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SYNTHESIS OF CONDUCTING BLOCK AND GRAFT COPOLYMERS WITH POLYETHER SEGMENTS

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Abstract: Synthesis of block and graft copolymers containing polyether and conducting polypyrrole sequences were described. Pyrrole moieties were incorporated at the chain ends of polytetrahydrofuran and polysiloxane and at the side chains of polyethyl vinylether by ionic polymerization and appropriate chemical reactions. Subsequent electropolymerization with pyrrole through these moities yielded free standing films of the corresponding block and graft copolymers. The formation copolymers was evidenced by FTIR spectroscopy and extraction with solvent of the precursor homopolymers. The thermal and morphological properties were also characterized. The two surface of the copolymer films generally differ in appearance, the surface at the solution side being cauliflowerlike or wrinkled, whereas the surface at the electrode side smooth. Conductivies of the copolymers were comparable with that of the pure polypyrrole.

INTRODUCTION

Conducting organic polymers has received growing interest because of their wide range applications in various fields [1]. These materials are often termed as synthetic metals due to the fact that they combine chemical and mechanical properties of the polymers with the electronic properties of the metals and semicunductors. Polypyrrole is one type of the polymer among a general type of conducting polymers that include polyacetylenes, polythiophenes, polyanilines, polyphenylenes, polycarbazoles, polyquinolines and polyphtalocyanines. Pyrrole systems have several attractiveness over the other conducting polymers. These include the chemical and thermal stabilty of the pyrrole based polymers and abilty of the preparation of derivatives with a range of conductivies. However, two major limtiations of polypyrroles are inabilty to process and poor mechanical and phsical properties. In order to improve their various properties several methods were proposed. Among them block and graft copolymerization is an elegant way to combine the conducting polypyrrole with the conventional polymers. For example, polystyrene-*g*-

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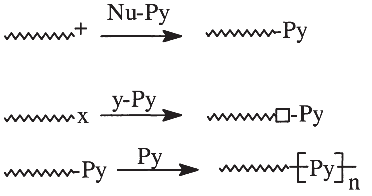
polypyrrole [2] and poly(mehyl methacrylate)-*g*-polypyrrole [3-5] were prepared by electrochemical and combination of chemical and electrochemical methods, respectively.

In this paper, we will describe our approach to synthesize polypyrrole with soft polyether segments. In this approach, two mutually exclusive polymerization mechanisms, namely conventional ionic and electrochemical polymerizations, are sequentially combined. The elecroactive pyrolle moieties were introduced polymers by either termination of cationic polymerization by suitable nucleophile or chemical reaction of the related compunds with the preformed polymers The overall procedure is described below.



(1)

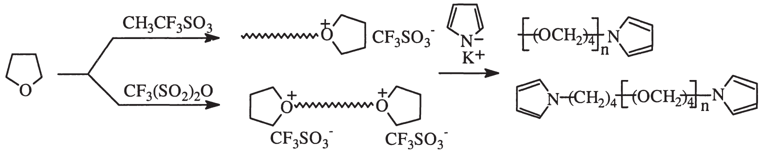
(2)

(3)

Py = pyrrole, Nu = nucleophile, x and y = mutually reactive functional groups

POLYPYRROLE/POLYTETRAHYDROFURAN BLOCK COPOLYMERS

Living polymerization allows the preparation of various well-defined polymers with functional end groups. It is known that tetrahydrofuran can be polymerized without chain transfer and termination reactions under closely controlled conditions [6]. The oxonium group of the living chain can react with nucleophiles and thus gives rise to a variety of functional groups [7-9]. Polytetrahydrofuran (PTHF) with one or two terminal pyrrole groups was prepared [10, 11] by the living polymerization of tetrahydrofuran (THF) using methyl triflate and triflic anhydride as mono- and bifunctional initiators, respectively, according to the following reaction:



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The living propagating chains readily react with potassium salt of pyrrole.The results are collected in Table 1. Based upon the comparision of the ratio of pyrrole protons at 6.4-7.1 ppm to protons of –OCH_2 of PTHF at 3.4 ppm, the functionalization of the polymers were calculated. UV spectra of the polymers show chracteristic absorbance of pyrrole moieties.

