

Anionic Polyurethane Ionomer for One-Step Electrosynthesis of Conductive Composites

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SYNOPSIS

A water soluble ionomer with sodium propanesulfonate groups was prepared based on a linear polyurethane with high content of —NHCOO— structures. This compound was used both as macromolecular electrolyte and dopant ion in electrochemical polymerization of pyrrole, obtaining a molecular level polypyrrole–propanesulfonate polyurethane composite with electroconductive properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

An increased attention has been paid in the last few years to composites based on conductive polymers, due to the necessity to improve the mechanical properties of this compounds group with vast application fields.^{1,2} Among various methods used for obtaining conductive composites, some involving ionic polymers as partners were mentioned. These present electrostatic interactions with conductive polymer matrix, which can be used in chemical or electrochemical synthesis. Electrochemical synthesis of conducting composites can be performed by two methods: inclusion of conductive polymer in an ionomer film predeposited on the surface of the electrode (two-step method) and direct electrosynthesis of composite from a solution containing both the dispersed ionomer and monomer precursor of conductive polymer (one-step method).² Thus the doping ability of heterocyclic polymers is exploited, the ionic polymer acting as dopant ion.

Some anionic polymers were successfully used for one-step synthesis of conductive composites, as polyvinylsulfate,^{3,4} butadiene–styrene sulfonated copolymer,³ Nafion,⁵ sulfonated acrylic polymers,³ carboxylic polymers, and sulfonated polystyrene.⁶ Recently, Gieselman and Reynolds⁷ have synthesized molecular composites based on poly-

pyrrole with poly(*p*-phenyleneterephthalamido)propanesulfonate as ionic partner.

In the present paper synthesis of a polyurethane anionomer with high content of ionic groups was carried out by derivatization of a support polyurethane. This ionomer was tested as macromolecular electrolyte in electrochemical polymerization of pyrrole. To our knowledge polyurethane ionomers have not been used till now for preparing composites with heterocyclic polymers.

EXPERIMENTAL

Support polyurethane was synthesized by a classical polyaddition reaction, using prepolymer technique from dehydrated polyethylenedipate (PEA) with $M = 2000$ (2 g), freshly distilled diphenylmethane diisocyanate (MDI) (1.5 g) and anhydrous 1,4-butanediol (BD) (0.45 g). All these compounds were commercial materials.

A method described by Ding et al.⁸ was used to prepare polyurethane ionomers. A 5% DMF solution of neutral polyurethane was treated for 15 min at $-5-0^{\circ}\text{C}$, under argon, with stoichiometric quantities of NaH, counted on the basis of the —NH—COO— group content in order to obtain the desired degree of substitution. In this way, a sodate polyurethane solution was obtained. An equivalent quantity of 1,3-propanesultone was then added, maintaining low temperature. After 2 h heating at 50°C , ionic polymer was isolated by ethylether

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Table I Characterization of Electrochemical Polymerizations of Pyrrole

Composite	Solvent	Electrolyte	$C_m (M)^a$	$C_e (M)^b$ (SO_3^- groups)	Durate (h)	I (mA)
PUAPy-I	H ₂ O	PUA-3	0.2	0.05	4	2
PUAPy-II	H ₂ O	PUA-3	0.2	0.05	12	2
TsOPy	H ₂ O	TsONa	0.2	0.10	4	2

^a C_m = monomer concentration.

^b C_e = electrolyte concentration.

precipitation, and repeated washing with the same unsolvent.

DMF was dried on molecular sieves (4 Å) and freshly distilled from BaO before use. NaH was used as a 50% suspension in mineral oil.

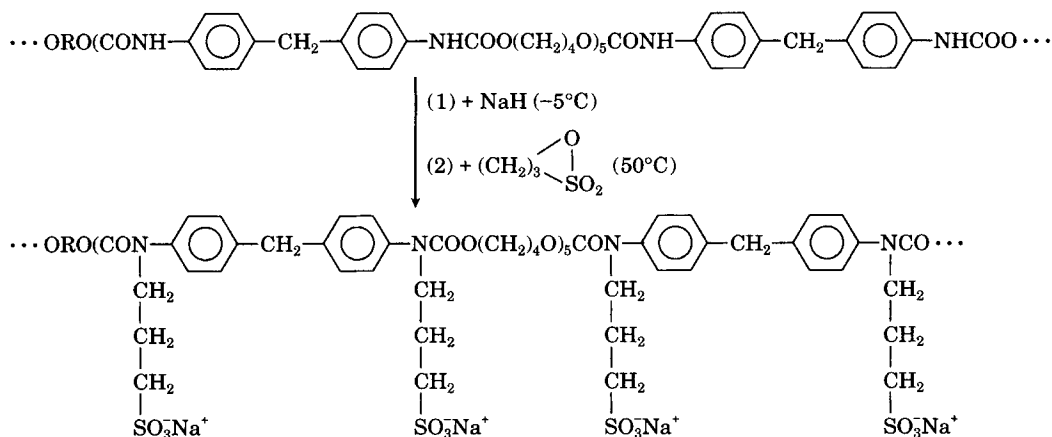
Electroinitiated polymerizations of pyrrole were carried out in galvanostatic conditions, in a double-compartment cell with two Pt electrodes. These had 2 cm² plane surfaces and were at a 10 cm distance. Some parameters of the polymerization process are presented in Table I. The electrical current was maintained constant by means of a MICM CCPAS 1045-01 source of stabilized current.

