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Surface conducting particles by oxidative copolymerization of pyrrole pendant groups and pyrrole in emulsion

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Summary

Poly(styrene-co-(p-vinylbenzyl 4-(3-pyrrolyl)-4-oxobutyrate)) (PSt-VBPOB) containing 16.7 mol% of p-vinylbenzyl 4-(3-pyrrolyl)-4-oxobutyrate (VBPOB) was synthesized by emulsion polymerization. Pyrrole was coupled onto pyrrole moiety of PSt-VBPOB via oxidative polymerization using $FeCl_3$ as a catalyst. Two kinds of conducting polymers, PSt-VBPOB-ox-Py (S) and PSt-VBPOB-ox-Py (E), were prepared. PSt-VBPOB-ox-Py (S) was prepared in THF solution. On the other hand, PSt-VBPOB-ox-Py (E) was obtained in the emulsion. The conductivity of PSt-VBPOB-ox-Py (E) (1.590 S/cm) was much higher than that of PSt-VBPOB-ox-Py (S) (0.022 S/cm). The mechanisms of electrical conductivity enhancement in PSt-VBPOB-ox-Py (E) is proposed. In the PSt-VBPOB-ox-Py (S) particles, polypyrrole was uniformly distributed throughout the particles. On the other hand, polypyrrole links are mainly located on the surface of the PSt-VBPOB-ox-Py (E) particles, giving surface conducting particles.

Introduction

Numerous attemps for structural modification of insulating thermoplastics to render conducting properties have been reported. An interesting subject is a styrene monomer containing pendant pyrrole ring in the side chain. A conducting polymer can be prepared by coupling pyrrole with pendant pyrrole moiety contained in the styrenic polymers. Castelvetro et al. (1) reported a conducting polymer derived from N-vinylpyrrole. Recently, Stanke et al. (2~4) studied the 2-(N-pyrrolyl)ethyl methacrylate and they investigated the electrical properties of the polymers. Nazzal and Street (5) reported the grafted polypyrrole onto the polystyrene backbone by electrochemical polymerization. Some other authors also studied the synthesis of N-substituted polypyrrole, however, N-substituted pyrrole leads to a steep decrease in the conductivity, and to an increase in oxidation potential of the resulting polymer (6). Rahman et al. studied the ordered mono and multilayers of 3-hexadecyl pyrrole by using Langmuir-Blodgett techniques (7). Ruckenstein obtained polyaniline-polystyrene composites starting from an emulsion in which a solution of sodium dodecyl sulfate in water constitutes the continuous phase and a solution of aniline

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and polystyrene in benzene the dispersed phase (8). We synthesized poly(p-vinylbenzyl 4-(3-pyrrolyl)-4-oxobutyrate) (PVBPOB) and studied its electroactive properties of the conducting polymer obtained from the oxidative α–α' coupling of the neighboring pendant pyrrole rings. However, the conductivities of the resultant oxidized polymers were low (9). In this paper, a method for preparing the surface conducting particles will be introduced. The spherical particles were obtained by emulsion copolymerization of styrene and a pyrrole-containing monomer. The surface of the particles became conductive by the oxidative polymerization of pendant pyrrole unit with pyrrole monomer in the emulsion.

Experimental

Materials: p-Vinylbenzyl 4-(3-pyrrolyl)-4-oxobutyrate (VBPOB) was prepared as described earlier in our previous papers (9). Pyrrole was distilled under reduced pressure and stored at 4 °C in the absence of light prior to use. Styrene was used as received. Anhydrous acetonitrile (ACN) was refluxed and distilled over P_2O_5 under a blanket of nitrogen. Tetrahydrofuran (THF) and chloroform were dried over sodium metal and CaH_2, respectively. Distilled and deionized water was employed.

Measurements: ^{1}H-NMR spectra were recorded on a Bruker SY-200 spectrometer. FT-IR spectra were recorded on a Bio-Rad model FTS 165 as KBr pellets. Differential scanning calorimetry (DSC) measurements were carried out on a DuPont 2100. Conductivities were determined by the standard four-probe method on a pressed pellet using Keithley 236 source & measure unit and Yokohama 2553 voltage & current device. Scanning electron micrographs (SEMs) were examined by a Hitachi 530 electron microscope.

