

CONDUCTIVE COMPOSITES FROM POLYPYRROLE ELECTROPOLYMERIZED IN A POLYURETHANE MATRIX

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ABSTRACT

In order to improve the mechanical properties of polypyrrole, composites were made by electropolymerizing polypyrrole in a polyurethane matrix. Polypyrrole/polyurethane (PPY/PU) composite films containing ClO_4^- , BF_4^- or $\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3^-$ counter ions were made in a variety of solvent systems and characterized by SEM, electronic conductivity, FTIR, and mechanical properties. Composite films showing much greater flexibility than pure polypyrrole were obtained, but their electronic conductivities were substantially lower. Measured conductivities ranged from 0.001 to 8 S/cm, tensile strengths from 44 to 592 psi, and elongation to failure from 3 to 70%.

INTRODUCTION

It is well known that polypyrrole PPY films, synthesized by electrochemical polymerization, show high electrical conductivity with good stability in air^[1-3], but the mechanical properties of PPY need to be improved.

One way of improving the flexibility of the conducting polymer is to make a composite material by electropolymerizing polypyrrole in a matrix of another polymers. Recently, Niwa, Tamamura and Paoli et al.^[4,5] have synthesized the conductive plastic composite of PPY-poly(vinyl chloride) and studied the electrical properties of the conductive composite (PPY/PVC), Lindsey and Street^[6] have studied the conductive composites from PPY and polyvinyl alcohol (PPY/PVA).

In this paper, we describe an electrically conductive composite polypyrrole/polyurethane (PPY/PU), which was obtained by the electrochemical polymerization of pyrrole in a polyurethane matrix. The composite of PPY/PU were characterized by FTIR, SEM, electronic conductivity, and mechanical properties.

EXPERIMENTAL

1. Preparation of the composites

Polypyrrole/polyurethane (PPY/PU) composites were prepared by the electrochemical polymerization of pyrrole onto a PU coated electrode, usually nickel, gold, or indium-doped tin oxide (Indalux-Sandus Roe), at a constant current density. The PU films were coated from a tetrahydrofuran (THF) solution of a PU and pyrrole (PY) solution of commercial Estane R5714-1 Resin (Polyether-

based polyurethane resin B. F. Goodrich).

The electrochemical polymerization was carried out in various solvent mixtures: acetonitrile (ACN)/water (H_2O) (99/1); ACN/ethylene glycol (EG) (50/50); and EG/ H_2O which contained 0.2 M of freshly distilled pyrrole and various electrolyte salts including tetraethylammonium fluoroborate (Et_4NBF_4), tetramethylammonium fluoroborate (Me_4NBF_4) or perchloric acid (HClO_4). The one compartment glass cell was equipped with a Nickel counter electrode. The amount of PPY in the composite was varied by changing the electropolymerization time. The thickness of the initial PU film was controlled by adjusting the concentration of the resin solution. All electropolymerizations were carried out using a PARC Model 173 Potentiostat/Galvanostat.

Pyrrole was purified by distillation over NaOH under N_2 ; the other chemicals were A. R. grade and used without further purification. Water was purified using a reverse osmosis distillation system.

2. Characterization of composites

- (1). The thickness of film was measured by a Digital micrometer to a precision of $\pm 10 \mu\text{m}$.
- (2). Infrared Spectra; The infrared spectra were obtained on a Digilab Model FTS-14 Fourier Transform Spectrophotometer. Each spectrum was recorded at a resolution of 8 cm^{-1} with a total of 10 scans. The spectra were stored in the system's memory for further data manipulation. The frequency scale is calibrated in the reported frequency of 1 cm^{-1} . All the samples were in KBr powder. In order to ensure complete removal of water, the pellets were kept in a vacuum oven at 120°C over a period of time, until the spectra no longer changed.
- (3). Scanning electron micrographs (SEM) were obtained using Cambridge Model 35—CF Instrument at room temperature.
- (4). Conductivity: The electrical conductivity was measured by a four point-probe contact instrument.
- (5). Mechanical Properties: The mechanical properties were measured by an Instron Model 1123 mechanical tester.
- (6). Electrochemical Experiments: Instrumentation for electrochemical experiments consisted of a PARC Model 173 potentiostat/galvanostat and PARC Model 175 wave form generator and Yokogawa 3033 Y-X-T Recorder. All electrochemical experiments were performed using a three electrode configuration in a two-compartment glass cell containing Au counter and SCE reference electrode separated from the working electrode compartment by a Luggin capillary and closed wetted tap. Solution were deoxygenated with nitrogen.

