Investigation of the Electroactivity, Conductivity, and Morphology of Poly(pyrrole-*co*-*N*-alkyl pyrrole) Prepared via Electrochemical Nanopolymerization and Chemical Polymerization

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ABSTRACT: The copolymerization of pyrrole (Py) with *N*-ethyl pyrrole, *N*-butyl pyrrole, and *N*-octyl pyrrole (NOPy) was carried out by electrochemical and chemical oxidation. In the electrochemical method, copolymer thin films with different feed ratios of monomers were synthesized by the cyclic voltammetry method in a lithium perchlorate (LiClO$_4$)/acetonitrile (CH$_3$CN) electrolyte on the surface of a glassy carbon working electrode. The deposition conditions on the glassy carbon, the influence of the molar ratios of the monomers on the formation of the copolymers, and the electroactivity of the copolymers were investigated with cyclic voltammetry. Nanoparticles made of a conjugate of the copolymers with different feed ratios of monomers were prepared by chemical polymerization (conventional and interfacial methods) in the presence of iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O) as the oxidant. Nanostructural copolymers with higher conductivities were synthesized by simple tuning of the preparation conditions in a two-phase medium. Fourier transform infrared spectroscopy, scanning electron microscopy, and four-probe conductivity measurement techniques were applied for the characterization of the obtained copolymers. The conductivity of the obtained copolymer by an interfacial method with chloroform as the organic phase was 20 times higher than the copolymer obtained via an interfacial method with toluene as the organic phase and 700 times higher than the copolymer prepared by the conventional method (for a molar ratio of 70 : 30 Py : NOPy). © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 124: 3956–3962, 2012

Key words: conducting polymers; copolymers; electrochemistry; polypyrroles

INTRODUCTION

Polypyrrole (PPy) is one of the most studied conducting polymers because of its high conductivity, thermal and environmental stability, and relative ease of synthesis.[1–4] Nevertheless, few applications have been reported because conducting polymers based on PPy exhibit poor physical and mechanical properties and are not soluble in common solvents. Numerous studies have been carried out to investigate the different properties of conducting polymers, focusing on the electrical properties.[5–7]

A number of investigations have targeted the copolymerization of heterocyclic compounds of different types, such as aniline–pyrrole (Py),[8] aniline–thiophene,[9] and thiophene–Py.[10] The aim of these studies was to correlate the composition of the copolymerized mixture and the final electrochemical, physical, and morphological properties of the resultant copolymer. Alternative methods of improving the mechanical and physical properties of the conducting PPy for a wider range of applications make the study of the Py monomer an active field of research.[11]

In this regard, 3-substituted Py's with *n*-alkyl side chains up to 22 carbons in length were used as precursors for conductive polymers because of the solubility of the resultant polymers in most common organic solvents.[12] The use of conducting polymers to fabricate conductive textiles is a new and exciting field that is relatively untapped for its commercial potential for smart materials. PPy can be processed readily into textiles; however, some problems need to be surmounted before the true commercialization of PPy-coated textiles. Some of these impediments are stability, brittleness, and insolubility. The insolubility of conducting polymers has been overcome by chemically chemical modification of the Py monomer. It was shown that poly(3-alkyl pyrrole) polymers are soluble in most polar organic solvents.[13,14] The electrochemical behavior of *N*-substituted Py with different functional groups and substituent sizes was investigated in the early 1980s.[15] Some

research groups focused on the copolymerization of Py and *N*-substituted Py's by chemical oxidation.[16] However, only a few studies have been reported on the copolymerization of *N*-alkyl substituted Py's by chemical and electrochemical oxidation. Chen-Yang et al.[17] reported the copolymerization of Py with *N*-hydroxyalkyl pyrrole and the characterization of the resulting copolymer electrodeposited on a stainless steel surface. However, to the best of our knowledge, there has been no report on the chemical or electrochemical oxidative copolymerization of Py with *N*-butyl pyrrole (NBPy) and *N*-octyl pyrrole (NOPy) or *N*-ethyl pyrrole (NEPy) until now. In this article, the copolymerization of Py with NEPy, NBPy, and NOPy with various monomer ratios is reported. The obtained copolymers were characterized by a variety of electrochemical and spectroscopic techniques. The morphology and the conductivity of the copolymers were evaluated by scanning electron microscopy (SEM) and the four-point probe method, respectively. Also, herein, we report the synthesis of NEPy, NBPy, and NOPy monomers and the morphological evolution and conductivity of poly(pyrrole-*co*-*N*-alkyl pyrrole) [poly(Py-*co*-NAPy)] prepared by interfacial chemical oxidative copolymerization from monomer mixtures of NEPy, NBPy, and NOPy with Py in the presence of toluene or chloroform solvents and iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O) as the oxidant.

