to appear at 593 nm and continually increased in intensity. With further oxidation, the intensity of this new characteristic transition began to decrease and was accompanied by a simultaneous shift to higher energies.

In another study, Johnson and Park²² studied the early stages of aniline oxidation employing spectroelectrochemical and rotating ring disk electrode experiments in a H_2SO_4 solution. The results indicated that a large amount of the head-to-tail dimer, the aniline tetramer, as well as oligomers formed in solutions of high aniline concentrations. The aniline tetramer was then immediately electrooxidized to its radical cation, which absorbed at about 550 nm. The spectroscopic results obtained in this study showed that the shorter polyaniline chains (similar to tetraaniline structure) absorb at 555 nm and do not display a blue shift. The

longer polyaniline chains, on the other hand, absorb at around 740 nm and show no blue shift, as was the case for polyaniline. It can thus be concluded from the above UV-vis spectra that thiophene units enter into the structure, forming an aniline-based copolymer, and that polyaniline chains are interrupted by the incoming thiophene units to give polyaniline chains of various lengths.

The experiments were repeated with increasing amounts of thiophene to 400 mM in a polymerization solution containing aniline, thiophene, and HBF_4 and the UV-vis spectra of the films obtained were found to be similar to those of the copolymer B [Fig. 2(b)], not to that of the expected polythiophene [Fig. 2(c)]. It can thus be assumed that aniline becomes oxidized more readily because of its lower oxidation potential and that the catalytic effect of thiophene cation radicals at more positive oxidation potentials operates. As a result of this catalytic effect, polyaniline-based copolymer film is obtained instead of the expected polythiophene-based copolymer.

Figure 3 shows SRR spectra of the homopolymers and copolymers after the reduction of freshly prepared films (at 0.0 V versus Ag/AgCl) in a blank solution containing 15 mM HBF_4 at 0.00 V versus Ag/AgCl. Figure 4 shows SRR spectra of the same samples after oxidation of the same films at 1.0 V versus Ag/AgCl in the blank solution containing 15 mM HBF_4 . All the bands in Raman spectra of copolymers A and B are also present in the spectrum of polyaniline when it was oxidized at 1.0 V versus Ag/AgCl [compare Fig. 3(b,c) with Fig 4(a)]. The bands of copolymer B are broader than those of copolymer A in both the reduced and oxidized forms [compare Fig. 3(b) with Fig. 3(c) and Fig. 4(b) with Fig. 4(c)]. There are mainly three differences between the spectrum of the oxidized polyaniline and the spectra of copolymers A and B. The spectra of copolymers A and B contain bands at 700, 1047, and 1456 cm^{-1} , which are also present in the spectrum of polythiophene, assignable to the symmetric in-plane ring deformation mode, the in-plane C–H deformation mode, and the symmetric C=C intraring stretching mode of polythiophene, respectively.²³ The intensity of these bands, especially that at 1456 cm^{-1} , increase with an increasing thiophene concentration [compare Fig. 3(c) with Fig. 3(d)]. These results show that the number of thiophene units in these copolymers increase with an increasing thiophene concentration in the polymerization solution.

The SRR spectrum of copolymer C contains all the polythiophene peaks in the reduced form [Fig. 3(d,e)]. There is only one different band at 830 cm^{-1} in the reduced form, which is also present in the spectrum of polyaniline, assignable to benzene ring symmetric stretching.^{24,25} When copolymer C is oxidized at 1.0 V versus Ag/AgCl in a blank solution containing 15 mM

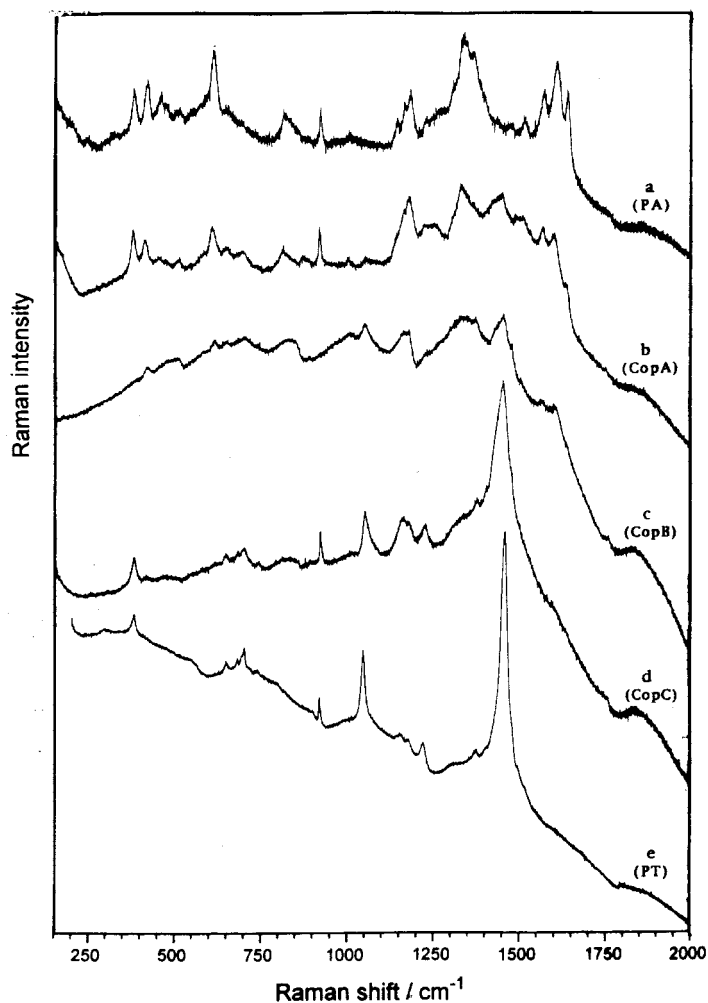


Figure 3 Raman spectra of (a) polyaniline, (b) copolymer A, (c) copolymer B, (d), copolymer C, and (e) polythiophene after reduction at 0.0 V versus Ag/AgCl in a blank solution containing 15 mM HBF_4 , $P_L = 100$ mW, and $L_0 = 647.1$ nm.

