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### CONDUCTING MULTIPHASE BLOCK COPOLYMERS OF POLYPYRROLE WITH POLYTETRAHYDROFURAN AND POLYTETRAHYDROFURAN-*b*-POLYSTYRENE

Serhan Öztemiz<sup>a</sup>; Levent Toppare<sup>a</sup>; Aysen Önen<sup>b</sup>; Yusuf Yagci<sup>b</sup>

<sup>a</sup> Department of Chemistry, Middle East Technical University, Ankara, Turkey <sup>b</sup> Department of Chemistry, Istanbul Technical University, Istanbul, Turkey

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# CONDUCTING MULTIPHASE BLOCK COPOLYMERS OF POLYPYRROLE WITH POLYTETRAHYDROFURAN AND POLYTETRAHYDROFURAN-*b*-POLYSTYRENE

Serhan Öztemiz and Levent Toppare\*

Department of Chemistry  
Middle East Technical University  
06531 Ankara, Turkey

Aysen Önen and Yusuf Yagci

Department of Chemistry  
Istanbul Technical University  
80626 Istanbul, Turkey

Key Words: Polypyrrole, Graft Copolymers, Conducting Polymers, Constant Potential Electrolysis

## ABSTRACT

Living bifunctional azo-polytetrahydrofuran (azo-PTHF) was terminated with pyrrolyl potassium salt to yield a polymer with electrochemically active functional end groups. This polymer is further used to synthesize polytetrahydrofuran-polystyrene (PTHF-*b*-PS-*b*-PTHF) block copolymer. These polymers are electrochemically blocked with polypyrrole using constant potential electrolysis (PPy/Azo-PTHF and PPy/PTHF-*b*-PS-*b*-PTHF). Two different solvent-electrolyte pairs were used during electrolysis. Characterizations of pristine and the blocked

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\* Author to whom correspondence should be addressed.

copolymers are based on Cyclic Voltammetry (CV), Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermal Gravimetry Analysis (TGA), Scanning Electron Microscope (SEM) Nuclear Magnetic Resonance Spectroscopy (NMR) and Gel Permeation Chromatography (GPC). Conductivities were measured using a four-probe technique.

## INTRODUCTION

Conducting polymers, because of their unusual properties, have attracted great interest in recent years. Despite the short history, they have found a place in various application areas such as rechargeable batteries, nonlinear optics, gas separation membranes, gas sensors, and enzyme immobilization [1-6]. But these applications are limited due to the poor mechanical properties and processabilities of conducting polymers. In order to compensate for this lack, many ways have been suggested. Making composites by the use of an insulating polymer as the host matrix improved the mechanical properties and have been extensively used [7-10]. And also, it has been found that some electrochemically synthesized composites have different behaviors other than that of the simple mechanical mixture of the two polymers, which was ascribed to a better homogeneity, to a possible hydrogen bonding and also to the formation of graft polymers to a certain extent [11]. An alternative method to improve the mechanical and physical properties is to synthesize graft or block copolymers which have better defined structures. For this, polymeric initiators with functional groups within or at the end of the chain are used [12-15]. Most of the efforts for the preparation of polymeric initiators have focused on living polymerization techniques, which involves quenching of living polymer ends with a reagent having functional groups [16-17].

In this paper, we describe the synthetic approach to preparing polytetrahydrofuran and polytetrahydrofuran-*b*-polystyrene with pyrrole end groups. These polymers were electrochemically polymerized with pyrrole using two different solvent-electrolyte systems. This should allow the synthesis of H-type block copolymers consisting of rather long insulating polymer chains, which should supply the necessary flexibility to the polymer. On the other hand, the polypyrrole blocks maintain the electrical conductivity with the same order of magnitude with that of a pristine polypyrrole.

## EXPERIMENTAL

### Materials

Pyrrole (Merck) was distilled before use and stored at 4°C. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and acetonitrile (AN) were purchased from Merck and used without further purification. Tetrabutylammonium tetrafluoroborate (Merck), p-toluene sulfonic acid (Sigma) and AgSbF<sub>6</sub> (Fluka) were used as received.

Tetrahydrofuran (THF) (Merck) was dried over KOH, distilled over sodium wire and finally distilled over sodium diphenylketyl just before use. Solvents were purified by conventional drying and distillation procedures and kept over molecular sieves. 4,4'-Azobis(4-cyanovaleryl chloride) (ACPC) was prepared from the corresponding diacid according to a previously described procedure [18].

### Synthesis of Azo Containing PTHF Terminated with Pyrrole (P1)

The polymerization of THF was carried out in bulk at 0°C under nitrogen atmosphere. Initiation of the polymerization of THF was induced by adding 5 ml stock solution of ACPC to 5 ml stock AgSbF<sub>6</sub> solution so as to adjust the final concentration of AgSbF<sub>6</sub> to be  $3 \times 10^{-2}$  mol/l. After 12 minutes, living polymerization of PTHF was terminated by the addition of an excess amount of potassium salt of pyrrole (as suspension in dichloromethane) into the reaction mixture and stirred overnight. The solution was centrifuged to separate insoluble salt, and the polymer was poured into a large amount of MeOH/water (3:1, v/v) and cooled for precipitation. Finally, the precipitated polymer was filtered off and dried under vacuum.