EXPERIMENTAL

Materials

Py (Merck, Germany) was distilled under reduced pressure and kept at 0°C before use. Ethylbromide, butylbromide, octylbromide, and tetrahydrofuran (THF); all from Fluka, Germany were distilled before use. Chloroform and toluene (Merck), FeCl$_3$·6H$_2$O (Merck), potassium metal (Merck), methanol (Fluka), and lithium perchlorate (LiClO$_4$; Merck) were used as received without further treatment.

Synthesis of the NEPy, NBPy, and NOPy monomers

NEPy, NBPy, and NOPy were synthesized from Py. A typical preparation process was as follows: To a well-stirred mixture of 0.16 mol of potassium metal in 50 mL of dry THF, 0.14 mol of Py in 10 mL of THF was added under refluxing over 30 min; then, the mixture was refluxed for another 3 h. Then it was cooled in a water bath. To a stirred mixture, 15.10 mL (0.14 mol) of butylbromide was added over 30 min; then, the mixture was stirred for 24 h at room temperature. The mixture was kept stirring overnight, and then, the solvent was evaporated and

the resulting precipate dried (73%). The product was an oily sample that tended to darken on standing. The *N*-alkyl pyrroles (NAPy's) were purified by preparative layer chromatography (PLC) on silica gel using n-hexane: acetone (5 : 1) as eluent. Nitrogen gas was bubbled through the solutions before and during the reaction.

^{1}H-NMR (hexadeuterated dimethyl sulfoxide, δ, ppm): 6.70 (2H, Py–H$_{2,5}$), 5.95 (2H, Py–H$_{3,4}$), 3.86 (t, 2H, N—CH$_2$—), 1.64 (m, 2H, N—CH$_2$CH$_2$—), 1.22 [m, 2H, N—(CH$_2$)$_2$—CH$_2$—], 0.88(t, 3H, —CH$_3$).

Electrochemical preparation process of the PPy, poly(N-ethyl pyrrole) (PNEPy), poly(N-butyl pyrrole) (PNBPy), poly(N-octyl pyrrole) (PNOPy), and poly(Py–NAPy) copolymers

Electrochemical experiments were carried out in a convenient three-electrode cell. A glassy carbon plate with an area of 0.039 cm^2 was used as the working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Cyclic voltammograms (CVs) were recorded by an ATOLAB instrument (Ecochemie B. V., Utrecht, The Netherlands). The molar ratios of Py to NAPy (Py : NAPy) were selected to be 10 : 90, 25 : 75, 50 : 50, and 75 : 25. A typical preparation process was as follows: 0.1*M* monomer(s) and 0.1*M* LiClO$_4$ in acetonitrile (CH$_3$CN) were electropolymerized by the application of sequential linear potential sweeps with a scan rate of 10 mV/s between −0.4 and +0.9 V versus Ag/AgCl. The copolymer films were deposited through 30 cycles for the polymerizations in all supporting electrolytes. After deposition, the films were washed with 0.1*M* supporting electrolytes without any monomers. Throughout the studies, anaerobic conditions were maintained with a nitrogen gas atmosphere.

Preparation of the Py copolymers with NEPy, NBPy, and NOPy by chemical oxidation

Chemical synthesis (method 1)

PPy, PNEPy, PNBPy, PNOPy, and poly(Py-*co*-NAPy) were synthesized by a conventional chemical oxidative polymerization process, and the molar ratios of Py to NAPy (Py : NAPy) were selected to be 90 : 10, 70 : 30, 50 : 50, 30 : 70, and 10 : 90.