Table 1. Preparation of pyrrole terminated polytetrahydrofuran.

Polymer	Initiator (mol l^{-1})	Time (min)	Conv. (%)	M_n	M_w/M_n	*F*
Py-PTHF-1	$CH_3CF_3SO_3$ (1.2 x 10^{-2})	40	12	13000	1.5	1
Py-PTHF-2	$CH_3CF_3SO_3$ (1.2 x 10^{-2})	80	20	27000	1.7	1
Py-PTHF-Py-1	$(CF_3SO_2)_2O$ (1.2 x 10^{-2})	20	10	30000	1.3	2.01
Py-PTHF-Py-2	$(CF_3SO_2)_2O$ (2.44 x 10^{-2})	35	20	13800	1.5	1.98

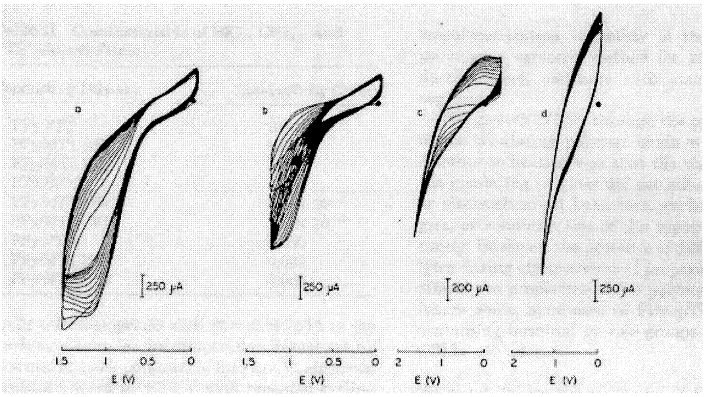
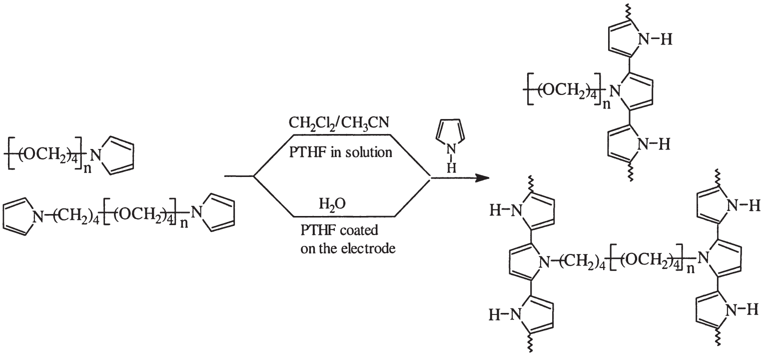


Figure1. Cyclic voltammograms of (a) TS^- doped PPy, (b) TS^- doped Py-PTHF-1, (c) BF_4^- doped PPy and (d) BF_4^- doped Py-PTHF.

The polymers obtained this way were not electroactive themselves as was confirmed by the cyclic voltammetry analyses. The absence of detection of any redox peak indicated that crosslinking through the pyrrole moieties was not possible. Different situation was, however, encountered when poyrrole was added to the solution. An electroactivity increasing with the number of scans was observed (Figure 1). Thus, these polymers were transformed into block copolymers containing pyrrole and THF segments by electropolymerization via single- or two-step procedures. In the single-step procedure, polymerizations were performed on a bare Pt electrode by using a conventional three-electrode electrochemical cell and BF_4^- or ClO_4^- as supporting electrolytes. Pyrrole, PTHF and electrolyte were dissolved in an appropriate solvent. Notably, sufficient amount of films were formed in much shorter times when ClO_4^- was used. In the two-step procedure, however, mono or bifunctional PTHFs were coated on the Pt electrode and subsequently pyrrole was polymerized electrochemically. Electrochemical synthesis of block copolymers yielded free standing films which were easily peeled off from the electrode surface.



