

Polypyrrole–vinyl aniline modified cyclohexanone formaldehyde resin copolymers: a comparative study of the resin preparation

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ABSTRACT: In this study, the synthesis of polypyrrole-*b*-vinyl aniline modified cyclohexanone formaldehyde resin (PPy-*b*-CFVAnR) block copolymers by a combination of condensation polymerization and chemical oxidative polymerization processes was examined. First, a cyclohexanone formaldehyde resin containing vinyl aniline units [4- vinyl aniline modified cyclohexanone formaldehyde resin (CFVAnR)] was prepared by a direct condensation reaction of 4-vinyl aniline and cyclohexanone with formaldehyde in an *in situ* modification reaction. CFVAnR and pyrrole (Py) were then used with a conventional method of *in situ* chemical oxidative polymerization. The reactions were carried out with heat-activated potassium persulfate salt in the presence of *p*-toluene sulfonic acid in a dimethyl sulfoxide–water binary solvent system; this led to the formation of desired block copolymers. The effects of the oxidant–monomer molar ratio, dopant existence, addition order of the reactants, and reaction temperature on the yield, conductivity, and morphology of the resulting products were investigated. PPy-*b*-CFVAnR copolymers prepared with a resin-to-Py molar ratio of 1:40 showed conductivity in the range 3.7×10^{-1} to 3.8×10^{-2} S/cm. Oxidant-to-Py molar ratios of 0.5 and 1.0 were proposed to be the optimum stoichiometries for higher conductivity and yield, respectively, of the copolymer. The morphology of the copolymer (PPy-*b*-CFVAnR) was investigated with environmental scanning electron microscopy analyses. The results indicate that the surface of the copolymer was composed of well-distributed nanospheres with average particle diameters of 60–85 nm. Also, the synthesized PPy-*b*-CFVAnR had a higher thermal stability than the pure CFVAnR. The chemical composition and structure of the PPy-*b*-CFVAnR copolymers were characterized by Fourier transform infrared spectroscopy and measurement. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 42841.

KEYWORDS: conducting polymers; copolymers; resins

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INTRODUCTION

Conducting polymers, such as polypyrrole (PPy) and polyaniline, have attracted much interest because of their diverse structures, special doping mechanism, excellent environmental stability, good solution processability, corrosion resistance, and high conductivity.^{1–3} Among numerous conducting polymers, PPy is one of the most promising. PPy has aroused increasing attention because of its practical applications, which are based on its unparalleled architectural diversity and flexibility, excellent environmental stability, high conductivity, relatively low density, and ease of preparation.⁴ However, PPy is brittle, and it has a poor mechanical strength; this inhibits its capacity for mass production. One of the global approaches for overcoming these limitations of PPy is to prepare a copolymer with a ketonic resin through the introduction of PPy into other ketonic resins of polymer matrices and to significantly change their physical properties; this makes the samples more soluble, ambient, and physically active.^{5,6} The conductivity and other properties of these polymers

depend on the conditions of their preparation. Although insoluble PPy showed no glass-transition temperature (T_g), the produced conductive PPy–ketonic resin copolymers were soluble in organic solvents and had various T_g values. Therefore, by the inclusion of the ketonic resin segments, PPy possessed a T_g and solubility.⁷ The same method was used to prepare conductive silicone TEGOMER–PPy copolymers.⁸

The chemical oxidative polymerization of pyrrole (Py) or aniline in aqueous media is a widely used preparation method, mainly because of its technical simplicity.⁹ The conductivity and other properties of these polymers depend on the conditions of their preparation. Persulfate salts, ammonium, potassium, sodium, and so on are well-known reagents for *in situ* chemical oxidation. Although persulfate anion has a high oxidation–reduction potential, it is usually activated by heat, ultraviolet light, a high pH, or transition metals to generate sulfate radicals.¹⁰ The persulfate ion ($S_2O_8^{2-}$) has a standard oxidation potential (E°) of 2.01 V, but when it is activated by heat (40–60°C) or a transition metal,

Table I. Effect of the DMSO Content in the DMSO–H₂O Solvent Mixture on the Yield and Conductivity of the PTSA-Doped PPy

Polymer	$n(\text{KPS}):n(\text{Py})^a$	DMSO (vol %)	[PTSA]	Yield (g)	Yield (%)	Conductivity (S/cm)
PPy-1	0.5	—	0.24	0.17	59	20.8
PPy-2	0.5	25	0.24	0.16	55	19.6
PPy-3	0.5	50	0.24	0.14	48	6.1
PPy-4	0.5	75	0.24	—	—	—
PPy-5	1.0	—	0.24	0.33	114	12.5
PPy-6	1.0	25	0.24	0.32	110	6.4
PPy-7	1.0	50	0.24	0.25	86	1.0
PPy-8	1.0	75	0.24	—	—	—

^a n : Number of moles.

sulfate radicals (SO_4^-) are generated; these are stronger oxidants ($E^\circ = 2.6 \text{ V}$).¹¹ When persulfate is used for *in situ* chemical oxidation applications at relatively low temperatures (e.g., $<20^\circ\text{C}$), the oxidation reactions are usually less aggressive because of the slow generation rate of SO_4^- .¹² Persulfates are common catalysts for polymerization processes, and usually, water (H_2O) is used as the reaction media. It is known that persulfates can oxidize amine groups to radical cations, which react with the Py monomer and, in last stage, form PPy. In this case, the Py–ammonium persulfate (APS) molar ratio was 1:5, and it was determined that the ratio had an effect on the conductivity and solubility of the polymer. When a high amount of oxidant was used, a high conductivity and a poorer solubility were obtained.¹³ Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) is used to generate free radicals and is generally applied at about 3 mol to 1 mol of Py.¹⁴ Blinova *et al.*¹⁵ oxidized Py with APS in the presence of equimolar quantities of hydrochloric acid at 20°C . It was determined that the optimum stoichiometry for the oxidant–monomer molar ratio was 1.25. The results show that some sulfate and hydrogen sulfate anions coming from the initiator were placed on the polymer chains as counter ions.