A typical preparation process was as follows: 0.01 mol of monomer(s) was added to 100 mL of an aqueous solution of FeCl$_3$·6H$_2$O (0.03 mol) under vigorous stirring. The mixture was stirred at room temperature for 6 h. The precipitated black powder was filtered and washed with distilled water and methanol until the filtrate became colorless and was then dried in a vacuum-drying cabinet at 60°C for 24 h.
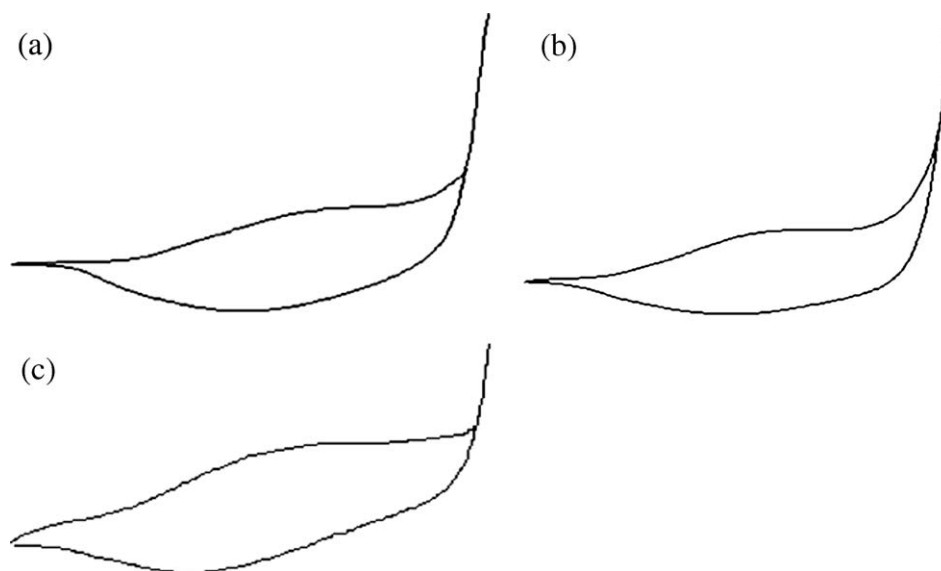
Figure 1 CVs recorded during the synthesis of the copolymers [Py : NEPy = (a) 10 : 90, (b) 25 : 75, and (c) 50 : 50] between the scanning potential values of -0.4 and $+0.9$ V versus Ag/AgCl with a scan rate of 10 mV/s in the 30th cyclic.

Nanostructures synthesis (method 2)

Poly(pyrrole-*co*-*N*-ethyl pyrrole) [poly(Py-*co*-NEPy)], poly(pyrrole-*co*-*N*-butyl pyrrole) [poly(Py-*co*-NBPy)], and poly(pyrrole-*co*-*N*-octyl pyrrole) [poly(Py-*co*-NOPy)] nanostructures were synthesized by an interfacial chemical oxidative polymerization, and the molar ratios of Py to NAPy were selected to be 10 : 90 and 30 : 70.

A typical preparation process was as follows: 0.01 mol of monomer(s) was added to 100 mL of toluene or chloroform; 100 mL of a precooled $0.03M$ $FeCl_3 \cdot 6H_2O$ aqueous solution was added very slowly to the previous solution for oxidative interfacial polymerization. The reaction mixture (two phase-solution) was kept for 24 h at room temperature. The precipitated powder was filtered and washed with distilled water and methanol until the filtrate became colorless; it was then dried in a vacuum-drying cabinet at $60°C$ for 24 h.

Characterization

SEM images were collected by an LE440I, Oxford, UK scanning electron microscope. The conductivity of the polymers was measured at room temperature via a standard four-probe apparatus (Azar Electric Co., Tabriz, Iran). Fourier transform infrared (FTIR) spectra of the samples were recorded by a Bruker Tensor, Germany, 27 FTIR spectrophotometer with KBr pellets.

RESULTS AND DISCUSSION

Investigation of the electrochemical behavior of the poly(Py-*co*-NAPy) copolymer

Figures 1(a–c) represent the CVs recorded during the copolymerization of Py with NEPy in a $0.1M$ $LiClO_4$/

CH$_3$CN solution at room temperature. The CVs were recorded through the cycling of the potential between -0.4 and $+0.9$ V at a scan rate of 10 mV/s for 30 cycles at ratios of 10 : 90, 25 : 75, and 50 : 50.

All of the samples demonstrated electrochemical activity, which was characterized by the typical reduction and oxidation peaks. The electropolymerizatin of the NEPy, NBPy, and NOPy monomers was only performed in the presence of Py. Therefore, at least 10% Py monomer was needed for the electropolymerization of the NAPy's. According to Figure 1 (a–c), the copolymers with more Py component had a higher electroactivity. The CV of PPy showed two anodic peaks at 0.51 V and a cathodic peak at 0.1 V, whereas the CVs of poly(Py-*co*-NEPy) indicated peaks at $E_{anodic} = 0.49$ V and $E_{cathodic} = 0.06$ V, which were different from the PPy redox. The current intensity corresponding to the anodic peak of the copolymers at different scan rates gradually increased for poly(Py-*co*-NAPy) with increasing portion of Py in the copolymer; this is shown in Figures 2 and 3.