### Polymerization of Styrene by Utilizing Azo-PTHF Initiator (P2)

A known amount of azo containing PTHF (50 g/l) was dissolved in toluene and 5.8 mol/l styrene was added. The solution was degassed with nitrogen and heated to 60°C for 3 hours. Finally, copolymer was precipitated in methanol and dried under vacuum.

### Synthesis of Conducting Block Copolymers

Block copolymer films of both P1 and P2 with polypyrrole were synthesized electrochemically in two different solvent-electrolyte pairs. Electrolyses were performed in a three-compartment cell equipped with platinum (Pt) foils

(1.5 cm<sup>2</sup>) as the working and counter electrodes and a luggin capillary reference electrode (Ag<sup>0</sup>/Ag<sup>+</sup>). A Wenking POS 73 Potentiostat was used to supply the constant potential for the syntheses.

Blocks were prepared by the electrochemical polymerization of pyrrole onto P1 and P2 coated electrode where either TBAFB (solvent is AN) or PTSA (solvent is water) were used as the supporting electrolytes. P1 and P2 were coated on the Pt electrodes by dipping the electrode in a solution of polymer dissolved in CH<sub>2</sub>Cl<sub>2</sub> and allowing the solvent to evaporate. The electrolysis solution contained 0.05 M dopant and 0.02 M pyrrole. Polymerization reactions lasted for 3 hours for both polymers.

The films were easily peeled off the electrode surface and washed with AN (for BF<sub>4</sub><sup>-</sup> doped films) and with water (with PTS<sup>-</sup> doped ones), and dried under vacuum. Then, the films were left in CH<sub>2</sub>Cl<sub>2</sub> in order to dissolve and get rid of the ungrafted polymers (P1 or P2).

GPC analysis was performed with a setup consisting a Waters 600 pump and 2 ultrastayragel columns (10<sup>4</sup>, 500 Å) with THF as the eluent at a flow rate of 1 mL min<sup>-1</sup> and a Waters differential refractometer (model 410). Molecular weights were calculated with the aid of polystyrene standards. <sup>1</sup>H NMR spectra were recorded on a Bruker 250 MHz instrument in CDCl<sub>3</sub>.

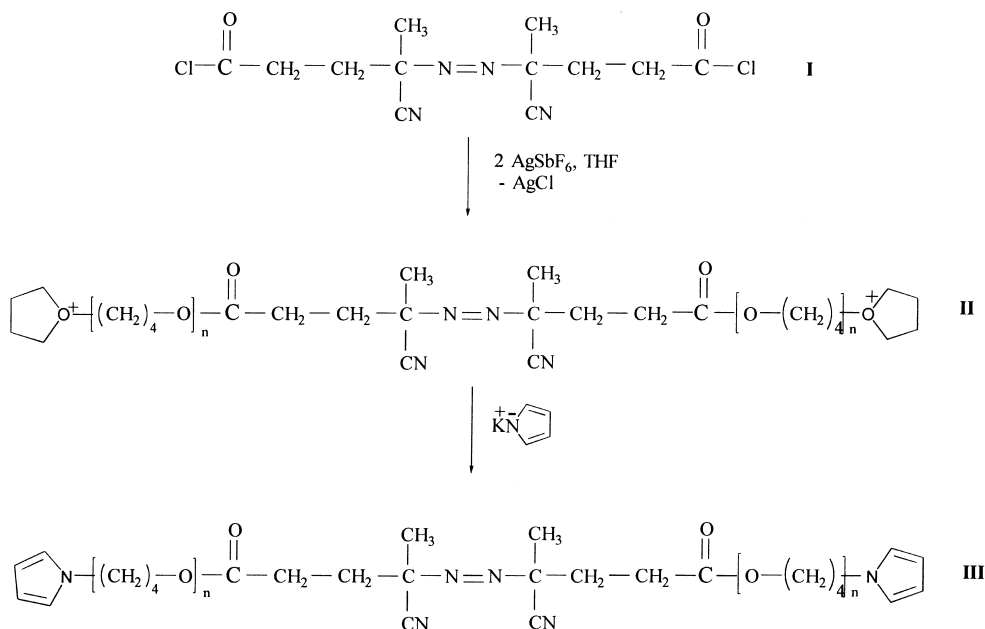
For the characterization of both precursor and grafted copolymers, CV, FTIR, DSC, TGA and SEM analyses were performed. To study the electroactivities of the polymers, a HEKA potentiostat/galvanostat was utilized. FTIR spectra of the films were recorded on a Nicolet 510 FT-spectrophotometer. Thermal behavior of the films were analyzed by DSC (Du Pont 2000) and TGA (TL-TGA 2000). SEM (JEOL JSM-6400) was used to observe the surface morphologies. Conductivities of the samples were measured using a four-probe technique.