Soluble PPy's doped with various bulky dopants (dodecyl benzene sulfonic acid, naphthalene sulfonic acid, and anthraquinone sulfonic acid) were synthesized by the reaction of Py and APS. The

reaction was carried out at 0°C for 36 h.¹⁶ Soluble copolymers from Py and *o*-toluidine were synthesized with APS under acidic conditions. The reaction was carried out for 24 h at ambient temperature. The monomer-to-oxidant molar ratio was 1:1.¹⁷ The oxidative polymerization of Py and 2-ethylaniline was carried out in an HCl solution at 10°C for 8 h. The oxidant(APS)–monomer molar ratio was 1:2.¹⁸ PPy-polymeric dopant composites were prepared in an aqueous solution at 0°C for 36 h. APS, dodecyl benzoic acid, and poly(2-acrylamido-2-methyl-1-propane sulfonic acid) were used as an oxidant, a dopant, and a co-dopant, respectively.¹⁹ The copolymerization was initiated with $\text{K}_2\text{S}_2\text{O}_8$ (1 mol % of the total monomer moles) at 65°C for 36 h, whereas APS (with a monomer–oxidant molar ratio of 1:1.5) was used for the initiation of PPy synthesis. Polypyrrole preparation was maintained at 0°C for 24 h.²⁰

The chemical oxidation reaction of 4-vinyl aniline modified cyclöhexanone formaldehyde resin (CFVAnR) with a persulfate initiator in dimethyl sulfoxide (DMSO) was studied previously. The reduction-oxidation process, radical decomposition of CFVAnR, and polymerization mechanism were described in the presence of $\text{K}_2\text{S}_2\text{O}_8$ under nonaqueous conditions.²¹ In this study, the *in situ* chemical oxidation polymerizations of Py in the presence of CFVAnR with potassium persulfate salt (KPS) in DMSO–H₂O (1:3) solutions were studied. *p*-Toluene sulfonic acid (PTSA)