As shown in Figure 3, the highest current intensities corresponding to the anodic peak observed for the copolymers Py with NAPy's was as follows: NEPy > NBPy > NOPy. This revealed that the increase in the current densities and electroactivity, in general, was strongly dependent on the long chain of the *N*-alkyl groups.

Characterization of the poly(Py-*co*-NAPy) copolymer prepared by chemical oxidation

Investigation the structure of the monomers and copolymers by FTIR spectroscopy

The FTIR spectrum of NBPy is shown in Figure 4. The band of $-NH$ Py did not appear at 3400 cm^{-1},
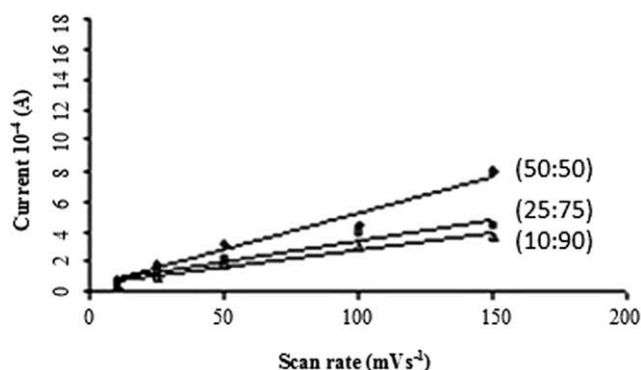
Figure 2 Curves of the electroactivity (current intensity vs scan rate) of Py–NEPy: (▲) 10 : 90, (●) 25 : 75, and (◆) 50 : 50.
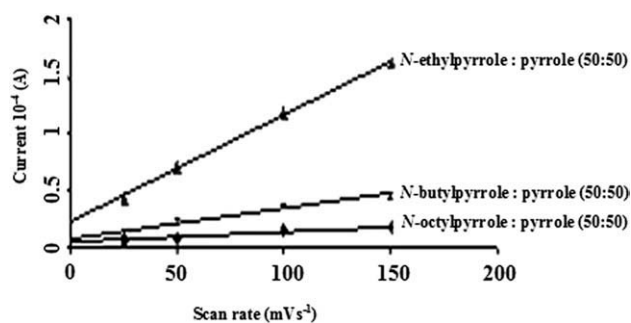

Figure 3 Curves of the electroactivity (current intensity vs scan rate) of Py–NAPy: (▲) Py : NEPy, (*) Py : NBPy, and (◆) Py : NOPy at molar ratios of 50 : 50.

and instead of that, bands stretching vibrations of aliphatic —CH appeared at 2950 and 2870 cm^{-1}.

The FTIR spectra of PPy and PPy-*co*-poly(*N*-alkyl pyrrole) (PNAPy) synthesized in FeCl$_3$·6H$_2$O are shown in Figure 5. A band at about 1700 cm^{-1}, characteristic of carbonyl groups, was found for all of the copolymers; this arose from the keto-enol tautomerism of the hydroxyl groups introduced on the ring by the nucleophilic attack of water during the preparation process.[18,19]

The FTIR spectra of the copolymers showed bands at 2960, 2925, 925, and 1026 cm^{-1}. These bands, which could be attributed to alkyl-group —CH starching, —CH out-of-plane deformation (925 cm^{-1}), and π

and —CH in-plane deformation (1026 cm^{-1}), were barely detected on the broad absorption wave centered at 1070 cm^{-1} of PPy. These observations suggest that not only Py–Py linkages but also some NAPy–Py linkages were formed, and therefore, the polymer resulting from the copolymerization from solution containing both Py and NAPy was a mixture of PPy and a random PPy–PNAPy copolymer.