## RESULTS AND DISCUSSION

### Pristine Polymers

Functional polytetrahydrofuran (PTHF) containing an azo group in the main chain and pyrrole groups at the chain ends was synthesized by the use of a difunctional azo-oxocarbenium initiator. Pyrrole groups were introduced by terminating the living polymerization with pyrrolyl potassium salt (compound III).

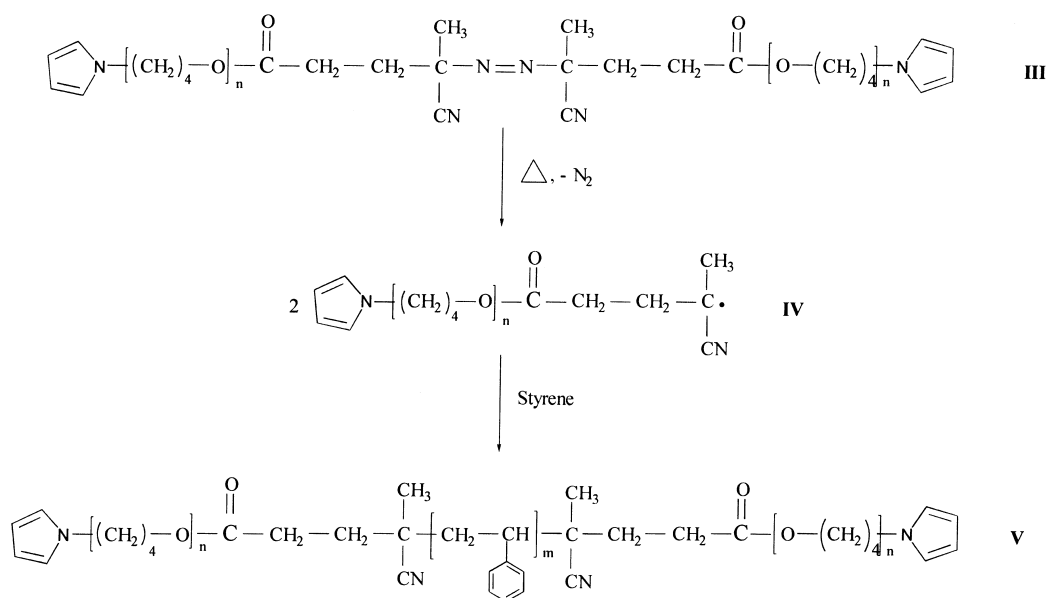
The <sup>1</sup>H NMR spectrum of the polymer (compound III) exhibits signals in the range of 6-7 ppm corresponding to aromatic protons of pyrrole in addition to characteristic PTHF signals. This polymeric initiator has a bifunctional character



**Scheme 1.** Synthesis of azo-PTHF (**III**), from ACPC (**I**) by living polymerization.

due to the presence of both the thermosensitive azo group and thermally stable, but electrochemically active pyrrole groups in the structure. Block copolymers of different structures can be obtained by utilizing this initiator in the presence of appropriate monomers. In the first step, this polymeric initiator was used in the thermal polymerization of styrene to obtain A-B-A type electrochemically active block copolymers. In this system, the type of block copolymer formed, depends greatly on the kinetic behavior of the particle monomer involved. Initiation of styrene polymerization by means of azo-pyrrole PTHF (compound III) was expected to yield A-B-A type block copolymer (compound V) having electrochemically active pyrrole groups at each end since termination occurs by radical-radical combination.

In a typical copolymerization experiment, azo-PTHF (compound III) was heated for 3 hours at 60°C in the presence of styrene (13.5 mol% of the initial styrene has been found to be consumed). The <sup>1</sup>H NMR spectrum of the block copolymer represents characteristic signals at 1.1-2.1 ppm (CH<sub>2</sub>), 3.4 ppm (OCH<sub>2</sub>), 6.3-7.2 ppm (C<sub>6</sub>H<sub>5</sub>). Block copolymer composition (compound V) was also calculated from <sup>1</sup>H NMR data and it was found that block copoly-



**Scheme 2.** Synthesis of PTHF-b-PS-b-PTHF (V), from azo-PTHF (III).

mer chains consisted of 70% PTHF and 30% PST. Experimental data for the synthesis of block copolymer involving cationic and free radical steps are given in Table 1.

In the second stage, these polymers were electrochemically blocked with polypyrrole using constant potential electrolysis (Schemes 3 and 4)

**TABLE 1.** Syntheses of Azo-PTHF and PTHF-b-PST Polymers with Pyrrole Terminal Groups by Sequential Cationic and Free Radical Polymerization

Polymer code	% Conversion	Mn <sup>a</sup>	Mw/Mn	Polymer Composition <sup>b</sup>	
				(%) PTHF	(%) PS
P1 <sup>c</sup>	16 %	92610	1.5	100	0
P2 <sup>d</sup>	13.5 %	270600	1.48	70	30