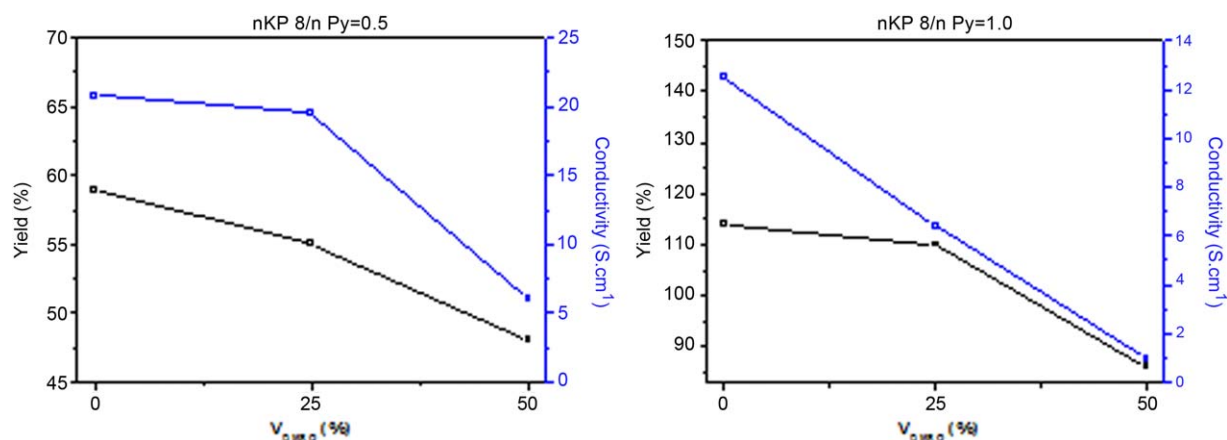
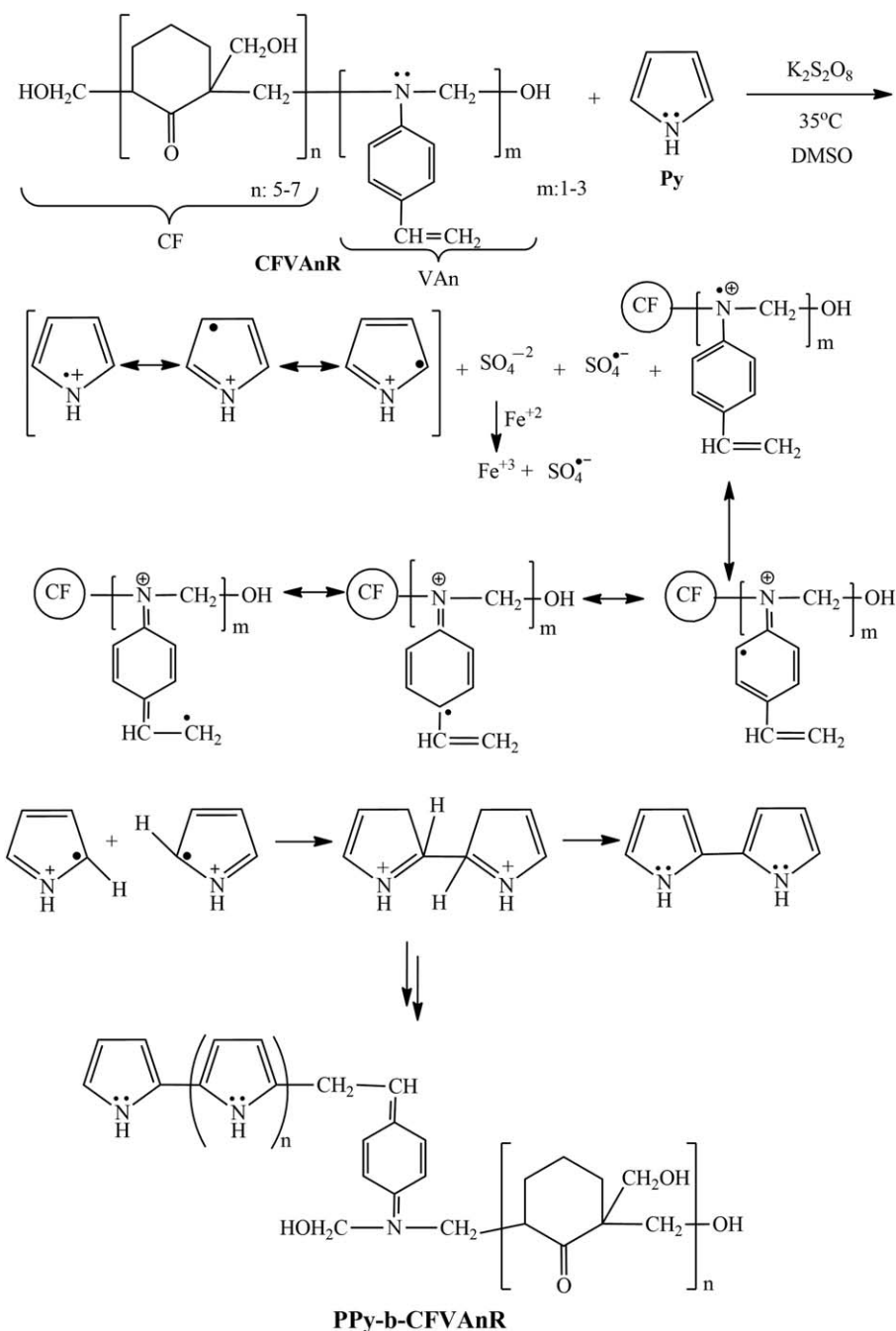


Figure 1. Effect of the DMSO content in the DMSO–H₂O solvent mixture on the yield and conductivity of the PTSA-doped PPy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. Formation of PPy-*b*-CFVAnR. CF: cyclohexanone formaldehyde resin; VAn: 4-vinyl aniline.

was used as a doping agent with a constant dopant–Py molar ratio of 3:1. The effects of the doping agent, heat-activated oxidant (KPS), addition order of the reactants, and molar ratio of KPS to Py on the resulting product were also examined.

EXPERIMENTAL

Materials

Py was purchased from Aldrich Chemical Co. $K_2S_2O_8$ was obtained from J. T. Baker Co. (Holland). PTSA monohydrate ($CH_3C_6H_5SO_3H \cdot H_2O$) was obtained from Alfa-Aesar, and DMSO was obtained from Merck (Germany). All of the chemicals

were used without further purification. CFVAnR was prepared according to procedures described elsewhere.²²

Methods for the Characterization of the Block Copolymers

Fourier transform infrared (FTIR) spectra in the range 500–4000 cm^{-1} were measured and recorded on a PerkinElmer Spectrum One FTIR model spectrophotometer [with an attenuated total reflectance (ATR) sampling accessory].

¹H-NMR spectroscopic analysis was obtained with a Varian spectrometer (500 MHz, Germany) with DMSO as the solvent and tetra methyl silane (TMS) as an internal reference.

Table II. Conductivity and Yield Values for the PPy and PPy-*b*-CFVAnR Copolymers

Polymer	Temperature (°C)	$n(\text{KPS}):n(\text{Py})^c$	$n(\text{Py}):n(\text{CFVAnR})$	[PTSA]	Yield (%)	Conductivity (S/cm)
PPy-b1	35	0.5	—	—	40	1.3×10^{-1}
PPy-b1-CFVAnR ^a	35	0.5	40	—	36	4.2×10^{-2}
PPy-b1-CFVAnR ^b	35	0.5	40	—	37	3.8×10^{-2}
PPy-b2	35	0.5	—	0.24	55	11.9
PPy-b2-CFVAnR	35	0.5	40	0.24	46	3.7×10^{-1}
PPy-b3	70	0.5	—	0.24	52	3.1
PPy-b3-CFVAnR	70	0.5	40	0.24	43	8.8×10^{-2}
PPy-b4	70	1.0	—	0.24	97	1.0
PPy-b4-CFVAnR	70	1.0	40	0.24	85	7.0×10^{-2}

^a The reactants were added simultaneously.