(6)

(7)

The mechanical properties of block copolymers were quite different from the pyrrole homopolymer. The block copolymers produced rubbery films. These films were soft but retained their shape when cut into strips. FTIR spectra of the block copolymers showed characteristic bands of the precursor PTHF, polypyrrole segment and also the dopants. Thermogravimetric analyses revealed that the block copolymers doped with p-toluene sılfonate (TS^-) were more resistant to heating when compared to BF_4^- and ClO_4^- in accordance with the thermal behaviour of pure polypyrrole. Block copolymers obtained from mono and bifunctional PTHF showed similar DSC paterns. Decomposition transitions of polypyrrole and the dopant were detected. Scanning electron microscopy (SEM) studies revealed that the surface appearance of the electrode and solution side depends on the type of electrolyte used. Smooth appearance in the electrode side and cauliflowerlike appearance, particularly with TS^-, dopant indicates that pyrrole groups grew towards the solution.

In contrast to the chain length, the electrolyte type significantly changed the conductivities. The highest conductivity, very close to that of pure PPy, was shown by BF_4^- doped polymers. The lowest conductivity was shown by ClO_4^- doped films. When TS^- was used as the supporting electrolyte, films had conductivity values of about 0.07 S/cm, which was also the conductivity of of TS^- doped pure PPy (Table 2).

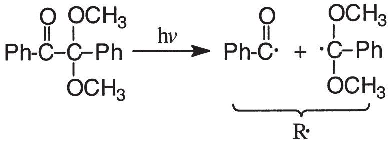
Table 2. Conductivities of the films doped with various dopants.

Polymer	Conductivity (S/cm)
PPy BF_4^-	0.56
PTHF-PPy-1 BF_4^-	0.56
PTHF-PPy-2 BF_4^-	0.14
PPy ClO_4^-	0.085
PTHF-PPy-1 ClO_4^-	5.5×10^{-3}
PTHF-PPy-2 ClO_4^-	9.2×10^{-3}
PPy TS^-	0.09
PTHF-PPy-1 TS^-	0.032
PTHF-PPy-2 TS^-	0.065

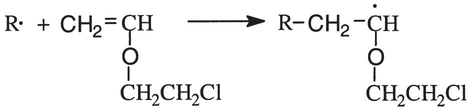
POLYETHYLVINYLETHER/POLYPYRROLE GRAFT COPOLYMERS

Vinylethers are readily polymerized by onium type photoinitiators. Both direct and indirect acting systems were found to be effective for the initiation [12]. Among various indirect acting systems radical promoted cationic polymerization is particularly useful and flexible way for the polymerization of vinyl ethers [13]. The operating wavelenght is extended to longer wavelenghts with the aid of free radical photoinitiators so that the absorption of the onium salt does not interfere with that of the chromophoric group of a particular monomer involved. For convenience, we have employed, 2,2-dimethoxy-2-phenyl acetophenone (DMPA) / diphenyl iodonium hexafluoro phosphate ($Ph_2I^+PF_6^-$) combination for the radical promoted cationic polymerization of 2-choloroethyl vinly ether (CEVE). Irradiation of solution of

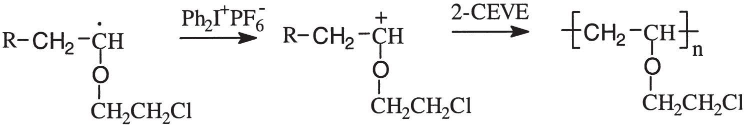
CEVE (6.6 mol l^{-1}) in methylene chloride containing DMPA (5×10^{-3} mol l^{-1}) and $Ph_2I^+PF_6^-$ (5×10^{-3} mol l^{-1}) at $\lambda = 350$ nm for 5 minutes produced a polymer with 98 % conversion. In this case the initiating species are formed by the oxidation of either or both primary and monomer adduct radicals.



