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Synthesis and Characterization of Polypyrrole Dispersions Prepared with Different Dopants

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Summary: Stable polypyrrole dispersions were prepared by chemical oxidative polymerization of pyrrole in an aqueous medium containing different anionic salts – sodium benzoate, potassium hydrogen phthalate and sodium hydrogen succinate. Results of the elemental analysis and FT-IR spectroscopy confirmed that the anionic salts are incorporated in the conducting polymers and functioned as the dopants. The retardation of pyrrole polymerization was observed when a certain amount of the salt was used as dopant. SEM images of polypyrrole dispersions indicate large spherical particles (150-180nm). The conductivity of polypyrrole composites has also been investigated.

Keywords: conducting polymer; dopant; morphology; polypyrrole

Introduction

In the last two decades a lot of research work has been done in the field of conducting polymers, such as polypyrrole (PPy) and polyaniline (PANI). As we know the general intractability of conducting polymers presents a serious problem, the preparation of polypyrrole in its colloidal forms has been sought to improve its processibility[1]. And in this case the selection of an appropriate stabilizer to provide the effective stabilizaton of colloidal system and to control the morphology and size of polymer particles is very important. Recently, a lot of polymers have been reported on being used as stabilizer for successful preparation of polypyrrole colloids by chemically oxidizing pyrrole in either water or other media, such as poly(vinyl pyrrolidone) (PVP)[2], poly(vinyl alcohol-co-acetate) (PVA)[3], poly(ethyleneoxide) (PEO)[4], poly(styrenesulfonate) (PSS)[5], poly(vinyl methyl ether) (PVME)[6], ethylhydroxycellulose[7], etc. In our pervious paper, we investigated the morphology of obtained polypyrrole particles, which were prepared by oxidative polymerization in the presence of PVME or crosslinked PVME microgels using water or aqueous ethanol as a dispersion medium. Spherical and needle-like polypyrrole particles were found when PVME and crosslinked PVME microgels were used as stabilizer,

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respectively[8]. In this paper, three different anionic salts – sodium benzoate, potassium hydrogen phthalate and sodium hydrogen succinate were used as dopants in the polymerization of pyrrole in the presence of PVME as stabilizer. The properties of the polypyrrole with respect to morphology, conductivity, stability, and processabiility were affected by the addition of these salts.

Experimental

Material

Pyrrole(Py) was purchased from Aldrich Chemical Crop., distilled under vacuum and stored in a refrigerator before use. Sodium persulfate ($Na_2S_2O_8$), sodium benzoate (Benzoate), potassium hydrogen phthalate (Phthalate) and sodium hydrogen succinate (Succinate) were obtained from Aldrich Chemical Corp. and were used as received. PVME was obtained as a 50 wt% aqueous solution (BASF, Lutonal® M40) and used as supplied. The weight-average molecular weight, M_w, was determined by static light scattering in butanone to be 57,000 g/mol.

Polymerization of pyrrole

PVME was dissolved in appropriate amount of water at 25°C in a reactor equipped with stirrer. Then pyrrole was added to the stirred solution and the reactor was purged with nitrogen for 15 min. Oxidant, which was first dissolved in water, was then added dropwise and the polymerization was allowed to proceed for 24 hours. The resulting stable dispersions were cleaned by dialysis (Millipore membrane 100 000 MWCO) to remove oxidant and by-products.

Measurement

The nitrogen content of PPy was determined by elementary analysis. IR spectra were recorded with Mattson Instruments Research Series 1 FTIR spectrometer. Dried polymer samples were mixed with KBr and pressed to form a tablet. The morphology of the samples was examined by scanning electron microscopy (SEM) using a Zeiss DSM 982 Gemini microscope. The conductivity measurements were made at room temperature using the standard two-point probe method.

Results and discussion

Table 1 gives detailed information of Py dispersion polymerization at room temperature. And in all runs stable PPy colloids were formed in the presence of different salts. By following the polymerization process, the results indicate that the effect of the presence of benzoate, phthalate and succinate on the rate of PPy formation is marginal (Fig. 1). Gill et at.[9] reported that the oxidation of aniline proceeds slowly when sodium dodecylbenzenesulfonate (DBSNa) was added to the reaction mixture. But, Kudoh[10] noted that Py polymerization was faster in the presence of an anionic surfactant. Our results show that retardation of the polymerization has been observed in all runs with salts, possibly as a consequence of the limited miscibility of monomer and salt solutions. Furthermore, it is also easy to see that the retardation of pyrrole polymerization is henced with the increase of the dopant's amount, which indicates a more active involvement of the anionic salt in the reaction course.