^b After 15 min, Py was added.

^c n : Number of moles.

Differential scanning calorimetry thermograms were obtained with a PerkinElmer DSC-6 instrument. The heating rate was 10°C/min under a nitrogen atmosphere.

Thermogravimetric analyses were performed with a PerkinElmer Diamond thermogravimetry/Diamond thermogravimetric analyses (DTA) instrument under a nitrogen atmosphere at a heating rate of 20°C/min up to 800°C temperature.

The morphologies of the products were examined with a scanning electron microscope (Phillips ESEM XL30 environmental scanning electron microscope/field emission gun).

The electrical conductivities of the solid products were measured with a four-point probe technique. For the measurement of the electrical conductivity of the products, thin pellets were prepared by compaction of the polymer powders under 10 tons of pressure. A typical sample diameter was 13 mm, and the thickness was 0.8 mm. To measure the electrical conductivity, the reaction product was compacted under 10 tons of pressure to obtain a thin pellet. Conductivity (σ) measurements were

performed with a four-probe technique with a Keithley 2400 model current source, multimeter, Lucas Labs 302 model probe holder, and SP4-85-TFS type probe and calculated with the help of the following equation:

$$\sigma = V^{-1} I (\ln 2 / \pi d_n)$$

where V is the potential (V), I is the current (A), and d_n is the thickness of the samples (cm).

Synthesis of PPy in the DMSO–H₂O Mixtures

Amounts of 2.54 g (13 mmol) of PTSA and 0.3 mL (4.3 mmol) of Py were dissolved in 29 mL of a DMSO–H₂O mixture and stirred for 30 min at ambient temperature. A calculated amount of K₂S₂O₈ dissolved in 26 mL of H₂O was added in one step to the acidic Py solution and stirred for 1 h at ambient temperature. PPy that was precipitated spontaneously was filtered off and washed with H₂O, methanol, and acetone. Finally, the polymer was dried at 45°C for 24 h. The experimental procedure was repeated in DMSO–H₂O mixtures with different compositions (25:75, 50:50, and 75:25 v/v) and pure H₂O; we kept the total solvent volume constant at 55 mL (PPy 1–8).

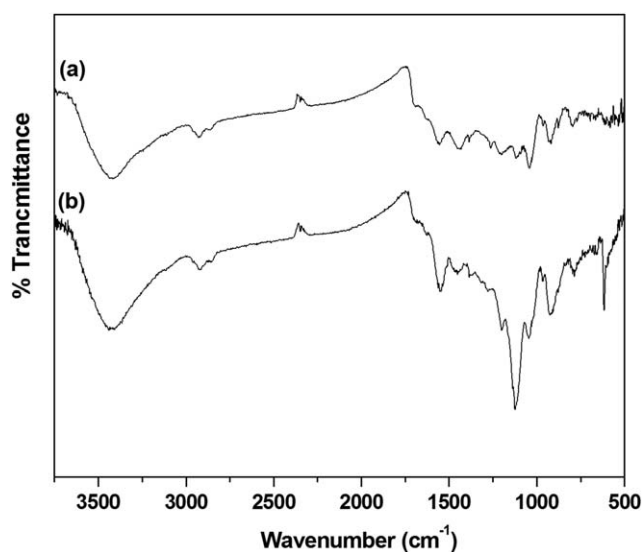


Figure 2. FTIR spectra of the copolymers: (a) PPy-b1-CFVAnR^a and (b) PPy-b1-CFVAnR^b.

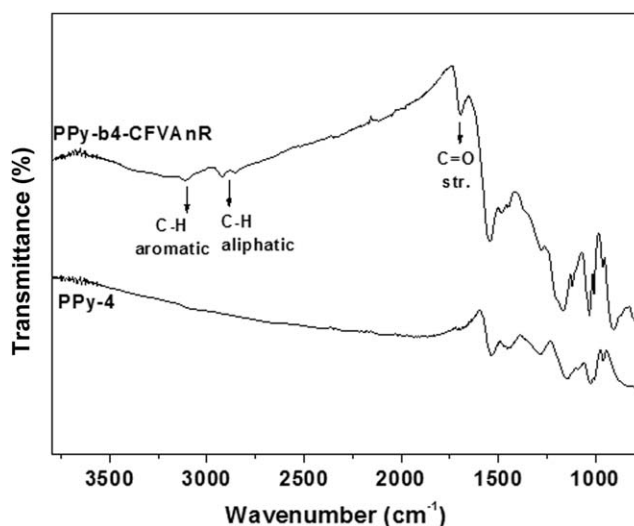


Figure 3. FTIR spectra of PPy-b4-CFVAnR and PPy-4.