<sup>a</sup> Determined by GPC

<sup>b</sup> Determined by <sup>1</sup>H NMR

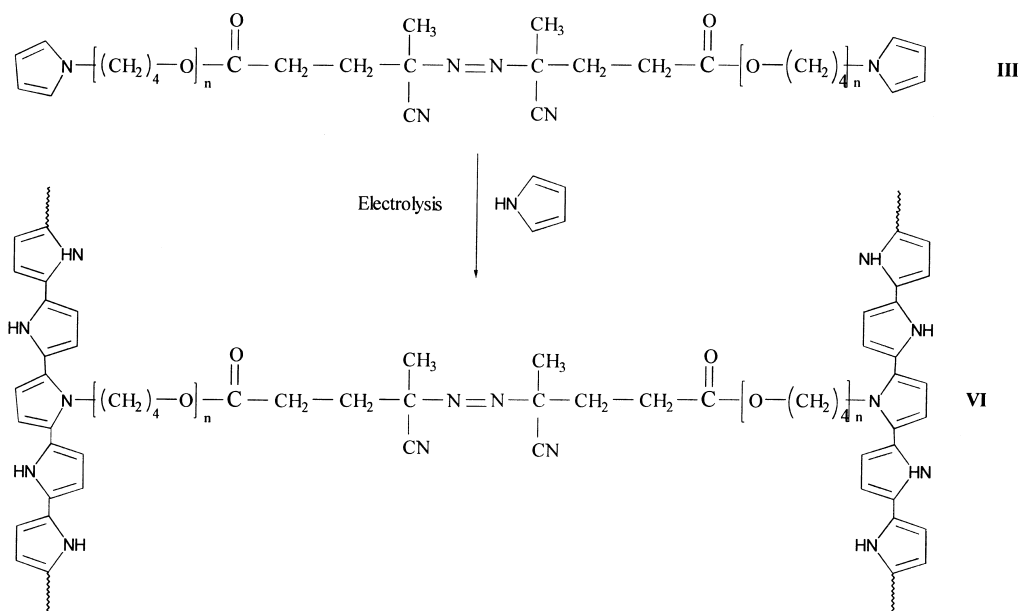
<sup>c</sup> Cationic Polymerization, 0°C, 12 minutes.

ACPC = 1.5 × 10<sup>-2</sup> mol l<sup>-1</sup>, AgSbF<sub>6</sub> = 3 × 10<sup>-2</sup> mol l<sup>-1</sup>, THF = 12.3 mol l<sup>-1</sup>.

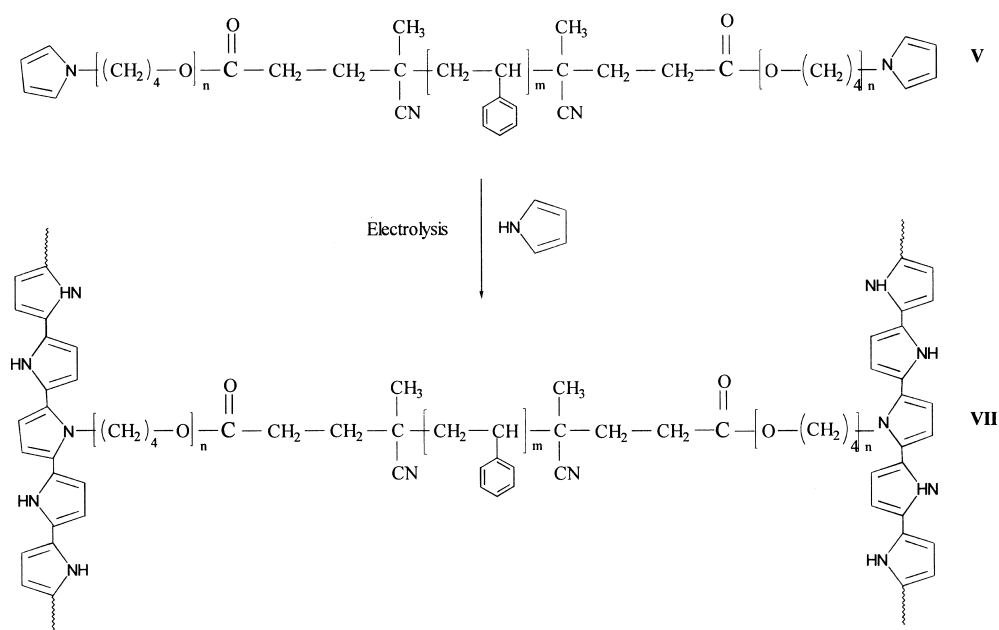
<sup>d</sup> Free Radical Polymerization, 60°C, 3 hours.

azo-PTHF = 50 g l<sup>-1</sup>, St = 5.8 mol l<sup>-1</sup>.

Solvent = Toluene.



**Scheme 3.** Synthesis of block copolymer of pyrrole with azo-PTHF by electrolysis.



**Scheme 4.** Synthesis of block copolymer of pyrrole with PTHF-b-PS-b-PTHF by electrolysis.



### Cyclic Voltammetry

Cyclic voltammetry experiments were performed for both TBAFB-AN and PTSA-water systems.

In the cyclic voltammograms of the pristine polymers P1 and P2, no detectable redox peak was observed. For this reason, it was concluded that no self propagation may occur and both polymers were electroinactive in that sense. But, upon pyrrole addition to the solution, an increasing redox peak appeared with increasing scan number, indicating a possible reaction between the polymers and pyrrole.