IR spectra of support polyurethane and of ionic polyurethanes were performed in KBr dispersions on a SPECORD-M 80 spectrophotometer. For polypyrrole polymer materials, IR spectra were recorded with an IFS-Brucker spectrometer, in KBr.

Electrical conductivities were measured on dry state samples, by the two-probe method, in the perpendicular direction to the layer plane.

RESULTS AND DISCUSSION

Synthesis of polyurethane ionomer is based on the capacity of polyamides and polyurethanes to be modified by reactions at amidic nitrogen atoms. After a preliminary metallation of polymer with sodium hydride, in appropriate conditions, different groups may be introduced instead of hydrogen.⁹⁻¹¹ Using this property, a polyurethane forerunner was derivatized, by deprotonation of nitrogen atoms from urethane groups, to form a sodate compound. This product was treated afterwards with propane sulfone, when ring opening occurred and sodium propane-sulfonate side groups were introduced, as follows:



A linear polymer support was used, having a high content of —NHCOO— groups. For its synthesis, polyaddition reaction between PEA ($M = 2000$), MDI, and BD, in molar ratios 1 : 6 : 5, was performed. Urethane structures are grouped together in large domains. Structural changes produced by ionic functionalization of polyurethane were evidenced in IR spectrum, where decreasing until disappearance

of 3300 cm⁻¹ band, characteristic for —NH— urethane groups was observed, concomitantly with the appearance of bands at about 1200 and 1050 cm⁻¹, attributed to SO₃⁻ groups.¹² Propane sulfone ring opening by active anionic positions from the polyurethane chain quantitatively occurs, and the proportion of introduced propane sulfonate groups can

Table II Synthesis and Characterization of Polyurethane Anionomers

Polymer	PU/PS Molar Ratio	S (%)	Sulfonation Degree (%)	Ionic Group (meq/100 g)	Water Solubility (%)	IR, SO ₃ ⁻ Bands (cm ⁻¹)
PUA-1	1/0.5	3.00	48.0	93	Unsoluble	1040, 1207
PUA-2	1/0.75	4.89	78.4	152	Unsoluble	1040, 1207
PUA-3	1/1	6.23	99.9	194	13.5	1040, 1207

be rigorously controlled by the ratio between reagent quantity and urethane nitrogen content, as shown in Table II.

The degree of substitution by sodium propane sulfonate groups was determined by elemental analysis data, reporting sulfur content to urethane group percent. The reaction conditions used prevent polymer degradation from producing.^{8,13}

Polyurethane ionomers having propanesulfonate groups were reported to present modified physicochemical and physicomachanical properties.^{8,13,14} One of the new properties introduced due to presence of ionic groups in macromolecules is a high hydrophilicity. Complete substitution of urethanic hydrogen in polyurethane used in this study has led to a polymer with a content of ionic groups of 194 meq/100 g, water soluble until about 14%. By its content of ionic groups, the polymer belongs to ionomer class. Its structure, characterized by presence of ionic fragments grouped together in big domains, so-called "clusters," determines its solubility by including water inside the "clusters." Thus hydrophobic effect of unpolar chain fragments is counteracted.

Water solubility of polyurethane ionomer with the above structure with all hydrogen atoms from urethane groups substituted by propanesulfonate, allowed it to be tested as a macromolecular electro-

lyte in electrochemical polymerization of pyrrole in aqueous medium. A 0.05 M solution of ionomer in water presents a good electrical conductivity. The distance between electrodes in polymerization cell was 10 cm, which argued for electrolyte qualities.

By passing of electrical current through ionomer and pyrrole solution, oxidative electropolymerization of heterocyclic monomer took place, and the polymer was obtained as a black film on anod. The quantity of deposited polymer is dependent both on the reaction time and current intensity.