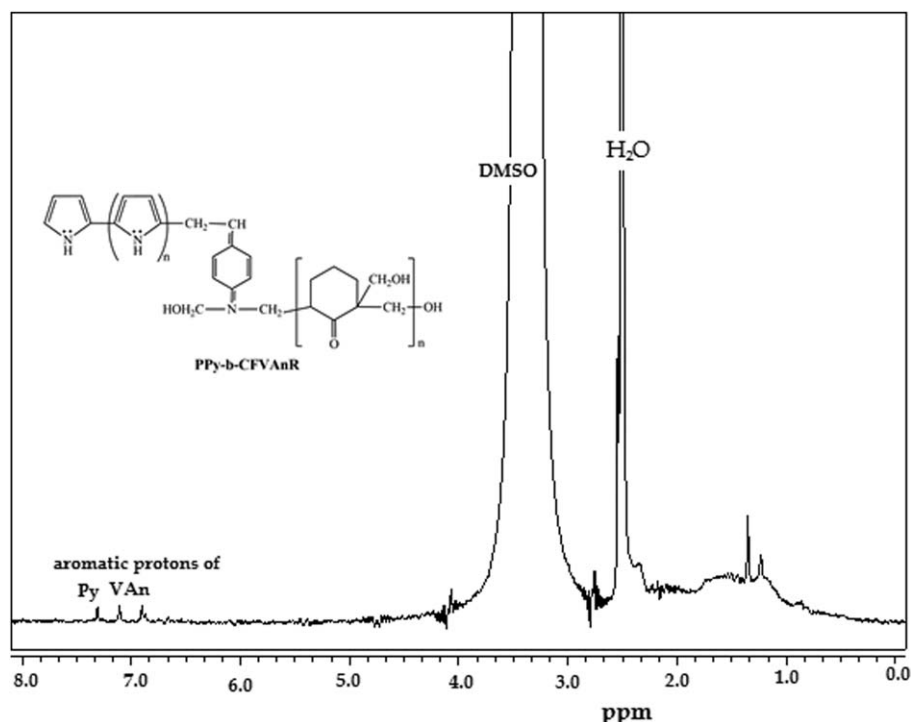


Figure 4. $^1\text{H-NMR}$ spectrum of polypyrrole-block-vinyl aniline modified cyclohexanone formaldehyde resin (PPy-b1-CFVAnR)^b.

Blank experiments were synthesized under the same conditions with a related copolymer in the absence of resin (PPy-b1 to PPy-b4).

Block Copolymer Synthesis of CFVAnR and Py by Heat-Activated KPS

An amount of 2.54 g (13 mmol) of PTSA was dissolved in 15 mL of H_2O ; then, 0.3 mL (4.3 mmol) of Py was added and stirred. A solution of 0.12 g (0.11 mmol; number-average molecular weight = 1105 g/mol) of CFVAnR in 14 mL of DMSO was added to the acidic Py solution and stirred for 30

min at room temperature. A calculated amount of $\text{K}_2\text{S}_2\text{O}_8$ dissolved in 26 mL of H_2O was added in one step to a mixture of the monomers and stirred for 1 h at 35°C (the product indicated by a superscript *a*) and 70°C (the product indicated by a superscript *b*). The product was filtered off, washed with DMSO, H_2O , methanol, and acetone. Finally, the polymer was dried at 45°C for 24 h.

RESULTS AND DISCUSSION

The block copolymers were prepared with a polypyrrole-*b*-vinyl aniline modified cyclohexanone formaldehyde resin (PPy-*b*-CFVAnR) by persulfate oxidation. Because the resin was soluble in DMSO and PPy had a good conductivity in an aqueous medium, a mixture of DMSO and H_2O was used for the synthesis of the copolymers. The copolymers did not contain any ketonic resin because they were washed with acetone, ethanol, and DMSO several times. The copolymer was slightly soluble in DMSO. First, the influence of the DMSO content in the solvent mixture on the yield and conductivity of PPy was investigated.

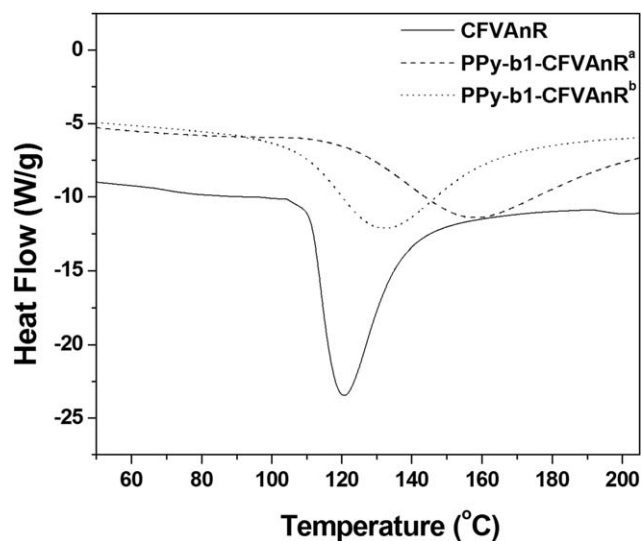


Figure 5. Differential scanning calorimetry diagrams of the PPy-b1-CFVAnR^a and PPy-b1-CFVAnR^b copolymers and the CFVAnR resin.