Table 1. The recipe of the polymerization pyrrole in water at 25°C.

Sample	Dopant	Dopant (g)	Pyrrole (g)	PVME (g)	$Na_2S_2O_8$ (g)	Water (g)	Stability
WP1-1	-	-	0,1	0,1	0,5	75	Stable
WP1-2	Na-benzoate	0,21	0,1	0,1	0,5	75	Stable
WP1-2a	Na-benzoate	0,043	0,1	0,1	0,5	75	Stable
WP1-2b	Na-benzoate	1,08	0,1	0,1	0,5	75	Stable
WP1-3	KH- phthalate	0,31	0,1	0,1	0,5	75	Stable
WP1-4	NaH-succinate	0,21	0,1	0,1	0,5	75	Stable

Table 2 shows the elemental composition of final products. And the results of elemental analysis show the reduction of the nitrogen content in the final products, which demonstrates the incorporation of dopants into PPy after Py polymerization.

Table 2. Elemental composition(wt%) of PPy prepared in the presence of dopants.

Sample	Dopant	C	H	N	S
WP1-1	None	56,46	4,98	12,90	0,59
WP1-2	Benzoate	49,80	5,64	7,69	3,11
WP1-3	Phthalate	56,09	5,24	11,12	1,48
WP1-4	Succinate	51,20	6,32	7,94	2,91

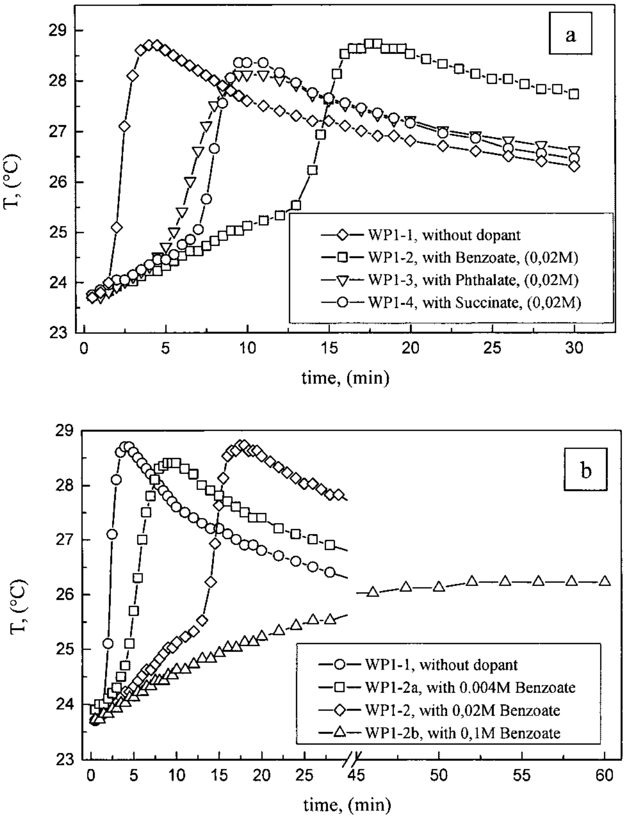

Figure 1. Temperature profile of the exothermic oxidation of pyrrole in the presence of various salts (a) and various amount of salts (b).

Moreover, the presence of anionic salts in PPy as dopants is also confirmed by a comparison of the infrared spectra of PPy prepared in the presence and absence of the salt (Fig.2). The peak at about 1452 cm^{-1} belonging to the carboxylate stretching of neat Na-benzoate is observed also in the spectra of polypyrrole polymer (WP1-2) prepared in presence of this salt. And the peaks at about 926 and 791 cm^{-1} are responsible for the δ(CH) and γ(CH) vibration of pyrrole, respectively. Similar results have been also investigated in the infrared spectra of polypyrrole prepared in the presence of other anionic salts.