### FTIR Analysis

FTIR spectra of P1 and P2 insulating polymers showed the characteristic C-O-C asymmetric stretching at  $1113\text{ cm}^{-1}$ . The two bands at  $2940\text{ cm}^{-1}$  and  $2866\text{ cm}^{-1}$  arose as a result of aliphatic  $\text{CH}_2$  vibrations. Additionally, two very sharp bands at  $763\text{ cm}^{-1}$  and  $707\text{ cm}^{-1}$  arose due to the benzene ring in the styrene units.

In order to investigate the graft copolymers, low dopant concentration ( $10^{-3}\text{ M}$ ) was used to synthesize the films since dopants' intensive peaks may obscure the characteristic peaks of P1 and P2.

Both P1/PPy and P2/PPy copolymers (doped with TBAFB) showed the characteristic bands of the pristine polymers. In addition, an intense band at  $1084\text{ cm}^{-1}$  was observed indicating the presence of dopant anions,  $\text{BF}_4^-$ , in the polymer chain.

PTSA<sup>-</sup> doped block copolymers showed a comparably crowded appearance between  $1600\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$ ; but, they still revealed the characteristic bands of the pristine polymers.

### Conductivities of the Films

Conductivities of the films, both electrode and the solution sides, were measured by using the four-probe technique. The results are given in Table 2.

When the electrode side and solution side conductivities of both TBAFB and PTSA doped films were compared, in each case, conductivities of the same order of magnitude were observed. That reveals the homogeneity of the films. Moreover, it indicates that the pyrrole chains are very long, and they show rather polypyrrole behaviour in terms of conductivity.

### Thermal Gravimetry Analysis

The thermal gravimetry analysis of P1 shows a small (7%) loss at  $181^\circ\text{C}$  and then the weight decreases gradually to 70% till  $400^\circ\text{C}$ . There occurs a great

TABLE 2. Conductivities of the Films

Polymer	Solution Side	Electrode Side
PPy/BF <sub>4</sub> <sup>-</sup>	22 S/cm	23 S/cm
PPy/PTSA	19 S/cm	19 S/cm
P1/PPy/BF <sub>4</sub> <sup>-</sup>	12 S/cm	12 S/cm
P1/PPy/PTSA	10 S/cm	10 S/cm
P2/PPy/BF <sub>4</sub> <sup>-</sup>	17 S/cm	16 S/cm
P2/PPy/PTSA	14 S/cm	15 S/cm

loss at 430°C and the weight decreases to 3.33% and stays constant till 1000°C. P2 reveals almost the same trend except the loss at 181°C. There occurs no characteristic weight loss till 400°C, but a great loss occurs at 433°C, and the weight drops to 1.4%.

Thermograms for graft copolymers of P1, with both dopants, showed nearly the same behavior with that of pure polypyrrole (Figure 1). The films with TBAFB lose 10% till 200°C, and gradually dropped to 60% till 600°C. But in the PTSA doped films, there was a characteristic loss at 347°C for pure PPy and at 350°C for P1/PPy graft, resulting from the decomposition of the dopant anion. At 1000°C, 57% and 58% of the films remained for TBAFB and PTSA doped ones, respectively.