RESULTS AND DISCUSSION

1. Electropolymerization

The electro-oxidation of pyrrole using a PU-coated Ni anode gives rise to brown-black composite films which can be peeled off from the electrode surface. These composite films are much easier to peel off than pure PPY films and are

flexible and self supporting.

Depending on the electropolymerization conditions three types of composite films could be prepared. At high current densities, a pure polypyrrole layer tended to form at the edges and underneath the polyurethane layer (at very high current densities gas evolution occurred with consequent buckling and/or detachment of the film). At lower current densities (1 mA/cm^2) and relatively short times (10 minutes) an apparently homogeneous composite is produced with the electrode side tending to be polypyrrole-rich and more conductive than the PU-rich solution side. It should be noted that when these films are drawn beyond a certain point the polypyrrole regions separate while the PU regions continue to elongate. This suggests that at some submicroscopic level the polypyrrole is incorporated in domains, and is not homogeneous on a molecular level.

At low current densities and long polymerization times the polypyrrole tends to grow on both the inside (electrode) and outside solution surfaces of the composite film. The polypyrrole region can be grown to a thickness many times that of the original composite.

(1) Constant current polymerization

Table 1 shows the PPY/PU composites prepared in various solvent systems with various electrolyte at a current density of 15 mA/cm^2 . The measured conductivities of the PPY/PU composite films range from 10^{-1} to 10^{-3} S/cm . The measured tensile strengths and elongations of the PPY/PU composites range from 44 to 592 psi and 3 to 70% respectively. The composites are clearly related to the solvent system in which the polymerization is carried out. The best tensile strength was 592 psi for the PPY/PU composite film which was prepared from the $\text{H}_2\text{O}/\text{EG}$ (50/50) solvent system. This solvent system was excellent for preparing the highest tensile strength and the homogeneous PPY/PU composites as shown in Fig. 1. With the PU-coated nickel electrode in the $\text{H}_2\text{O}/\text{HClO}_4$ system, the PU film always peeled off from nickel electrode so that this solvent system was not appropriate to prepare PPY/PU composite.

Even though the best mechanical properties of PPY/PU composite films were obtained from the $\text{H}_2\text{O}/\text{EG}$ solvent system, the measured conductivities of these films was only 10^{-3} – 10^{-2} S/cm . In an attempt to improve these values, the

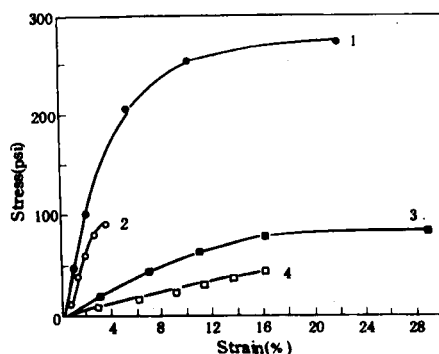


Fig. 1 Stress-strain curve for PPY/PU composite films prepared from different solvent systems.

1. PPY/PU (BF_4^-) from $\text{H}_2\text{O}/\text{EG}$ 2. PPY/PU (BF_4^-) from $\text{H}_2\text{O}/\text{ACN}$
3. PPY/PU (BF_4^-) from EG/ACN 4. PPY/PU (ClO_4^-) from $\text{H}_2\text{O}/\text{HClO}_4$