Conductivity

The conductivity values for different ratios of copolymers are presented in Table I. The conductivity of PNAPy was low compared to that of PPy. The main reason seemed to be the stereochemical
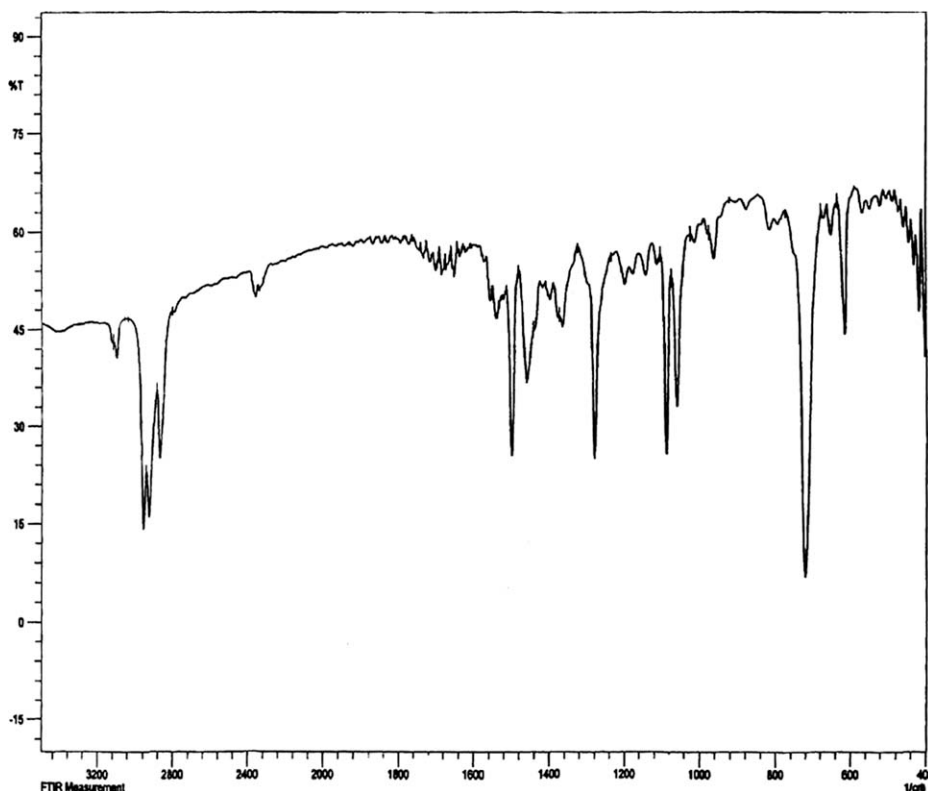

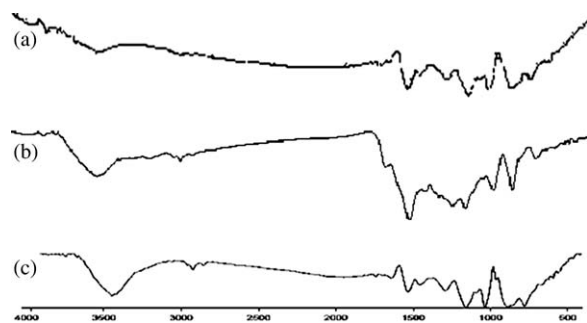**Figure 4** FTIR spectrum of the NBPy monomer.

Figure 5 FTIR spectra of (a) poly(Py–NEPy), (b) poly(Py–NBPy), and (c) poly(Py–NOPy) at molar ratios of 30 : 70.

differences between these two conducting polymers. Oxidized PPy had an almost planar structure with a low ionization potential because of the strong delocalization of π electrons. For the PNAPy's, we presumed that the planarity of the oligomeric and polymeric oxidized forms of the PNAPy's was prevented through steric van der Waals repulsion interactions by alkyl groups. The electrical characteristic of PPy-co-PNAPy suggested that the presence of longer alkyl chains reduced the conjugation length in the copolymer backbone, which in turn, lowered the concentration of charge carrier/conductivity and, thereby, resulted in a wider depletion width and better junction behavior.[20]

The electrical conductivity of the nanostructured copolymers increased in comparison with that of the copolymers prepared via method 1. However, from these results, it was obvious that the nanostructured copolymers prepared via the interfacial method may

have had more conjugated and regular backbone structures. Also, when control copolymers of similar compositions were prepared by an alternative approach, the conventional copolymerization method from Py and NAPy monomer mixtures, the resulting poly(Py-co-NAPy) was less conductive. Such results showed that the conventional polymerization (method 1) created an irregular backbone and, thus, led to poor conductivity. However, this result reflected the electrical transport in the semiconducting polymer system and was usually limited by interchain hopping. This was consistent with the microscopic investigation, which showed a slightly higher density for the interfacial materials. The conductivity of the copolymers in the case of the two methods also decreased in the following sequence: Py-co-NEPy > Py-co-NBPy > Py-co-NOPy.