Table III. Thermogravimetric Analysis Data for PPy-b1-CFVAnR

Sample	Weight loss from 25 to 550°C (%)	Weight loss from 25 to 760°C (%)	Temperature at 40% weight loss (°C)	Temperature at 50% weight loss (°C)
PPy-b1-CFVAnR ^a	40	73	531	608
PPy-b1-CFVAnR ^b	37	55	567	692

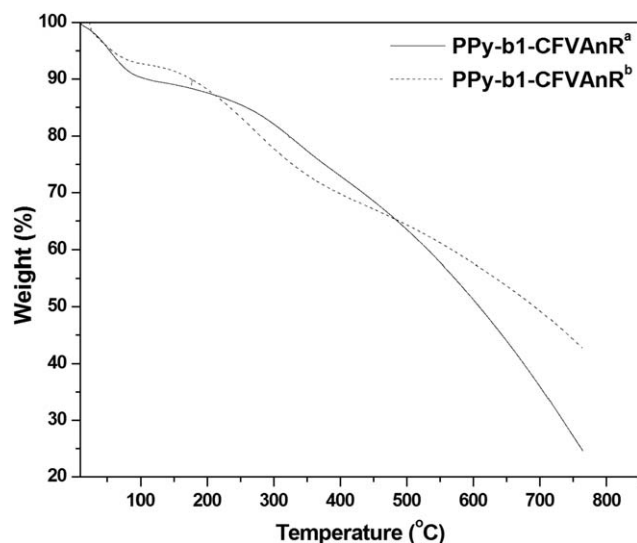


Figure 6. Thermogravimetric analysis thermograms of PPy-b1-CFVAnR^a and PPy-b1-CFVAnR^b.

PPy's were prepared in H₂O and with three different DMSO–H₂O combinations (25:75, 50:50, and 75:25 v/v) at ambient temperature. The results obtained for the PTSA-doped PPy's are presented in Table I and Figure 1. The conductivities of the PPy's were found to be in the range 1–20 S/cm, with the highest values for samples prepared in the pure H₂O without DMSO. The conductivity and yield of PPy decreased as the DMSO–H₂O ratio increased. The maximum values were obtained for PPy prepared in a DMSO–H₂O mixture with a volume ratio of 25:75. The spontaneous precipitation of PPy was not observed when the DMSO–H₂O volume ratio was 75:25. The yield of PPy was calculated in terms of the weight percentage with respect to the amount of Py. A high yield of PPy (86–114 wt %) was obtained with the use of a KPS–Py molar ratio of 1:1.

Formation of PPy-*b*-CFVAnR

The reduction-oxidation process and radical formation of CFVAnR was described in the presence of K₂S₂O₈.²¹ The initial step in the redox reaction of vinyl aniline and Py were thought to be the formation of radical cations at the nitrogen atom.

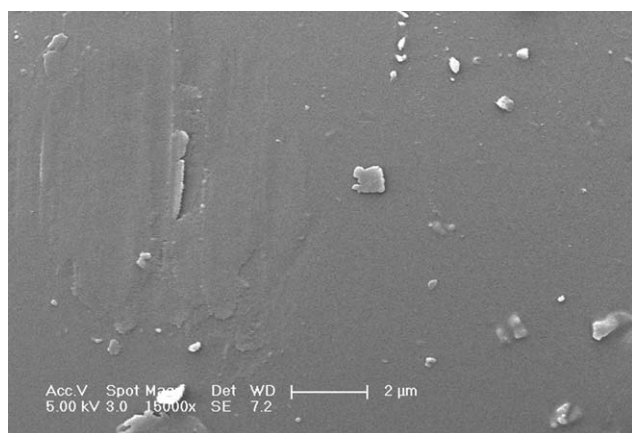


Figure 7. Scanning electron micrographs of CFVAnR.

Polymerization in solution can also proceed by the oxidation of vinyl aniline by K₂S₂O₈ to form radical cations, which can resonate with the aromatic group of CFVAnR in the proposed mechanism for chemical oxidation. The second-step mechanistic possibility in the initiation step is the formation of the vinyl radical of resin–Py cation radical and radical attached onto a natural monomer molecule. In the termination step, the resin radical may combine with the Py cation radical chain or other resin radical to produce PPy-*b*-CFVAnR in the proposed reaction mechanism for chemical oxidative polymerization. The reaction details are shown in Scheme 1.

The block copolymers were prepared with a resin–Py molar ratio of 1:40 and two different oxidant–Py molar ratios (1:1 and 0.5:1). The reactions were carried out at 35 and 70 °C with or without a dopant. The solid-state conductivities at room temperature and yield of the polymers are listed in Table II. The results are compared in terms of the reaction temperature, KPS–Py ratio, use of dopant, and addition order of the monomers. Increasing the temperature resulted in a decreased copolymer yield and a conductivity that could be explained by the formation of soluble oligomers. When the KPS–Py ratio was increased, PPy's and copolymers with both a higher yield and lower conductivity values were obtained. The results indicate that the conductivity and yield of the polymers synthesized in the presence of PTSA increased considerably.

The structures of the PPy-*b*-CFVAnR copolymers were identified by ATR-FTIR spectroscopy. The spectra of PPy-b1-CFVAnR^a and PPy-b1-CFVAnR^b are outlined in Figure 2. These copolymers did not contain PTSA. The spectra of PPy-b4-CFVAnR and PPY-4 are shown in Figure 3. The IR spectra of all showed strong absorption bands at 3450 cm⁻¹, including stretching vibrations of both –OH groups of methylols and –NH groups. A weak absorption band characteristic of the carbonyl linkage appeared at 1700 cm⁻¹ and was assigned to C=O stretching vibrations. Aliphatic hydrogens of methylene bridges between nitrogen and carbon were observed as peaks at 2800–2950 and 1450 cm⁻¹; these were similar to the methylene bridges of CFVAnR [Figures 2(a, b) and 3]. Aromatic ring vibrations of aniline –C=C– appeared as a doublet peak at about