Table 1 PPY/PU Composites prepared in various solvent systems

Solvent	Electrolyte / Pyrrole (0.1 M) (0.2 M)	Time (Min.)	Thickness of Film (mm)	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	Tensile Strength (psi)	Elongation at Break (%)
H ₂ O	HClO ₄	2	0.035	1.32×10^{-1}	273	56.5
H ₂ O	HClO ₄	5	0.095	4.8×10^{-2}	103	24
H ₂ O	HClO ₄	10	0.11	3.2×10^{-2}	44	16
H ₂ O/ACN* (1/99)	Et ₄ NBF ₄	2	0.025		345	8.75
H ₂ O/ACN (1/99)	Et ₄ NBF ₄	5	0.04	4.37×10^{-3}	172	3
H ₂ O/ACN (1/99)	Et ₄ NBF ₄	10	0.115	9.15×10^{-2}	87	3.75
EG**/ACN (50/50)	Et ₄ NBF ₄	2	0.07	5.5×10^{-2}	153	74
EG/ACN (50/50)	Et ₄ NBF ₄	5	0.115	1.7×10^{-2}	82	29
EG/ACN (50/50)	Et ₄ NBF ₄	10	0.145	1.4×10^{-1}	69	7.5
H ₂ O/EG (50/50)	Me ₄ NBF ₄	2	0.02	2.8×10^{-2}	592	47
H ₂ O/EG (50/50)	Me ₄ NBF ₄	5	0.04	1.1×10^{-2}	590	28.25
H ₂ O/EG (50/50)	Me ₄ NBF ₄	10	0.095	2.5×10^{-3}	275	22

* ACN=acetonitrile

** EG=ethyleneglycol

concentration of pyrrole was increased, the current density of polymerization was decreased, and the solvents used for casting the PU film on the electrode were changed. The experimental results for this set of composites is shown in Table 2. The results from Table 2 show that when the PU films are cast from a PU solution of pyrrole and tetraethylammonium fluoroborate the conductivity of the PPY/PU composites is approximately 10^{-1} S/cm , better than other casting solvents. But the PPY/PU composite films so produced were brittle. This can be attributed to their greater PPY content resulting from the more efficient introduction of pyrrole during casting rather than slowly by diffusion through the film from the electropolymerization solution as in the previous case.

PPY/PU toluenesulfonate composites and polypyrrole toluenesulfonate were prepared in mixtures of ethyleneglycol and acetonitrile solvents. The results in Table 3 show that the best conductivity of PPY/PU toluenesulfonate composite (PPY side = 8.5 S/cm , PU side = 6.8 S/cm) was obtained. In this sample which contained 97.7% polypyrrole and 2.3% PU (obtained by dissolving out the PU with THF) the thickness increased approximately 42 times after polymerization. It must be concluded that much of this film was pure PPY probably formed on both

Table 2 PPY/PU Composites prepared from various solvent casting PU film on electrode

Solvent * with stirring	Electrolyte Pyrrole (M/M)	Current Density (mA/cm ²)	Time (Min.)	PU Film from Solvent	Thickness of PU/PP film (mm)	Conductivity (Ω ⁻¹ cm ⁻¹)	Tensile Strength at Break (psi)	Elongation (%)
EG/H ₂ O (50/50)	<u>Me₄ NBF₄ (0.1 M)</u> Pyrrole (1 M)	0.6	20	Pyrrole	0.007	1.98 × 10 ⁻³	362.5	17
EG/H ₂ O	<u>Me₄ NBF₄ (0.1 M)</u> Pyrrole (1 M)	0.6	90	Pyrrole	0.017	1.9 × 10 ⁻³	236.35	6.5
EG/ACN (50/50)	<u>Me₄ NBF₄ (0.1 M)</u> Pyrrole (1 M)	1	35	Pyrrole+ Me ₄ NBF ₄	0.02	1.7 × 10 ⁻¹		
EG/ACN	<u>Me₄ NBF₄ (0.1 M)</u> Pyrrole (1 M)	1	120	Pyrrole+ Me ₄ NBF ₄	0.17	1.4 × 10 ⁻¹		
EG/ACN (50/50)	<u>Et₄ N (CH₃ C₆H₄SO₃) (0.1 M)</u> Pyrrole (1 M)	1	60	THF+ Pyrrole	0.07	1.7 × 10 ⁻¹	249.4	4
EG/ACN	<u>Et₄ N (CH₃ C₆H₄SO₃) (0.1 M)</u> Pyrrole (1 M)	1	60	Pyrrole	0.085	1.14 × 10 ⁻²		
EG/ACN	<u>Et₄ N (CH₃ C₆H₄SO₃) (0.1 M)</u> Pyrrole (1 M)	1	60	Pyrrole + Me ₄ NBF ₄	0.057	1.46 × 10 ⁻¹		