With changing solvent (CHCl$_3$ instead of toluene) from a nonpolar to a polar solvent, high-quality uniform copolymers were prepared. This indicated a difference in the morphology and packing of the products.[21] SEM images of the product revealed the transition from nanofibers to agglomerates as the amount of the less polar solvent increased. As nanofibers can pack loosely, they appear to have a higher volume. Agglomerates pack much more densely; therefore, they appear to occupy less volume.

Morphological studies

SEM images of poly(Py-co-NEPy), poly(Py-co-NBPy), and poly(Py-co-NOPy) with different molar ratios of

TABLE I
Electrical Conductivity (S/cm) for PPy-co-NEPy, Py-co-NBPy, and Py-co-NOPy at Different Composition Ratios

| Molar ratio of the monomer, homopolymers, and copolymers	Conductivity (S/cm)		
	Method 1 (conventional method)	Method 2 (interfacial method in toluene)	Method 2 (interfacial method in chloroform)
PPy	0.54	—	—
PNEPy	0.0001	—	—
NEPy-co-Py (90 : 10)	0.0037	—	—
NEPy-co-Py (70 : 30)	0.005	—	—
NEPy-co-Py (50 : 50)	0.0083	—	—
NEPy-co-Py (30 : 70)	0.07	—	—
NEPy-co-Py (10 : 90)	0.4	—	—
PNBPy	—	—	—
NBPy-co-Py (90 : 10)	0.0035	0.035	—
NBPy-co-Py (70 : 30)	0.004	0.073	—
NBPy-co-Py (50 : 50)	0.0065	—	—
NBPy-co-Py (30 : 70)	0.03	—	—
NBPy-co-Py (10 : 90)	0.22	—	—
NOPy-co-Py (90 : 10)	0.001	0.024	—
NOPy-co-Py (70 : 30)	0.0014	0.039	0.9
NOPy-co-Py (50 : 50)	0.004	—	—
NOPy-co-Py (30 : 70)	0.013	—	—
NOPy-co-Py (10 : 90)	0.034	0.73	3.18
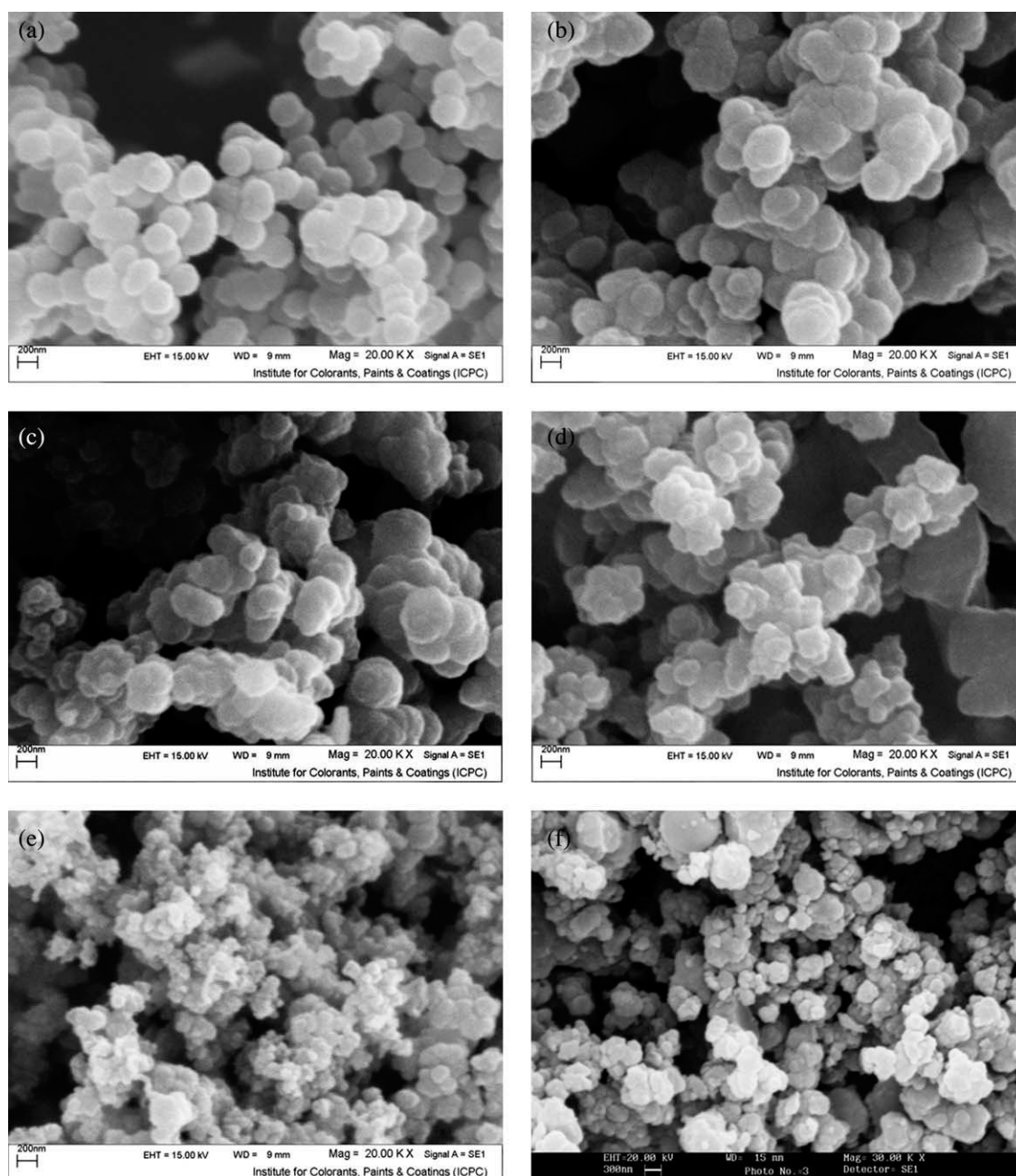
Figure 6 SEM images of PPy-*co*-PNOPy prepared by method 1 at ratios of (a) 100 : 0, (b) 10 : 90 by method 2, (c) 10 : 90 in toluene, (d) 30 : 70 in toluene, and (e) 30 : 70 in chloroform and (f) PPy-*co*-PNBPy prepared by method 2 at a ratio of 30 : 70 in toluene.