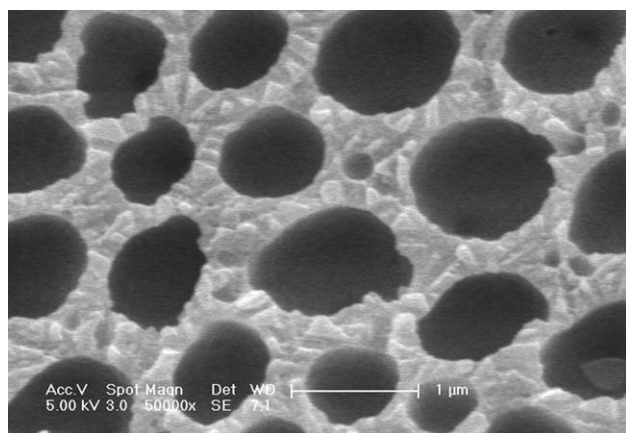


Figure 8. Scanning electron micrographs of chain extended of vinyl aniline modified cyclohexanone formaldehyde resin (CE-CFVAnR).

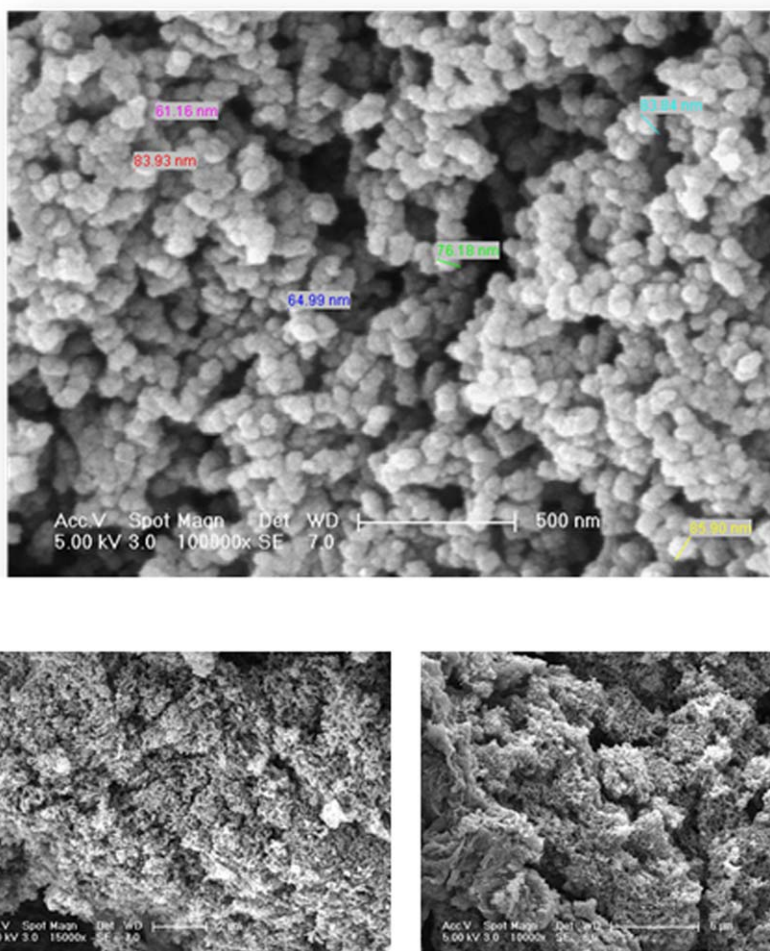


Figure 9. Scanning electron micrographs of PPy-b1-CFVAnR^a. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1600 cm^{-1} , and the out-of-plane stretching vibrations of $=\text{C}-\text{H}$ showed a peak at 650–750 cm^{-1} . The vinyl vibrations of $-\text{C}=\text{C}-$ appeared as peaks at 1516 and 1384 cm^{-1} , and the out-of-plane stretching vibrations of $=\text{C}-\text{H}$ showed a peak at 950–900 cm^{-1} . In general, the two bands located at 1565 and 1619 cm^{-1} , characteristic of the stretching vibrations of $-\text{C}=\text{C}-$, and various bands between 1475 and 1236 cm^{-1} , which were due to the vibration modes of the Py ring, were observed in addition to three bands situated at 1045, 968, and 922 cm^{-1} , which were related to the in-plane and out-of-plane vibration modes of $\text{N}-\text{H}$ and $\text{C}-\text{H}$ (line b). We observed that all of the characteristic absorption bands described previously were observed except for the in-plane and out-of-plane vibration modes of PPy doped with dopant anions at 500–1000 cm^{-1} ; this may have been due to side reactions during polymerization (Figure 3).

