

Sulfonated Polyurethane Anionomer–Polypyrrole Molecular Composite

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Received 15 July 1996; accepted 15 March 1997

ABSTRACT: Preparation of a molecular-level composite of sulfonated polyurethane ionomer and polypyrrole (PUA–PPy) was performed by electrochemical polymerization of pyrrole in aqueous solution of polyurethane anionomer and was confirmed by compositional and Fourier transform infrared analysis. The effects of anionomer concentration and of electrochemical reduction process were followed, and it was forecasted that the composite could behave as a cation exchanger. Some results of thermal analysis were also presented. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 591–595, 1997

Key words: polyurethanes; anionomer; polypyrrole; molecular composite; electrosynthesis

INTRODUCTION

Synthesis and properties of the composites based on conductive polymers have been a field of increasing interest in the past years. An attractive way for the preparation of these conductive composites is heterocycle electropolymerization in the presence of a solubilized macromolecular electrolyte, with covalently bound anions to a polymer chain.¹ Electroconductive polymers precipitate on the anode surface and incorporate ionic macromolecules as charge-compensating dopant, with the two polymer backbones being intimately mixed.

Polypyrrole is one of the most widely studied conducting polymers due to its easy synthesis and overall interesting properties, and there is already some work examining one-step electrosynthesis of its molecular composites. Many anionic polymers, like as polyvinylsulfate,^{2–4} butadiene–styrene sulfonated copolymer,² Nafion,⁵ sulfonated acrylic polymers,² carboxylic polymers,²

sulfonated polystyrene,^{6–8} sulfonated polyamides and copolyamides,^{9–11} and sulfonated polysiloxanes⁸ have served as water-soluble partners for above synthesis.

We reported previously¹² the preparation of a water-soluble polyurethane ionomer with sodium propanesulfonate groups and the obtaining of a conductive molecular composite with pyrrole, when the anionomer was tested as macromolecular electrolyte and dopant ion in aqueous electrochemical polymerization.

In this article, we examine the more detailed structure and thermal properties of this type of composite, as well as the effects of some synthesis conditions.

EXPERIMENTAL

Polyurethane ionomer with sodium propanesulfonate groups was prepared by reaction between a linear polyurethane support, *N*-modified firstly with NaH, and 1,3-propane sultone, using a method described by Ding et al.¹³ Synthesis and structure of this anionomer were reported previously.¹² The ionic groups content of polymer was

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Journal of Applied Polymer Science, Vol. 66, 591–595 (1997)

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CCC 0021-8995/97/030591-05

Table I Synthesis of Sulfonated Polyurethane–Polypyrrole Composites

Composite	Electrolyte	C_m (M) ^a	C_e (M) ^b	Polymerization Time (h)	Reduction Time (h)
PUAP _y -11 _{ox} ^c	PUA	0.4	0.01	8	—
PUAP _y -12 _{red}	PUA	0.4	0.01	5	5
PUAP _y -21 _{ox}	PUA	0.4	0.03	8	—
PUAP _y -22 _{red}	PUA	0.4	0.03	4	4
PUAP _y -31 _{ox}	PUA	0.4	0.05	8	—
PUAP _y -32 _{red}	PUA	0.4	0.05	4	5.5
TsOPy-1 _{ox}	TsONa	0.4	0.045	8	—
TsOPy-1 _{red}	TsONa	0.4	0.045	4	5.5

^a Monomer concentration.

^b Electrolyte concentration (SO₃⁻).

^c ox = Oxidized; red = reduced.

194 meq/100 g, determined by sulfur analysis. Water solubility, at 25°C, was about 14 wt %.¹⁴

Pyrrole (Aldrich Chemical Co.) was purified immediately before use by passing it through activated alumina. This procedure was repeated until a colorless liquid was obtained. Water used in electropolymerization was double-distilled.

Electroinitiated polymerizations of pyrrole were carried out in galvanostatic conditions. Two platinum sheets of 2 cm² as electrodes were immersed in the polymerization cell and separated by 10 cm. The electrical current was maintained constant by means of a MICM CCPAS 1045-01 source of stabilized current. Intensity was always 2 mA. Water was used as solvent and polyurethane ionomer with propanesulfonate groups (PUA) as macromolecular electrolyte. Three concentrations of PUA were tested, as presented in Table I. A polymerization with sodium tosylate as electrolyte and dopant was performed also (samples TsOPy). Reduced samples were obtained by inversion of electric current polarity.