Py to NAPy are shown in Figures 6. During the copolymerization of Py with NAPy, quasi-spherical structures were formed by the agglomerated particles. The SEM images illustrated that the formation of nanostructured copolymers was realized via a simple interfacial nucleation mechanism. The polarity of the organic phase and the concentration of oxidant influenced the diffusion role of the monomer from the organic phase to the aqueous phase.

Therefore, we obtained PPy-*co*-PNAPy nanostructures with nanoparticle morphologies and higher conductivity by tuning the preparation conditions in a two-phase medium. A comparison of the copolymer morphologies showed that the particle size of the copolymers could be reduced by the interfacial method and a selective organic solvent during the polymerization of Py with the NAPy monomers.

An investigation of the obtained copolymers' morphology (Fig. 6) showed that the diameter of the copolymer particles prepared by method 1 was about 250 nm, whereas the diameters of the copolymer particles prepared by method 2 in toluene and chloroform were about 200 and 150 nm, respectively.

This difference in the particles sizes revealed that the polarity of the organic phase and the type of method influenced the morphology of the obtained particles.

Interfacial polymerization represents one effective method for suppressing secondary growth.[22] Hence, the interface between the immiscible aqueous organic layers did not contribute directly to the nanoscale formation; it simply separated nanoscale formation from secondary growth.

CONCLUSIONS

NEPy, NBPy, and NOPy monomers were synthesized with higher purity. The electrocopolymerization of these monomers with Py was performed by a cyclic voltammetry method. The electrochemical studies indicated that all of the obtained copolymers were electroactive. Also, chemical copolymerization of these monomers with Py was performed via two different methods (conventional and interfacial). The conductivity measurement showed that the obtained copolymers with a nanoparticle morphology prepared by the interfacial method with chloroform as an organic phase were approximately 20 times higher than the copolymer obtained in toluene as an organic phase and 700 times higher than the copolymer obtained from the convention method.

IR spectral data indicated a linear correlation between the ratio of absorbances of the symmetrical and asymmetrical hydrocarbon stretching modes and the alkyl chain length.

The conductivity of the copolymers was inversely correlated with the alkyl chain length; that is, the shorter the chain was, the more conducting the copolymeric films were.

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