Preparation of PSt-VBPOB: 10 ml of water was placed in a 100 ml flask and the oxygen dissolved in water was evacuated by passing a steady stream of nitrogen through the reaction vessel. 0.13 mmol of sodium dodecyl sulphate (SDS) was introduced into the flask, with stirring. 2 mmol of VBPOB dissolved in 10 mmol of styrene was added and the reaction mixture was stirred until emulsified solution was formed. 0.03 mmol of potassium persulfate (KPS) was introduced into the reaction mixture. Emulsion copolymerization was carried out at 80 °C for 8 h. The latex was coagulated by addition of 0.1 g of calcium chloride. The polymer was filtered with suction through a sintered-glass funnel, and washed with water to remove calcium chloride. The dried polymer was dissolved in THF, precipitated in methanol and was dried in vacuo to give 1.45 g (87% yield) of PSt-VBPOB. FT-IR (KBr) (cm^{-1}): 3409 -NH stretching, 3027 =C-H stretching, 2924 C-H stretching, 1779, 1734 C=O stretching, 1650 C=C stretching, 1493 benzene ring stretching, 1453 CH_2 scissoring, 1159 C-O stretching and 758 =C-H out-of-plane bending.

Preparation of PSt-VBPOB-ox-Py (S): 0.803 g of PSt-VBPOB (1 mmol of VBPOB and 5 mmol of styrene) was dissolved in 30 ml of THF. 1 mmol of pyrrole and 4.8 mmol of $FeCl_3$ in 30 ml of ACN were added into the reaction mixture. The reaction mixture was allowed to continue stirring for 5 h at room temperature. Immediately after introducing the $FeCl_3$, the solution turned dark and became bluish black. The oxidized copolymer, PSt-VBPOB-ox-Py (S), was precipitated in methanol. Collecting on a Büchner funnel by filtering, the resulting black powder was washed with methanol until the filtrate became colorless. The product was dried in vacuo at 40 °C for 24 h.

Preparation of PSt-VBPOB-ox-Py (E): 2 mmol of pyrrole was added into the emulsion of PSt-PVBPOB when the copolymerized reaction mixture cooled down to room temperature. 9.6 mmol of $FeCl_3$ was introduced and stirred for 5 h. Calcium chloride was added to coagulate the product. PSt-VBPOB-ox-Py (E) was washed with methanol and dried in vacuo to constant weight.