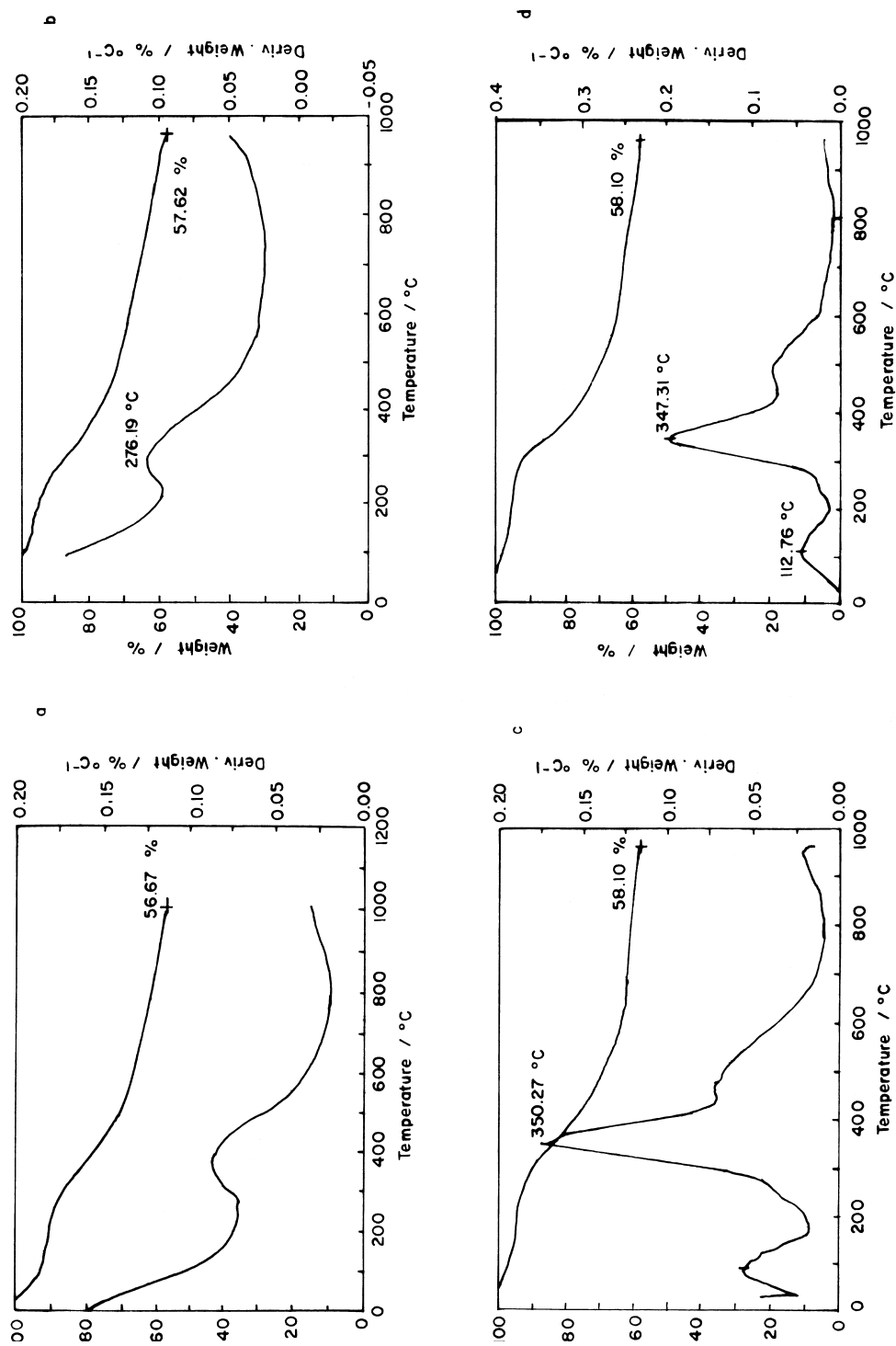
The trend was the same also for P2/PPy grafts. 53% of the film doped with TBAFB was remaining at 1000°C, whereas this number was 58% for the PTSA doped one. TGA analyses reveal that insertion of PPy blocks to the PTHF does not alter the heat resistance of the polymers to an appreciable extent.

### Differential Scanning Calorimetry

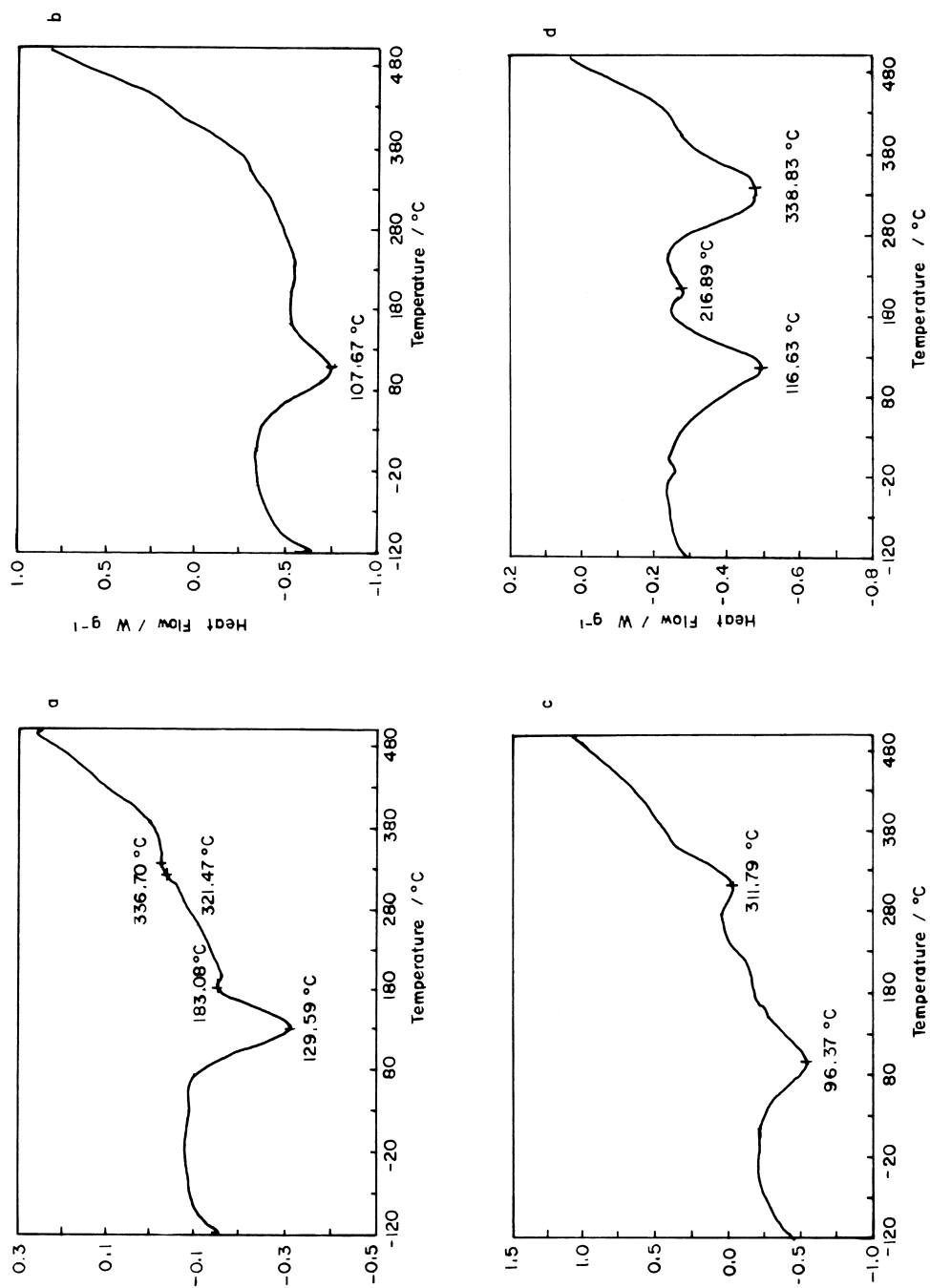
DSC curves of both the pristine polymers and the blocked ones were obtained by heating the samples from -120°C to 500°C at a rate of 10°C/min.