Fourier transform infrared (FTIR) spectra of polyurethane ionomer and of polypyrrole polymer materials were recorded with a Bruker IFS-48 spectrometer, in KBr dispersions.

Thermal analysis was performed on a Du Pont 2000 TA system, equipped with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TG curves were recorded between 20 and 600°C, with a heating rate of 20°C/min, under nitrogen purging. DSC data were obtained over temperature range of 20–200°C, which was scanned at a rate of 10°C/min.

RESULTS AND DISCUSSION

Electrosynthesis of Composites

For polypyrrole–polyurethane anionomer molecular composite, a conductivity of 4.5×10^{-6} S cm⁻¹

was reported by us,¹² a lower value than that for tosylate-doped polypyrrole. The existence of insulating domains, formed by big nonionic fragments of polyurethane ionomer, was proposed to cause this lowering. Based on this, we attempted to decrease the proportion of anionomer in the composite by the change of reaction conditions.

Oxidative electropolymerization of pyrrole was carried out in aqueous solutions, using different concentrations of polyurethane anionomer (Table I, samples PUAPy). A synthesis was performed with TsONa as dopant, and the polymer was studied comparatively.

Simultaneously with pyrrole oxidation and formation of the heterocyclic polymer matrix, orientation to the anode of the electrolyte anions, covalently bound on polyurethane backbones, was produced. An entanglement of macromolecular chains is formed and a composite is born, in which role of the anionomer is to maintain the charge neutrality. By compositional analysis, it was established that polyurethane is gravimetrically preponderant in composite (Table II). This fact may be due to high equivalent molecular weight (492) of the anions. The modification of macromolecular electrolyte concentration in aqueous solution had no notable effects on the doping degree defined by dopant–pyrrole molar ratio. Higher values of doping degree were obtained with polymer electrolyte (samples PUAPy) comparatively with TsOPy sample, and this could show that not all sulfonate anions of included ionomer were used as dopants for oxidized state of polypyrrole.

When polymers were electrochemically reduced by change of current polarity, a decrease in the sulfur content was always observed, consequently, on the release of the included anions. This lowering is very pronounced for small TsO⁻

Table II Characteristics of Polyurethane Anionomer-Polypyrrole Composites

Composite	S (%)	Composition				Dopant Ratio (A ⁻ mol/Pyrrrole mol)
		(g/100 g comp) A ⁻	(mol/100 g comp)			
			A ⁻	Pyrrrole		
PUAPy-11 _{ox}	4.67	71.80	0.146	0.420	0.348	
PUAPy-12 _{red}	3.91	60.11	0.122	0.595	0.205	
PUAPy-21 _{ox}	4.73	72.72	0.148	0.407	0.363	
PUAPy-22 _{red}	4.13	63.47	0.129	0.560	0.230	
PUAPy-31 _{ox}	4.79	73.64	0.150	0.393	0.381	
PUAPy-32 _{red}	4.44	68.24	0.138	0.474	0.291	
TsOPy-1 _{ox}	6.85	36.60	0.210	0.940	0.223	
TsOPy-2 _{red}	2.47	13.20	0.077	1.295	0.059	

anions. The downing of the anion to pyrrole ratio in composites shows that, by electrosynthesis, a part of polyurethane polyanion chains were only superficially included, being held very loosely by physical interactions, as Prezyna proposed also for polystyrenesulfonate-polypyrrole composite.¹⁵

The presence of anionic polyurethane in reduced composites proved that a material was obtained able to cathodic binding and anodic releasing of cations from medium, and this property could be further exploited.

Depending on the concentration of the electrolyte used in electropolymerization, some differences in reduced composites composition were observed. The most accentuated degrees of the molar ratio of anionomer to polypyrrole was evidenced for lower electrolyte concentrations (Table II), so performing pyrrole electropolymerization at a higher concentration of anionomer resulted in an increase of proportion of well entangled polyurethane chains in the composite and concomitantly in an enhancement of its ability to immobilize the cations from medium.