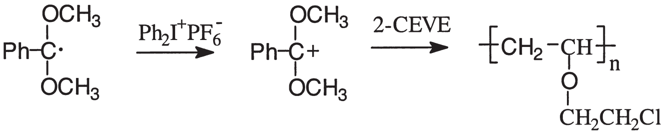
$$Ph\text{-}C(=O)\text{-}C(OCH_3)_2\text{-}Ph \xrightarrow{h\nu} \underbrace{Ph\text{-}\dot{C}(=O) + \cdot C(OCH_3)_2\text{-}Ph}_{R\cdot} \tag{8}$$



$$R\cdot + CH_2{=}CH(OCH_2CH_2Cl) \longrightarrow R\text{-}CH_2\text{-}\dot{C}H(OCH_2CH_2Cl) \tag{9}$$

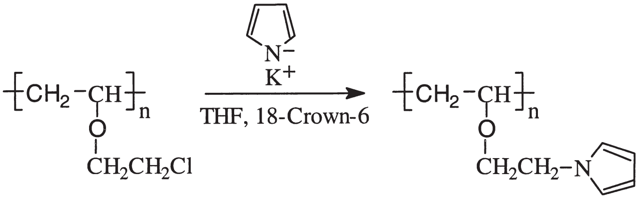


$$R\text{-}CH_2\text{-}\dot{C}H(OCH_2CH_2Cl) \xrightarrow{Ph_2I^+PF_6^-} R\text{-}CH_2\text{-}\overset{+}{C}H(OCH_2CH_2Cl) \xrightarrow{2\text{-}CEVE} \left[CH_2\text{-}CH(OCH_2CH_2Cl)\right]_n \tag{10}$$



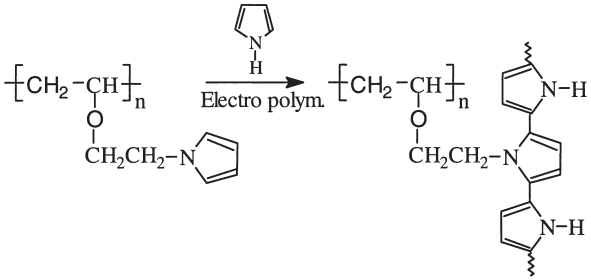
$$Ph\text{-}\dot{C}(OCH_3)_2 \xrightarrow{Ph_2I^+PF_6^-} Ph\text{-}C^+(OCH_3)_2 \xrightarrow{2\text{-}CEVE} \left[CH_2\text{-}CH(OCH_2CH_2Cl)\right]_n \tag{11}$$

PCEVE thus obtained was converted to pyrrole derivative (polypyrrolethyl vinyl ether, PPEVE) by reacting with pyrroyl potassium in THF in the presence of 18-crown-6.



(12)

Structure of PPEVE was confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectral and thermal analyses. Glass transition temperature of PCEVE increased from –6.67 °C to 4.13 °C by such modification indicating that PPEVE is relatively more rigid than the corresponding prepolymer. Moreover, subtitution increases the thermal stability as demonstrated with TGA studies. Electropolymerization of pyrrole with PPEVE was performed in both in organic solution and water as described for PTHF.



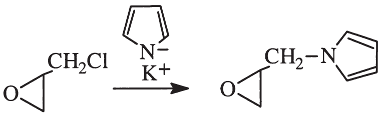
(13)

Although the chemical incorporation of polyether with polypyrrole in both cases was evidenced by the treatment of the graft copolymers with solvents and IR spectral analysis, DSC studies revealed that electropolymerization in organic solution yielded graft copolymers with higher pyrrole contents. The morpholoy of the graft copolymers were different than that of the pure PP. Electrode side of the pure PPy produced under the same experimental conditions exhibit wrinkled surface whereas the corresponding surface of the graft copolymer is smooth [14].

No weight loss is recorded upon washing the graft copolymers with the solvent of PPEVE. Conductivities of washed and unwashed graft copolymer films were almost the same.

POLYSILOXANE / POLYPYRROLE BLOCK COPOLYMERS

Excellent properties of polysiloxanes regarding high flexibility, high temperature resistance and solubility prompted us to modify the properties of polypyrrole by similar electrochemical blocking process of polysiloxane with pyrrole. Many synthetic approaches for siloxane containing block and graft copolymers are based on organofunctional polysiloxanes as the starting materials [15]. Organofunctional polysiloxanes can be prepared [16] by several routes such as hydrosilation, chemical transformation and the cationic or anionic equilibration of cyclic siloxanes in the presence of a functional disiloxane acting as an end-blocking agent. Pyrrole functionalized polydimethylsiloxane (Py-PDMS-Py) was prepared by a multistep procedure according to the following reactions.