P1 showed a glass transition temperature at -67°C and well-defined melting peak at 43°C, whereas P2 had a glass transition temperature at 3°C. The melting of PTHF blocks in P2 occurred at 42°C.

Both TBAFB and PTSA doped block polymers revealed very different curves than the pure polypyrroles. TBAFB doped P2/PPy had one endothermic peak at 130°C and several shoulders between 180°C and 340°C (Figure 2a). But pure PPy had only an endothermic peak at 108°C (Figure 2b). PTSA doped P2/PPy had two endothermic peaks at 96°C and 312°C, whereas pure PPy had three peaks at 117°C, 217°C, and 339°C (Figure 2c and 2d). The differences thus, arose not only from the type of the dopant but also from the presence of the PTHF blocks, which in a way supports the presence of such chains in the end product.



**Figure 1.** TGA thermograms of a) P1 / PPy (TBAFB doped); b) PPy (TBAFB doped); c) P1 / PPy (PTSA doped); d) PPy (PTSA doped).



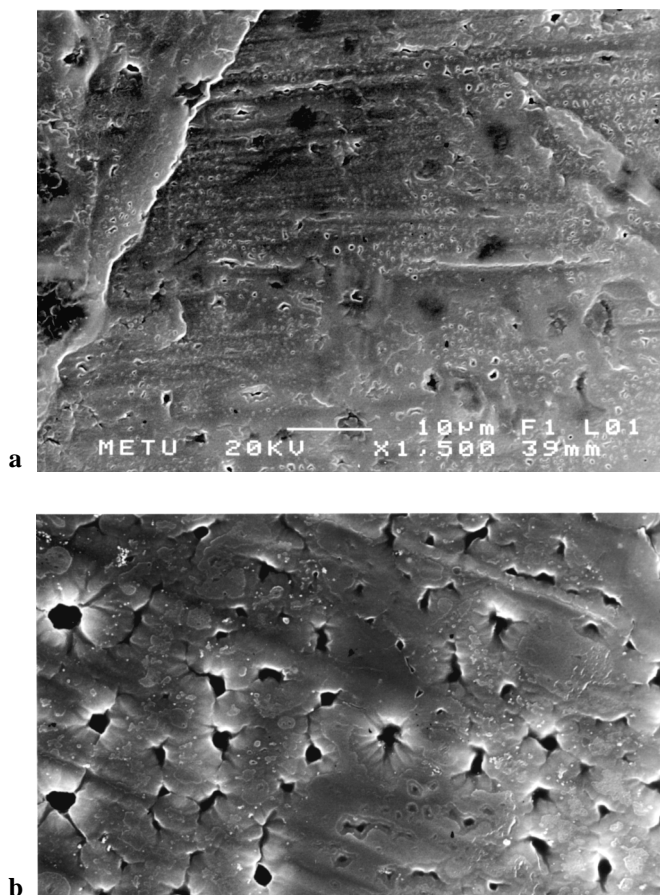
**Figure 2.** DSC curves of thermograms of a) P1/PPy (TBAFB doped); b) PPy (TBAFB doped); c) P1/PPy (PTSA doped); d) PPy (PTSA doped).