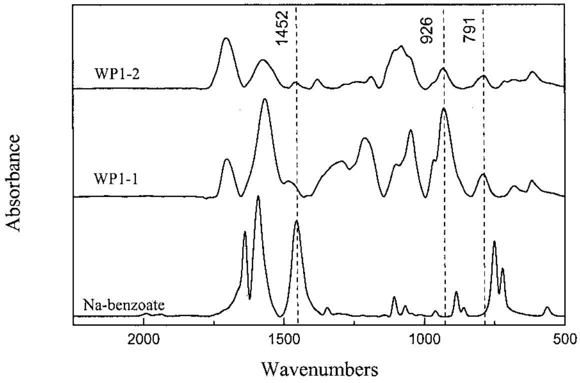

Figure 2. Infrared spectra of polypyrrole prepared with and without Na-benzoate and the spectrum of Na-benzoate.

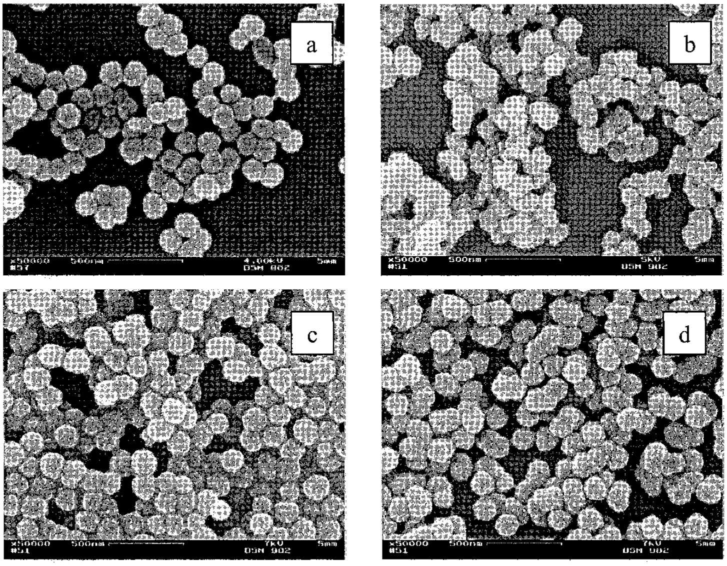

Figure 3. SEM images for sample (a) WP1-1, (b) WP1-2, (c) WP1-3, (d) WP1-4.

Electron microscopy images of polypyrrole colloids are shown in Figure 3. SEM investigations indicate that the morphology of obtained polypyrrole particles prepared in the presence of anionic salts are quite similar to the particles prepared in the absence of salt. In all cases, the spherical particles exhibit a "cauliflower" morphology, which was reported in other reviews[5,8]. Additionally, comparing the particle size of

PPy samples prepared with and without salts, it can be observed that larger particle size (about 180nm) is obtained by PPy samples prepared with salts and this observation can be explained by the slower rate of oxidation of Py polymerization in the presence of salt, which has been shown in Figure 1.

Tab. 3. Influence of presence of the dopants on conductivity of the PPy dispersions.

Sample	Py, (g)	PPy, (%)	σ, (Scm^{-1})
WP1-1	0,1	61,73	$8{,}5*10^{-9}$
WP1-2	0,1	36,80	$1{,}17*10^{-5}$
WP1-3	0,1	53,21	$4{,}55*10^{-7}$
WP1-4	0,1	40,00	$1{,}5*10^{-7}$

Table 3 shows the conductivity of PPy samples, which was measured at room temperature. The lower conductivity value obtained by PPy samples prepared without any dopant may due to the reason that PPy particles were covered by insulator out layer of stabilizer PVME, which resulted in the difficulties to transport the charge carriers. In the case of PPy prepared in the presence of dopants, an improvement of the conductivity has been observed even at much lower PPy loads. While phthalate and succinate were used as dopant, the conductivity of the final products increased by 1-2 orders of magnitude, and while benzoate was used, the conductivity increased by 3-4 orders.

Conclusions

Results of the elementary analysis, IR spectroscopy confirmed that the anionic salts were incorporated in the conducting polymers and functioned as the dopants. The retardation of pyrrole polymerization was observed when a certain amount of the salt was used as the dopant. SEM images show larger spherical PPy particles prepared in the presence of salts. The presence of dopants in polypyrrole enhances the conductivity, especially in the case of sodium benzoate, the conductivity of the final product has been improved by 3 orders.

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