HBF_4 , the peaks at 416, 1475, 1585, and 1623 cm^{-1} appear [Fig. 4(d)]. These peaks are assignable to ring stretching in the semiquinoidal structure, stretching vibrations of C=N groups, C=C stretching in the quinoid ring, and C—C stretching deformations of polyemeraldine,^{17,24–27} respectively. These bands are also present in the oxidized polyaniline [compare Fig. 4(a) and Fig. 4(d)]. In addition, the intensity of the peak at about 1169 cm^{-1} is higher than that in pure polythiophene and this peak is also present in the spectrum of oxidized polyaniline [compare Fig. 4(a,d,e)]. The higher intensity is due to the overlap of this band with the C—H in-plane deformation band in the quinoid ring. The observation of this same band in the polythiophene spectrum indicates that polymer chains are present as *cis* coplanar isomers as well as in a highly symmetrical *trans* conformation.²³

CONCLUSIONS

In an earlier study related to these films, the cyclic voltammograms did not provide any evidence for the

formation of copolymers.¹⁶ The cyclic voltammetric patterns were all rather similar to that of polythiophene but the peak currents were different from each other. DSC findings did provide, however, convincing evidence that the electropolymerization resulted in forming copolymers, not composites.¹⁰

The UV-vis spectra of freshly prepared, reduced, and oxidized copolymer B are, on the other hand, different from the corresponding spectra of the homopolymers. UV-vis spectra of copolymer B recorded at various electrode potentials did not reveal much of the typical behavior of polythiophene, which implies the absence of extended polythiophene blocks in the polymer. Thiophene units apparently enter into the structure of the polymer, forming, mainly, an aniline-based copolymer with polyaniline chains of various lengths. The longer polyaniline chains in the copolymer can be oxidized to pernigraniline electrochemically and chemically during deposition while the shorter chains remain in the emeraldine form.

The SRR spectra of copolymers A, B, and C show peaks characteristics of both the polyaniline and poly-

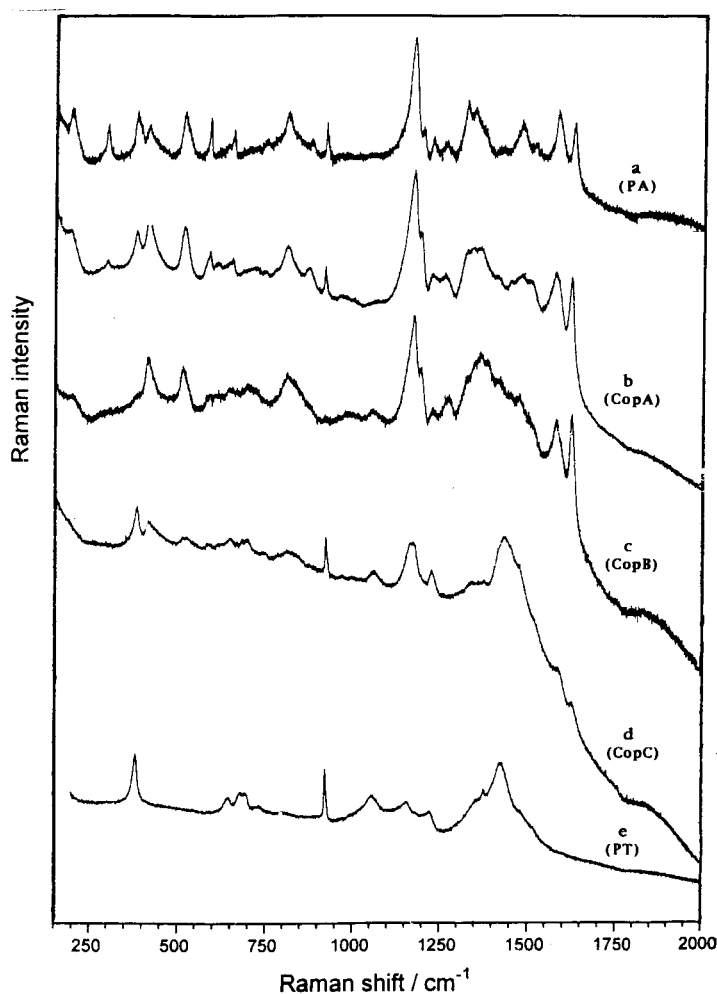


Figure 4 Raman spectra of (a) polyaniline, (b) copolymer A, (c) copolymer B, (d) copolymer C, and (e) polythiophene after oxidizing at 1.0 V versus Ag/AgCl in a blank solution containing 15 mM HBF_4 , $P_L = 100$ mW, and $L_0 = 647.1$ nm.

thiophene homopolymers. Therefore, the evaluation of the SRR spectra would lead to the conclusion that all of these copolymers are of the block copolymer type. However, the observed *in situ* conductivity properties¹⁶ and *in situ* UV-vis spectra do not correspond to the sum of those of the two individual homopolymers. These later findings eliminate the possibility that copolymers A, B, and C can be considered as block copolymers. It can only be concluded that copolymer B has a structure approaching that of the block copolymer, having longer polythiophene units and shorter polyaniline units than those of copolymer A and having longer polyaniline units and shorter polythiophene units than those of copolymer C.

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