### Surface Morphologies

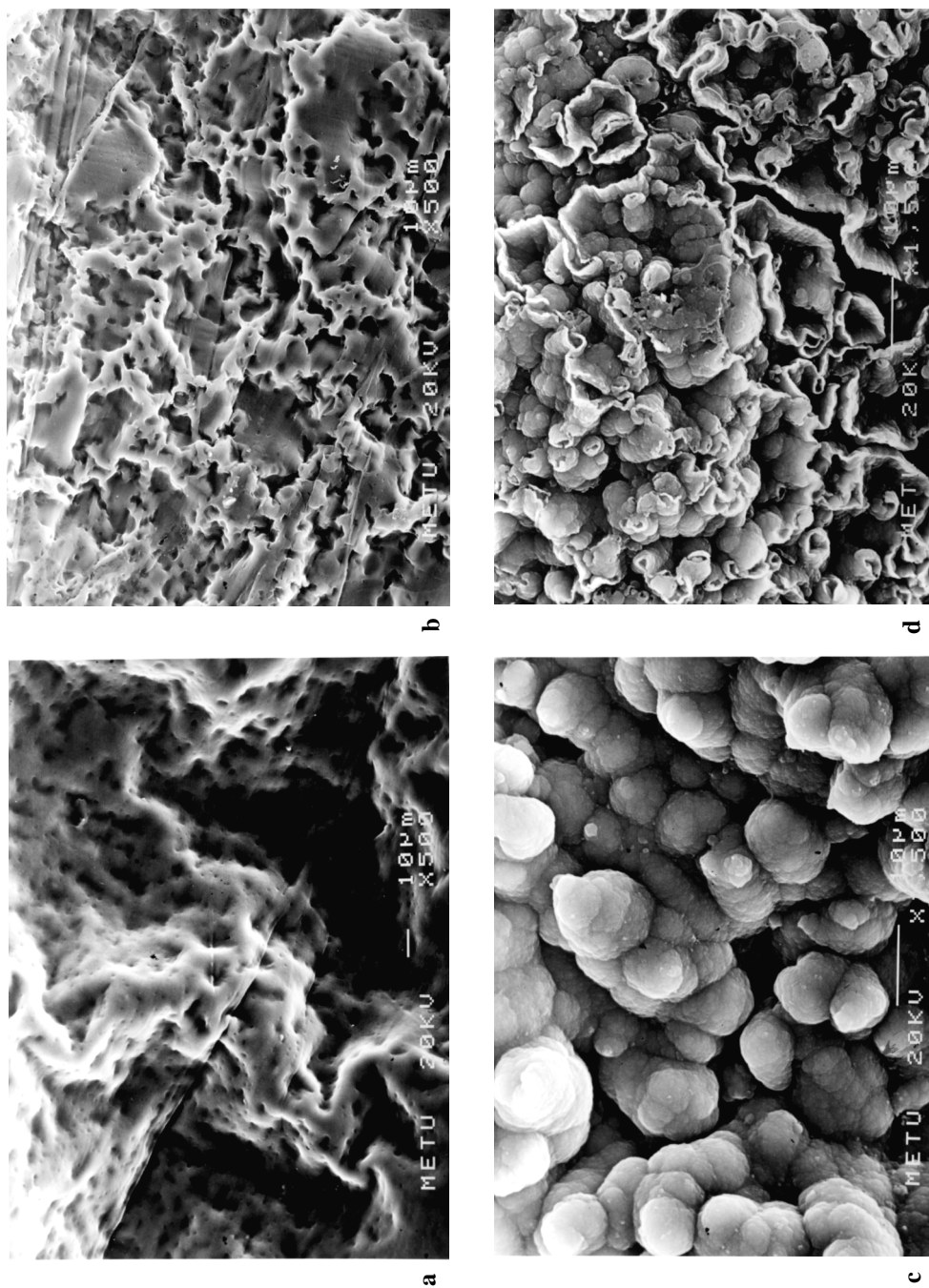
Scanning electron microscopy (SEM) studies were carried out to investigate the morphologies of the films by JEOL JSM-6400.

When the electrode side surface of the PTSA doped P1/PPy unwashed film (Figure 3a) was compared to the washed film (Figure 3b), some holes were observed in the washed films, resulting from the loss of the ungrafted P1.

When the electrode side of TBAFB doped P2/PPy unwashed film (Figure 4a) was compared to the washed film (Figure 4b), rather large losses were observed. Moreover, comparing the solution sides of the P2/PPy films (Figure 4c and 4d), it was observed that the usual cauliflower like structure of



**Figure 3.** SEM films - a) Electrode side of unwashed P1/PPy (PTSA doped); b) Electrode side of washed P1/PPy (PTSA doped).



**Figure 4.** SEM films - a) Electrode side of unwashed P2/PPy (TBAFB doped); b) Electrode side of washed P2/PPy (TBAFB doped); c) Solution side of unwashed P2/PPy (TBAFB doped); d) Solution side of washed P2/PPy (TBAFB doped).



the polymer is popped out in order to let the dissolved, ungrafted P2 to leave the film.

These results were already expected from the blocking percentages of the polymers (70% for P1 and 36% for P2).

## CONCLUSION

Block copolymers of azo-PTHF and PTHF-b-PS-b-PTHF having pyrrole units at both ends with polypyrrole was achieved in two different solvent-electrolyte pairs. Introduction of styrene units into the pristine polymers affects the grafting percentage. Although the polymers were not 100% blocked, thermally stable and electrically conducting polymer films were obtained.

## ACKNOWLEDGEMENTS

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