Table 3 Improved electrical properties of PPY/PU composites

Solvent *	Electrolyte Pyrrole (M/M)	Current Density (mA/cm ²)	Time (Min.)	Thickness of PP/PU Film (mm)	Conductivity (Ω ⁻¹ cm ⁻¹)	PU Film from Solvent
EG/ACN (50/50)	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.74 M)	2	270	0.2024	6.4 × 10 ⁻¹	THF+Pyrrole
EG/ACN	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.74 M)	1.5	360	0.207	5.98 × 10 ⁻¹	THF+Pyrrole
EG/ACN	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.74 M)	10	50	0.098	8.5	THF+Pyrrole
EG/ACN	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.74 M)	10	50	0.145	1.78	THF+Pyrrole
EG/ACN	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.74 M)	5	30	0.024	1.26	THF+Pyrrole
EG/ACN	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.5 M)	5	30	0.019	10	(Polypyrrole only)
EG/ACN	<u>Et₄N (CH₃C₆H₄SO₃) (0.1 M)</u> Pyrrole (0.5 M)	10	30	0.076	30	(Polypyrrole only)

* EG=Ethylene Glycol ACN=Acetonitrile

sides of a much thinner composite layer. The conductivity of another PPY/PU composite film was 1.26 S/cm (PPY side) and 1.03 S/cm (PU side). This film contained 74% polypyrrole and 26% polyurethane (by weight); the thickness here increased 2.8 times on electropolymerization.

(2) Constant voltage polymerization

Data for PPY/PU composites prepared at constant potential are shown in Table 3. All experiments in Table 4. were performed in a one-compartment cell using a PU coated nickel working electrode, a nickel counter electrode, and a SCE reference electrode in a Luggin capillary. An uncompensated junction potential is included in these measurements and is designated by (SCE). The results of Table 4 show that potentials should not be less than 0.8 V to prepared PPY/PU composites; PPY/PU films prepared at potentials less than 0.8 V had poor conductivity.

Table 4 PPY/PU Composites prepared in CH₃CN at constant potential

Solvent	Electrolyte Pyrrole (M/M)	Potential (v) (SCE)	Time (Min.)	Thickness of PP/PU Film (mm)	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)		PU Film from Solvent
					PP side	PU side	
CH ₃ CN	Me ₄ NBF ₄ (0.1 M) Pyrrole (1 M)	+0.65 V	140	0.048	2.24×10^{-3}	insulator	THF + Pyrrole
CH ₃ CN	Me ₄ NBF ₄ (0.1 M) Pyrrole (1 M)	+0.8 V	40	0.0415	3.2×10^{-3}	insulator	THF + Pyrrole
CH ₃ CN	Me ₄ NBF ₄ (0.1 M) Pyrrole (1 M)	+0.8 V	100	0.044	4.45×10^{-1}	1.52×10^{-1}	THF + Pyrrole with black carbon powders
CH ₃ CN	Me ₄ NBF ₄ (0.1 M) Pyrrole (1 M)	+1.0 V	30	0.132	1.43×10^{-1}	1.15×10^{-1}	THF + Pyrrole
CH ₃ CN	Me ₄ NBF ₄ (0.1 M) Pyrrole (1 M)	+1.0 V	40	0.098	3.78×10^{-1}	3.78×10^{-1}	THF + Pyrrole