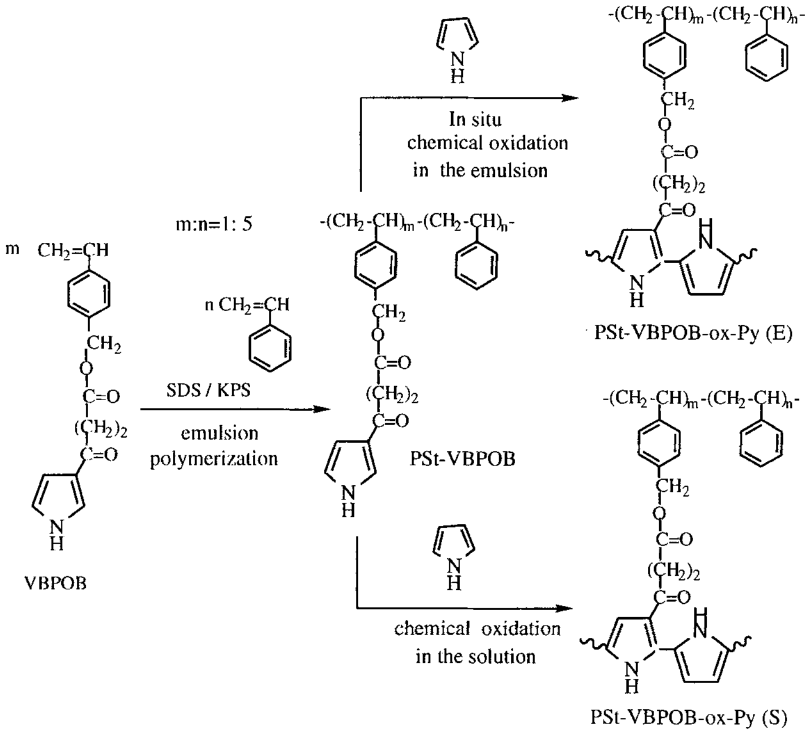

Fig. 1. Synthesis of conducting polymers via two different oxidative copolymerization methods.

Results and discussion

Fig. 1 represents synthesis of two conducting polymers, PSt-VBPOB-ox-Py (S) and PSt-VBPOB-ox-Py (E). Styrene and VBPOB were copolymerized by emulsion polymerization. The mole% of VBPOB in the copolymer (PSt-VBPOB) was 16.7 %. The average particle size of the copolymer was 0.1 μm in diameter. The absorption peak at 992 cm^{-1} which was found in both styrene and VBPOB, disappeared in the FT-IR spectrum of PSt-VBPOB. Vinyl proton signals discovered in both styrene and VBPOB, disappeared in the ^1H NMR spectrum of PSt-VBPOB. The oxidative coupling of PSt-VBPOB with pyrrole was achieved by adding pyrrole and $FeCl_3$.

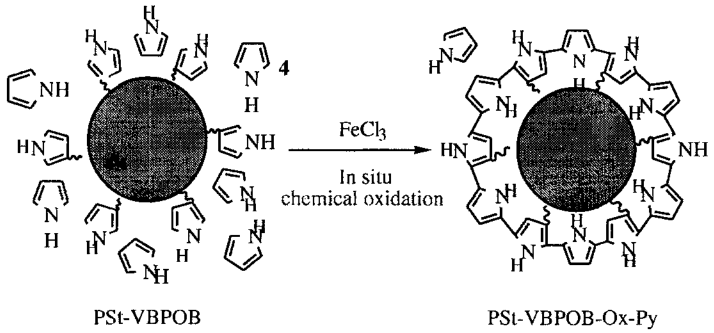

Fig. 2. Formation of polypyrrole on the surface of the emulsion particle.

A solution of PSt-VBPOB and pyrrole in an emulsion constitutes the dispersed phase, while an aqueous surfactant solution constitutes the continuous phase. The stability of the emulsion is ensured by the surfactant adsorbed upon the interface between the two phases. During the formation of copolymer particles in emulsion solution, relatively hydrophilic pendant pyrrole rings contained in PSt-VBPOB will be oriented to the surface of the emulsion particles, on the other hand, relatively hydrophobic styrenic polymer backbones will be located inside of the particles. The pyrrole monomer will be distributed near the surface of the emulsion particles. This will provide an opportunity for a rapid approach of the pyrrole monomer to the pyrrole unit contained in PSt-VBPOB, and for an easy oxidative polymerization at the water/oil interface. The formation of polypyrrole on the surface of the emulsion particle, can be schematically described in Fig. 2. During the oxidative polymerization, the α–α' coupling of pyrrole rings will take place at the surface of copolymer particles. These leads to a long conjugation length of polypyrrole in oxidized copolymer and to have a high connectivity in the polypyrrole links among particles. On the other hand, in the oxidized copolymer that was prepared from the THF solution, the oxidative coupling of pyrrole with pendant pyrrole unit of the PSt-VBPOB takes place randomly. The results of elemental analysis of the polymers are shown in Table 1.

Table 1. Elemental analysis of PSt-VBPOB, PSt-VBPOB-ox-Py (E) and PSt-VBPOB-ox-Py (S).