FTIR Analysis

FTIR analysis was used to characterize both the sulfonated polyurethane anionomer and the molecular polypyrrole composites obtained with it. Figure 1 shows FTIR spectra of the ionomer and the composite obtained in aqueous solution with 0.05 M electrolyte concentration, in initial form and after electrochemical reduction. The anionomer spectrum presents, beside the bands corresponding to polyurethane backbone, the characteristic absorption for SO₃⁻ groups, at 1040 and 1207 cm⁻¹. Spectra of the composites both in initial form and after electrochemical reduction put together the

bands from polypyrrole and polyurethane ionomer spectra, proving the formation of composite. There are absorptions at 1730–1700 cm⁻¹, due to urethane carbonyl, and at about 900 cm⁻¹, coming from polypyrrole. Between these wavelengths, the spectra show intensification and wideness of bands by superposition of absorptions. More evident is superposition of 1545 cm⁻¹ absorption band originating from polypyrrole over the polyurethane amide II band from 1520–1560 cm⁻¹.

Above 1700 cm⁻¹, the spectra of composites both in the initial form and after electroreduction, show a featureless tail, which is characteristic of the doped conductive form of the polypyrrole.^{16,17}

Thermal Analysis

Figure 2 shows TGA curves for the PPy-PUA composite before and after electrochemical reduction in comparison with those of PUA and PPy doped with sodium tosylate.

The temperature of 25% weight loss of composites is with about 50°C higher than of PUA. Above 450°C, the composites loss less of their weight both than PUA and PPy.

Whereas polyurethane anionomer and polypyrrole left 23 and 40% residue, respectively, PPy-PUA composites had a residue of 54%.

It can see that thermal stability of anodically obtained composite is somewhat better than that of polypyrrole down to 250°C and above 450°C. Thermal analysis data suggest that the inclusion of polypyrrole had not any detrimental effect on the stability of the ionomer, and thermal stability of PUA in composite is better than that of the pure ionomer.

DSC curves (Fig. 3) were performed between 20 and 200°C and, as is typical for polyurethanes,

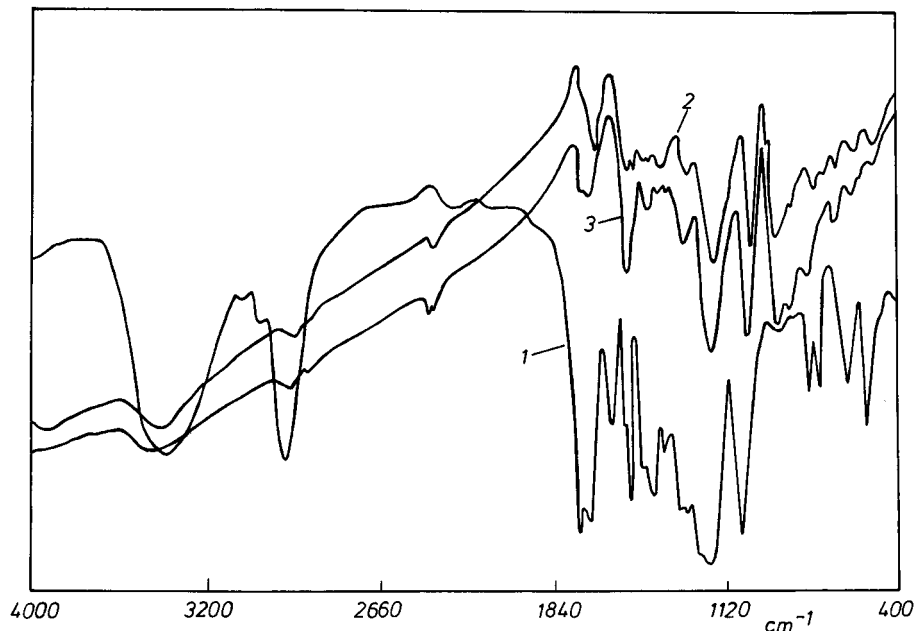


Figure 1 FTIR spectra of PUA (1), PPY-PUA composite in oxidized (2), and reduced form (3).

no evidence of a transition attributable to a hard phase glass transition was found for ionomer. For both the ionomer and composite, a broad endotherm was observed in DSC curves, as absorbed water is lost. This process is confirmed by weight loss in TG curves.