2. Conductivity and mechanical properties

The measured conductivities of PPY/PU composite films range from 10^{-3} to 8 S/cm, depending upon the thickness of the initial PU film and on the electropolymerization time. Table 4 shows the conductivity of a PPY/PU film which was prepared by electropolymerization at 0.8 V for 40 minutes to be $3.2 \times 10^{-3} \text{ S/cm}^{-1}$ (PPY side) and insulator (PU side). When the electropolymerization time was increased to 100 minutes, the conductivity increased to $4.45 \times 10^{-1} \text{ S/cm}^{-1}$ (PPY side) and 1.52×10^{-1} (PU side). The conductivity of the composites is directly proportional to the amount of polypyrrole present. In Table 3 the conductivity of PPY/PU toluenesulfonate composite is 8.5 S/cm (PPY side) and 6.8 S/cm (PU side); the thickness increased 12 times after electropolymerization. The conductivity of another PPY/PU toluenesulfonate composite film was 1.25 S/cm (PPY side) and 1.03 S/cm (PU side); in this case the thickness increased 2.8 times. The similar conductivity for both sides of the PPY/PU toluenesulfonate composites may indicate excellent homogeneity of the PPY/PU composites, or the formation of almost pure PPY layers on both

sides of the composites at long polymerization times.

The measured tensile strength and elongation of the PPY/PU composites ranged from 44 to 592 psi and 3 to 7% , depending on the electropolymerization time. Fig. 2 . shows the stress-strain curves for PPY/PU composite films obtained from H₂O/ACN (1/99) solution of pyrrole (0.2 M) containing the counter anion tetraethylammonium fluoroborate (0.1 M) after at different intervals of electropolymerization times. The experimental results show that the tensile strength of PPY/PU composite films decreases as the electropolymerization increases (i. e. as the PPY content increases).

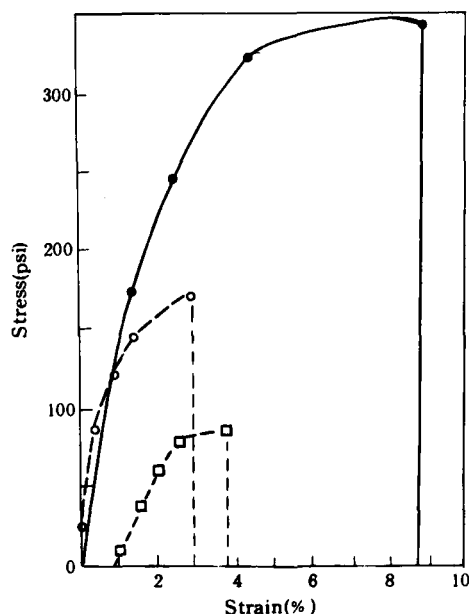
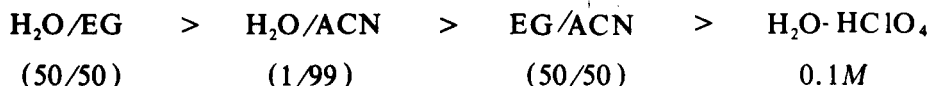


Fig. 2 Stress-strain curve for PPY/PU composite films with different electropolymerization times;
 ● — 2 mins ○ — 5 mins □ — 10 mins

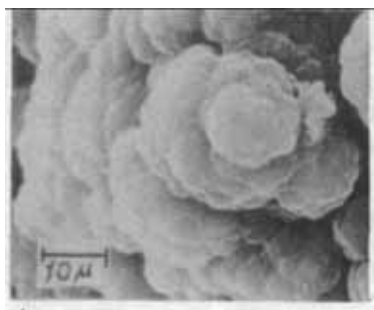
Fig. 1 is the stress-strain curves for PPY/PU composite films prepared from different solvent systems. The experimental results show that the best tensile strength of PPY/PU composite film is obtained from the H₂O/EG (50/50) solvent system. The tensile strength order of PPY/PU composite films obtained from different solvent systems is as follows :



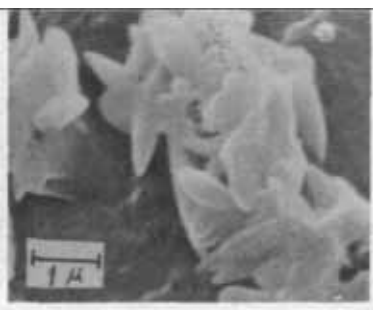
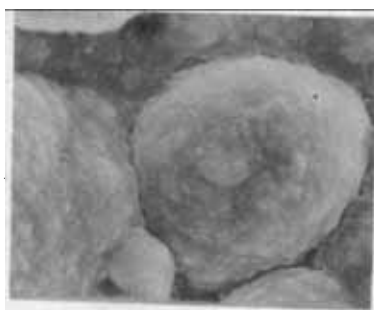
3. Infrared spectra of PPY/PU composites