Polymer	Conductivity (S/cm)	Calculated (%)			Found (%)		
		C	H	N	C	H	N
PSt-VBPOB	-	85.2	7.10	1.74	85.8	7.71	1.73
PSt-VBPOB-ox-Py (E)	1.590	84.5	6.70	3.23	84.1	6.44	3.34
PSt-VBPOB-ox-Py (S)	0.022	84.5	6.70	3.23	85.1	6.55	2.34

The N content in PSt-VBPOB-ox-Py (E) is higher than that in PSt-VBPOB-ox-Py (S). These results indicate that the degree of α–α' coupling of pyrrole with pendant pyrrole ring in PSt-VBPOB-ox-Py (E) is higher than that in PSt-VBPOB-ox-Py (S). Therefore, Pst-VBPOB-ox-Py (E) particles will enclosed with conjugated polypyrroles and these polymer leads to a high conductivity. As a results, the conductivity of PSt-VBPOB-ox-Py (E) reveals higher than that of PSt-VBPOB-ox-Py (S).

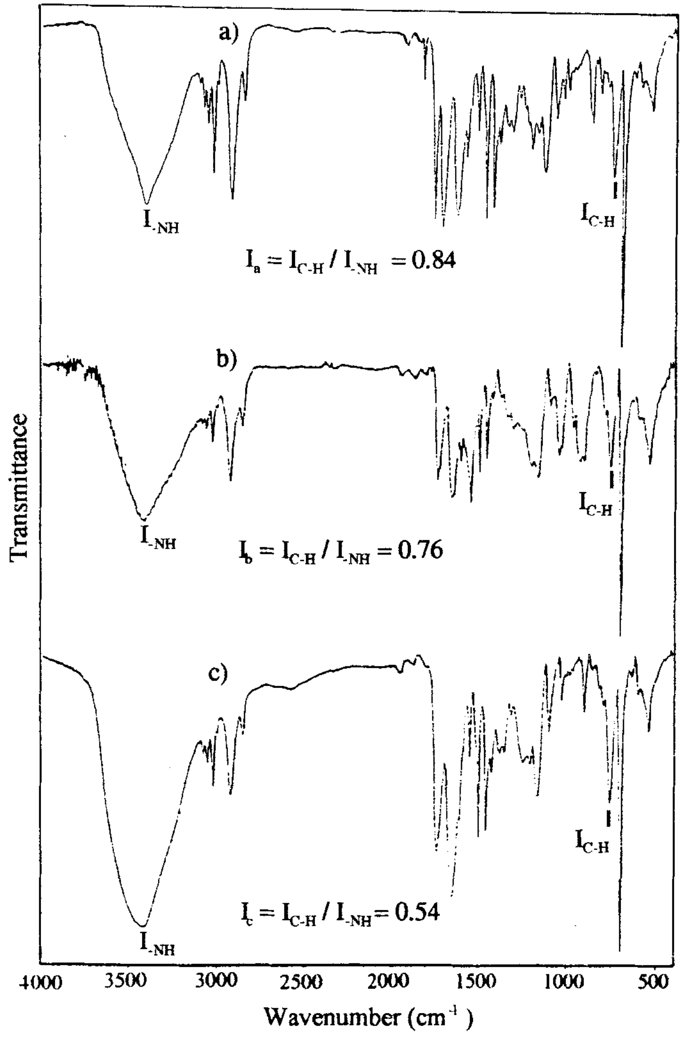

Fig. 3. FT-IR spectra of (a) PSt-VBPOB, (b) PSt-VBPOB-ox-Py (S) and (c) PSt-VBPOB-ox-Py (E).