The $^1\text{H-NMR}$ spectrum of PPy-b1-CFVAnR^b also confirmed the proposed structural formulas shown in Figure 4. The $^1\text{H-NMR}$ spectrum of PPy-b1-CFVAnR^b showed signals between 6.8 and 7.5 ppm, which were due to the aromatic protons of vinyl aniline and Py; signals between 3 and 4.5 ppm, which were due to the methylene protons of methylols; and signals between 1 and 3 ppm, which were due to the aliphatic hydrogens of cyclohexanone. The peaks that disappeared at 4.85 and

4.72 ppm were due to the vinylic protons of CFVAnR, which appeared as aliphatic protons at 2.48, 2.8, and 5 ppm.²¹

The thermal behavior of the copolymers were examined with a differential scanning calorimeter in the range 20–220°C (Figure 5). CFVAnR had a melting temperature of 120°C. PPy-b1-CFVAnR^a and PPy-b1-CFVAnR^b had T_g values of 136 and 119°C, respectively. The chemical oxidation reaction of CFVAnR and Py was expected to improve their thermal stability because of chain extension in the PPy copolymer backbone. The 50% weight loss temperature was assumed to be a measurement of the thermal stability, and the related results are presented in Table III and Figure 6. Figure 6 shows the weight loss of the PPy-b1-CFVAnR copolymer. We found that thermal stabilities of the copolymers were similar. Both began to lose weight at about 50°C and decomposed more rapidly. PPy-b1-CFVAnR^b was more stable than PPy-b1-CFVAnR^a at elevated temperatures because of the smaller weight loss around 700°C.

An environmental scanning electron micrograph for CFVAnR showed a continuously homogeneous and smooth resin suitable for use as a coating material. Figure 7 of the CFVAnR resin shows the scanning electron microscopy images of the interior porous structure and surface porous morphology of the oxidized CFVAnR. As shown in Figure 8, regular pores formed for

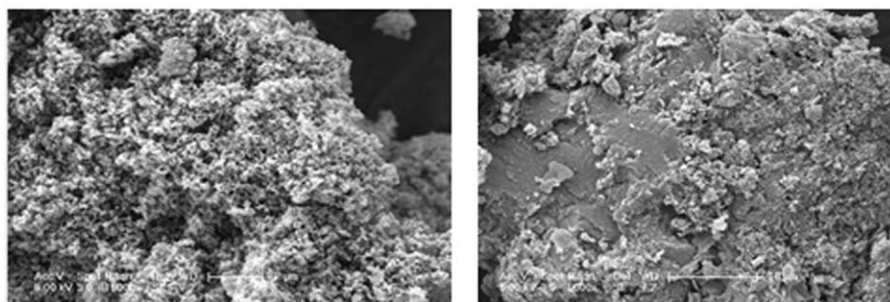
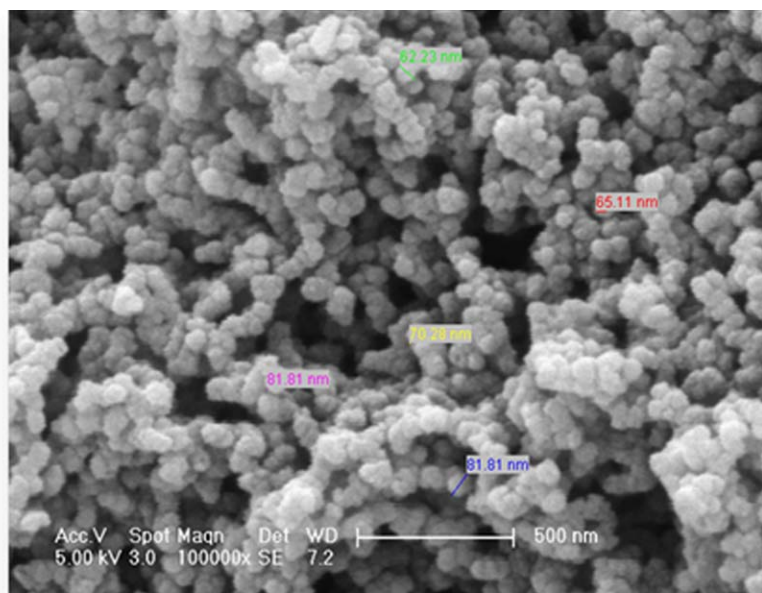


Figure 10. Scanning electron micrographs of PPy-b1-CFVAnR^b. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CECFVAnR without Py.²¹ Although the surface of CECFVAnR1 was close to a honeycomb appearance, particles were well-distributed and had an average size of 0.5–0.75 μm . With the PPy copolymers of CFVAnR, more ordered and smaller agglomerates were observed, as shown in Figures 9 and 10. Figures 9 and 10 show scanning electron microscopy images of the nanostructure and surface porous morphology of PPy-*b*-CFVAnR. An environmental scanning electron micrograph of the surface of copolymers was close to the familiar cauliflower appearance of PPy; the particles were well-distributed and had average sizes of 60–85 nm.

CONCLUSIONS

PPy-*b*-CFVAnR copolymers were prepared via the *in situ* chemical oxidative polymerization of Py with CFVAnR by the heat activation of KPS. The copolymers were obtained in DMSO–H₂O mixtures (1:3 v/v) at two different temperatures in the presence or absence of PTSA. The conductivity and yield values of these copolymers were varied through changes in the Py–KPS ratio, dopant addition, and reaction temperature. The highest conductivity value (3.7×10^{-1} S/cm) was obtained for the copolymer synthesized at low temperature with PTSA and a KPS–Py molar ratio of 0.5:1.0. Dopant insertion and an increase in the oxidant-to-Py ratio resulted in an increase in the product

yield. In addition, thermal analyses of the conducting copolymers showed T_g values at about 136 and 119°C; this suggested that the copolymers may have been thermally processable. Ketonic resin–PPy copolymers may be used in surface-coating applications, in which conductivity is also an important property. This copolymers may find a number of new applications in addition to existing PPy applications.

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