The PU film (Estane[®] 5714-1 resin), PPY (BF₄⁻), PPY (CH₃C₆H₄-SO₃⁻), and PPY/PU (BF₄⁻), PPY/PU (ClO₄⁻) composites were characterized by FTIR. The results of the spectra of PPY and PPY/PU composites all show the band at 3410 cm⁻¹ which is assigned to the N-H stretching mode, and the bands at 1550 , 1400 , 1300 , 1180 , 1040 , and 900 cm⁻¹ are characteristic of polypyrrole.

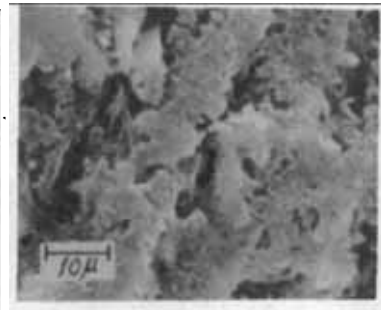
3-1-A



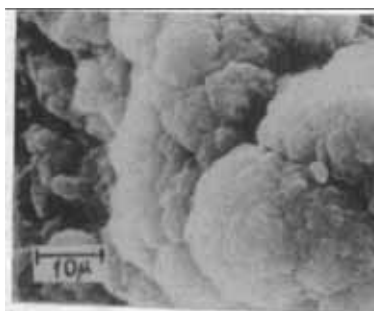
3-1-B

3-2-A
10μ

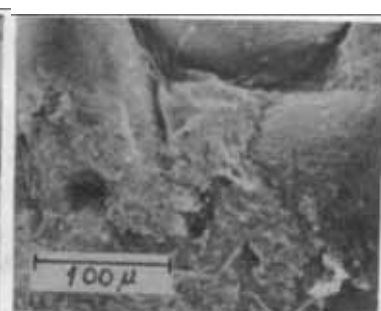
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3-3-A



3-3-B



3-4-A



3-4-B

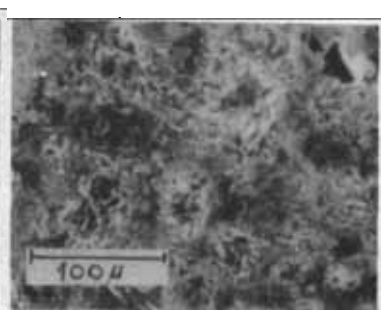


Fig. 3 SEM pictures of PPY/PU composite films formed from different solvent and different anions

Fig. 3-1 show the SEM of PPY/PU composite which is prepared from EG/H₂O (50/50).

Fig. 3-2 PPY/PU composite is prepared from H₂O/ACN (1/99).

Fig. 3-3 PPY/PU composite is prepared from EG/ACN (50/50).

Fig. 3-4 is the SEM of PPY/PU (CH₃C₆H₄-SO₃⁻) composite from EG/ACN (50/50) solvent system.

REFERENCES

- [1] Wynne, K. J. and Street, G. B., *Ind. Eng. Chem., Prod. Res. Dev.*, **1982**, 21, 23.
- [2] Diaz, A. F., Gastillo, J. I., Logan, J. A. and Lee, W-Y., *J. Electroanal. Chem.*, **1981**, 129, 115; Diaz, A. F. and Kanazawa, K. K. *J. Chem. Soc. Commun.*, **1979**, 635.
- [3] Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, M. D. and Kwak, J. J., *Synth. Met.*, **1981**, 1, 329.
- [4] Niwa, O. and Tamamura, T., *J. Chem. Soc. Commun.*, **1984**, 817.
- [5] Paoli, M. D.; Waltman, R. J.; Diaz, A. F., and Bargon, J., *J. Polym. Sci., Polym. Chem. Ed.*, **1985**, 23, 1687.
- [6] Lindsey, S. E., and Street, G. B., *Synth. Met.*, **1984/85**, 10, 67—69.