Fig. 3 represents the FT-IR spectra of PSt-VBPOB, PSt-VBPOB-ox-Py (S) and PSt-VBPOB-ox-Py (E), respectively. A decreased intensity of C-H out-of-plane bending of pyrrole groups (758 cm^{-1}), an increased intensity of the -NH stretching (3433 cm^{-1}) and an increased C=C stretching (1644 cm^{-1}) are shown in PSt-VBPOB-ox-Py (S) and PSt-VBPOB-ox-Py (E). A decreased intensity of C-H out-of-plane bending of pyrrole groups indicates the coupling reaction of pyrrole onto pendant pyrrole rings contained in the side chain of styrenic polymer. In addition, the relative intensities of C-H bending of pyrrole groups against those of -NH stretching revealed in order of $I_a > I_b > I_c$. It may be concluded that coupling reaction in PSt-VBPOB-ox-Py (E) take place more readily than in PSt-VBPOB-ox-Py (S). The C-N stretching vibration of PSt-VBPOB-ox-Py (E) at 1452 cm^{-1} is stronger than that of PSt-VBPOB-ox-Py (S). This suggests that the polypyrrole content of PSt-VBPOB-ox-Py (E) may be higher than that of PSt-VBPOB-ox-Py (S). The conducting polymers, PSt-VBPOB-ox-Py(E) and PSt-VBPOB-ox-Py (S) were completely insoluble in THF.

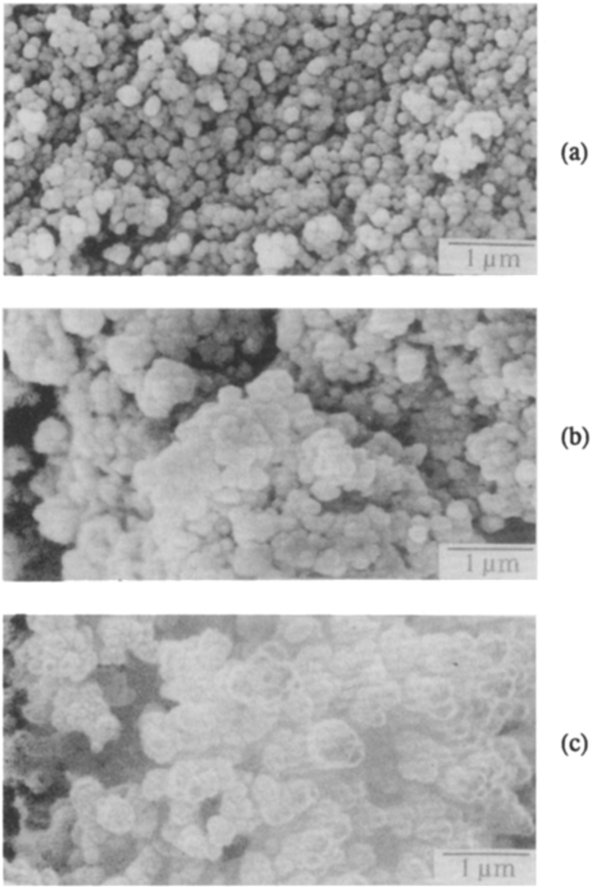

Fig. 4. Scanning electron micrographs (X 15,000) of (a) PSt-VBPOB, (b) PSt-VBPOB-ox-Py (S) and (c) PSt-VBPOB-ox-Py (E).

Fig. 4 shows scanning electron micrographs of PSt-VBPOB, PSt-VBPOB-ox-Py (S) and PSt-VBPOB-ox-Py (E). The morphology of PSt-VBPOB-ox-Py (S) and PSt-VBPOB-ox-Py (E) exhibited differently from that of PSt-VBPOB. The picture of the copolymer

PSt-VBPOB displays spherical particles. However, the picture of PSt-VBPOB-ox-Py (E) displays shrinked clusters of spherical particles with rough surface. The shrinked rough surface might be induced by the tension on the surface of emulsion particle during the oxidative coupling of pyrrole onto pendant pyrrole moiety. The particles of PSt-VBPOB-ox-Py (S) are of different sizes and have smooth surface of clusters.

Fig. 5 represents the thermal decomposition of PSt-VBPOB and PSt-VBPOB-ox-Py (E). PSt-VBPOB begin to decompose at 400 °C and shows 90 % weight loss at 500 °C, however, the polymer PSt-VBPOB-ox-Py (E) begins to decompose at 376 °C and the weight loss at 500 °C was 50 %. The high decomposition temperature of PSt-VBPOB-ox-Py (E) is ascribed to the crosslinking of pyrrole onto pendant pyrrole units of PSt-VBPOB. The glass transition point of polymer PST-VBPOB showed at 111 °C. However, the glass transition range of the PSt-VBPOB-ox-Py (E) was broad and inflected at 122 °C (Fig. 6). This indicates that pyrrole was chemically reacted with pyrrole unit in the side chain of PSt-VBPOB.