An endotherm appears in DSC curve of electro-

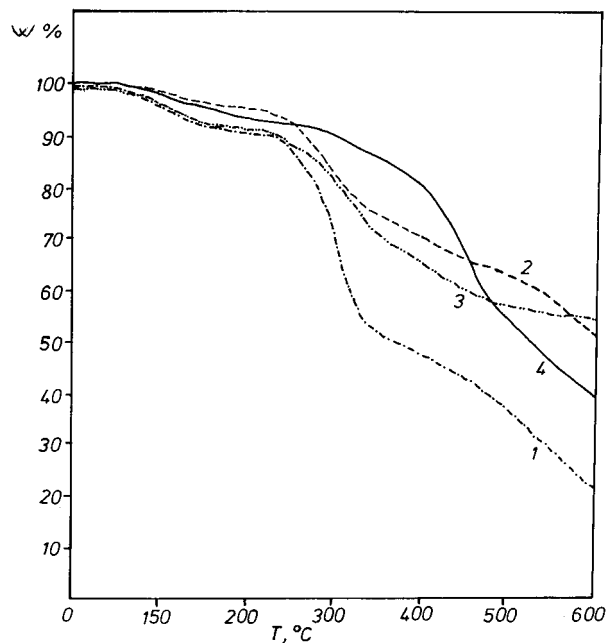


Figure 2 TG curves of PUA (1), PPY-PUA oxidized (2), PPY-PUA reduced (3), and PPY-TsO⁻ (4).

chemical reduced composites, at about 125°C. The origin of this endotherm is unclear. It may be related to a possible rearrangement of the ionic aggregates in anionomer, after the partial release of sulfonate groups by electrochemical compensation of polypyrrole positive charge. In this way, the anionic sulfonate groups are not more constrained by electrostatic interaction with polypyrrole chains, and better ordering and separation of ionic phase is permitted. It is known that primary driving force for phase separation in neutralized, sulfonated,¹³ or carboxylated¹⁸ polyurethane ionomers is aggregation of ionic groups. The above endotherm is absent in DSC curve of initial anionomer, but it can be observed by us for polyurethane anionomers with a lower content of ionic groups.¹⁹ On the other hand, the endotherm could be due to a possible T_g of undoped polypyrrole, as Truong and Ennis recently proposed.²⁰

CONCLUSIONS

Anionomer content of the electrochemical-synthesized polyurethane ionomer-polypyrrole molecular composite was not significantly modified by lowering the concentration of macromolecular electrolyte in polymerization cell from 0.05 to 0.01M. At a higher concentration of electrolyte in solution, a better entanglement between polypyrrole macromolecules and sulfonated polyurethane

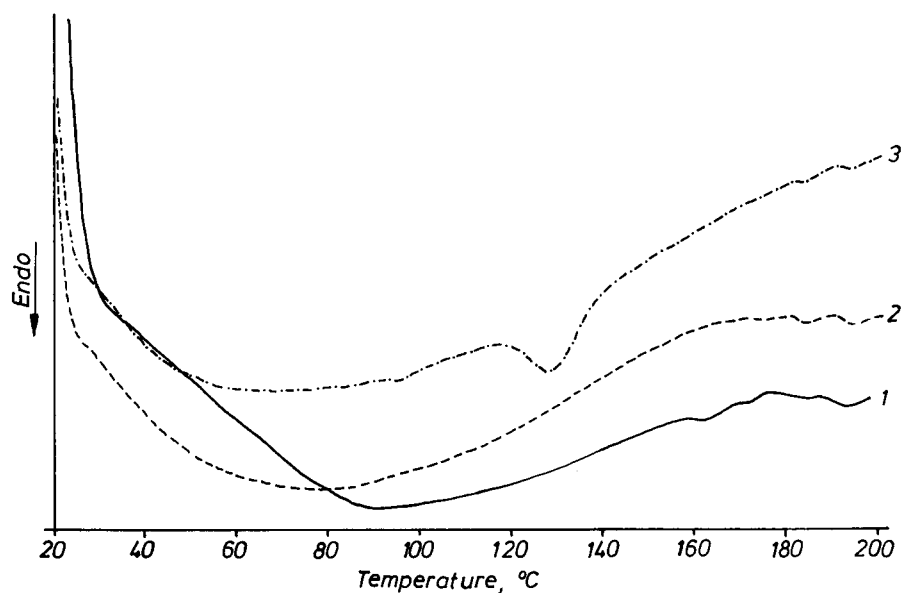


Figure 3 DSC curves of PUA (1), PPy-PUA composite in oxidized (2), and reduced form (3).

was obtained. As a result, more ionomer was found in this case in the composite after cathodic reduction, and an increased ability to immobilize the cations from medium was foreseen.

Thermal analysis shows that ionomer properties are not altered by polypyrrole presence, and, for some temperature ranges, enhanced behavior was evidenced for composites compared with individual polymers.

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