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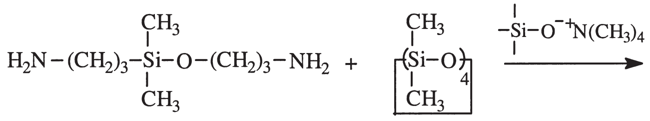

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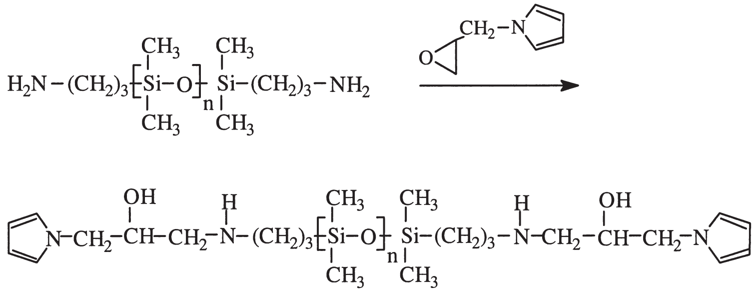
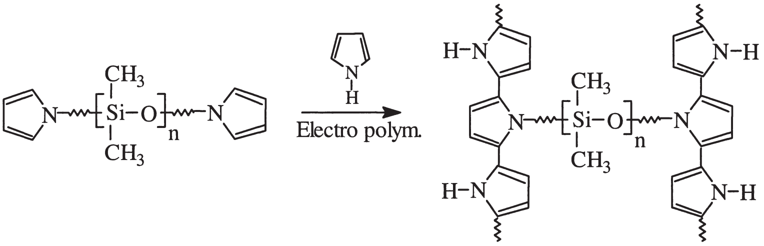


(16)

In this procedure, the functionalization agent *N*-glycidylpyrrole was prepared by reacting pyrrole salt with epichlorphydrin in the presence of 18-crown-6 in THF. The reaction of amino compounds with epoxy-terminated polysiloxanes is a known process for polysiloxane functionalization. For this purpose, the amino groups were attached to polysiloxane chain by anionic polymerization of octamethylcyclotetrasiloxane in the presence of 1,3-bis(aminopropyl)-1,1,3,3-tetramethylsiloxane as the end-blocking agent. The good agreement of the molecular weight values obtained by titration of the amino end groups (M_n=1100) and by vapour pressure osmometry (M_n=1210) confirms the presence of two functional groups per polymer chain and the absence of important amounts of high molecular weight cyclosiloxanes. In the subsequent step, this polymer was reacted with *N*-

glycidylpyrrole to yield pyrrole terminated polydimethylsiloxane (Py-PDMS-Py). The molecular weight of Py-PDMS-Py (M_n=1200) was calculated from the pyrrole content, as determined from the ^{1}H-NMR spectrum, and was found to be in good agreement with that of the amino derivative.

The block copolymers were then prepared by electrochemical polymerization of pyrrole on the surface of the electrode coated with Py-PDMS-Py.



(17)

The block copolymers doped with TS^- and BF_4^- were investigated by FTIR analysis. The characteristic Si-O-Si bands of the polysiloxane and C=C bands of polypyrrole at 1096 and 1023 cm^{-1} and 1550 cm^{-1}, respectively, were detected. Thermal behaviour of the block copolymer as studied by DSC and TGA depended on the type of dopant used. Although the size of the films was not suitable for the detailed tests, the electrolytic films were subjected to simple tests. They were foldable without any cracks on the surface.

The morphology of the films, as judged by SEM, was dependent of the electrode or solution side. The type of the dopant was shown to be also important determinant of the appearance of the surfaces. The electrode side of the block copolymer doped with TS^- was much smoother than that of the block copolymed doped with BF_4^-.

Conductivities of the solution and electrode sides of the block copolymer films were found to be the same. Conductivities of the block copolymers (doped either with TS^- and BF_4^-) were observed in the same order of magnitute (2-5 S/cm). This indicates the homogenity of free standing films.

In conclusion, main chain and side chain pyrrole functionalized polyethers have been successfully synthesized by ionic polymerization processes and chemical reactions. Block and graft copolymer films of the polyethers and polypyrrole were futher synthesized by electrochemical methods.

ACKNOWLEDGEMENTS

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