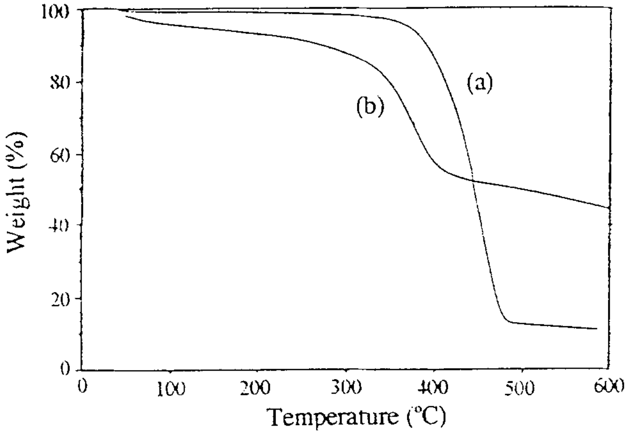

Fig. 5. TGA of (a) PSt-VBPOB and (b) PSt-VBPOB-ox-Py (E).

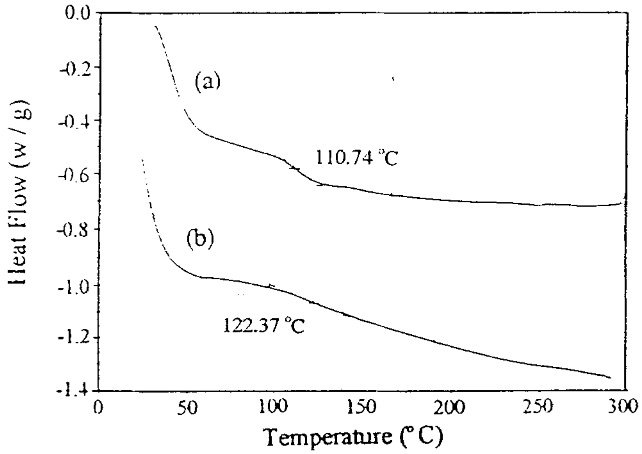

Fig. 6. DSC curves of (a) PSt-VBPOB and (b) PSt-VBPOB-ox-Py (E).

The conductivity of PSt-VBPOB-ox-Py (E) (1.590 S/cm) was 72 times higher than that of PSt-VBPOB-ox-Py (S) (0.022 S/cm). The higher conductivity of the oxidized copolymer prepared in the emulsion was ascribed to the higher content of polypyrrole on the surface of emulsion particles as shown with the intensities of C-H out-of-plane bending of pyrrole groups in FT-IR spectra. The polypyrrole layers of the particle prepared in the emulsion is more effectively distributed on the surface of the particle than that of the particle prepared in the solution medium.

Conclusions

Styrene and VBPOB were copolymerized by emulsion polymerization using SDS and KPS as an emulsifier and an initiator, respectively. Two conducting polymers, PSt-VBPOB-ox-Py (E) and PSt-VBPOB-ox-Py (S), were prepared in the emusion and in solution, respectively, via oxidative coupling of pyrrole monomer with pendant pyrrole unit of PSt-VBPOB using $FeCl_3$ as an oxidant. The conductivity of PSt-VBPOB-ox-Py (E) (1.590 S/cm) prepared in the emulsion exhibited much higher than that of PSt-VBPOB-ox-Py (S) (0.022 S/cm) prepared in THF solution. The SEM micrograph of PSt-VBPOB displays a spherical particles with uniform size. On the other hand, PSt-VBPOB-ox-Py (E) prepared in the emulsion showed shrinked clusters of particles with rough surface. It is likely that the polypyrrole is mainly located on the surface of particles and this leads to a much higher electrical conductivity in PSt-VBPOB-ox-Py (E).

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