Elemental analysis of anodic deposition showed inclusion of an appreciable quantity of sulfur (Table III). This comes from anionic sulfonate groups of macromolecular electrolyte, oriented to anod, which neutralize positive charges of oxidized heterocyclic polymer and act as dopant. Thus all polyurethane backbone is involved in building a tight network with polypyrrole macromolecules, and a molecular level composite structure is obtained.

From elemental analysis results, a dopant factor was counted, respectively, a ratio of anionic groups on a single pyrrole unit of 0.4, compared with 0.167 reported for one-step electrochemical synthesized polypyrrole, with polyvinylsulfate as dopant.⁴

The following schematic representation may be sketched out for the polypyrrole-anionic polyurethane composite structure:

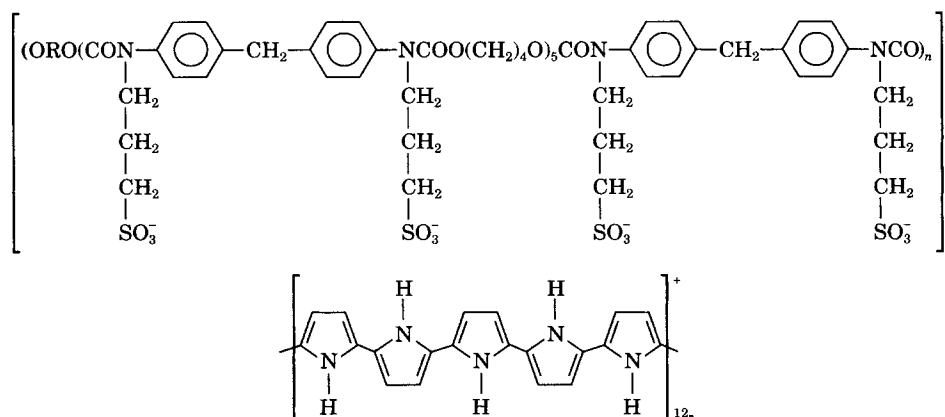


Table III Characteristics of Polypyrrole-Ionic Polyurethane Molecular Composites

Composite	$M_{A^-}^a$	S (%)	Composition (mol/100 g composite)		Dopant Ratio (A^- mol/pyrrole mol)
			A^-	Pyrrrole	
PUAPy-I oxidized	492	4.90	0.153	0.368	0.416
PUAPy-I reduced	492	4.74	0.148	0.404	0.366
PUAPy-II oxidized	492	5.50	0.172	0.230	0.737
PUAPy-II reduced	492	4.89	0.153	0.370	0.410
TsOPy oxidized	171	7.66	0.239	0.881	0.271
TsOPy reduced	171	2.47	0.077	1.295	0.059

^a A^- = dopant anion.

The doping degree may be easily controlled both by polymerization time and by the possibility of polarity inverting. Longer polymerization times determine increasing of this ratio (Tables I and III).

The current was kept almost constant all during electropolymerization; the small potential drops on the polymer thickness proved the electroconductive properties of composites. Electrochemical polymerization of pyrrole in aqueous medium in the presence of sodium *p*-toluenesulfonate (TsONa) was performed comparatively, when tosylate anion was included as dopant.

By inversion of current polarity electrochemical reduction of polypyrrole deposited on anod took place. Due to its large macromolecular size, the included macromolecular polyanion was not released from the heterocyclic polymer matrix. Sulfur content in the electroreduced product showed only a slight undoping, compared with that produced when tosylate was electrolyte and dopant (Table III). This fact suggests that after reduction composite can act as a cation exchanger, as was reported also when other ionomers were used.^{6,16}

Preliminary measurements of electrical conductivity were performed. Electrochemical reduced anionomer-polypyrrole composite (PUA-PyII) shows a conductivity of 4.5×10^{-6} S cm^{-1} , while the conductivity of TsO^- -doped polymer was 4.5×10^{-3} S cm^{-1} . A similar difference of conductivity was observed for other polypyrrole composite.³ A lower value of conductivity may be attributed to the existence of unionic parts of polyurethane ionomer, forming insulating domains in conductive material.

In conclusion, this paper presented synthesis of a water-soluble ionomer with sodium propanesulfonate groups, based on a linear polyurethane with high content of $-\text{NHCOO}-$ structures grouped together. This compound was used both as electrolyte and dopant ion in electrochemical polymeriza-

tion of pyrrole, obtaining a polypyrrole-propane-sulfonated polyurethane molecular composite with electroconductive properties.

Studies regarding other properties of molecular conductive composite are in progress now in our laboratory.

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