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Chemical synthesis of some Schiff base-type polymers containing pyrrole units

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Summary

The synthesis of three Schiff-base type monomers containing pyrrole units was performed. Their polymerization was carried out by chemical oxidation with $(NH_4)_2S_2O_8$. Some preliminary thermal and electrical properties were determined.

Introduction

Electrically conductive polymers have received considerable attention in recent years due to both theoretical aspects and practical applications [1,2]. Among these polymers a great deal of work was devoted to polyheterocycles, i.e., polypyrrole and polythiophene, prepared by chemical and electrochemical polymerization because they present an increased environmental and thermal stability in both conductive and neutral states. Unfortunately, important disadvantages of conducting polymers such as infusibility and insolubility in all known organic solvents are preserved in the case of polypyrrole and polythiophene. Therefore a variety of pyrrole and thiophene derivatives along with polymers derived from them have been synthesized in order to improve both the physical and electronic properties and solution and melt processability. The introduction of bulky substituents in β-position of the five- membered heterocycle was the most adequate method to achieve a molecular control of the properties of conducting polymers [3]. A less used direction was to obtain modified structures based on heterocycles by copolymerization.Thus, Hartel et.al [4] prepared polythiophenediylvinilene via a Wittig polycondensation reaction and Tanaka et. al [5] synthesized copolymers of thiophene and acetylene by electrochemical polycondensation of α,ω-dithienylpolyenes. Finally, Kossmehl and Greczmel have prepared poly(1,2-di(2-furyl)ethylene) by chemical oxidation of trans-1,2- di(2-furyl)ethylene with several inorganic oxidants [6].

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Copolymers containing thiophene and diacetylene units were synthesized using the Glesser coupling reaction from thiophene- based diethynyl monomers [7].

Fully aromatic polyazomethines have been known as an important class of thermally stable and highly conjugated materials. They were obtained by the conventional solution polycondensation of aromatic diamines with aromatic dialdehides and their electrical conductivity varies between 10^{-12} $\Omega^{-1}.cm^{-1}$(neutral state) and 10^{-7} $\Omega^{-1}. cm^{-1}$ (oxidized state)[8,9].

In this paper we report some results concerning the synthesis and characterization of polymers that combine the functionalities of pyrrole and Schiff bases containing alternating 2,2'- bipyrrole-diyl rings and azometine units in the main chain. Formally, the polymer structure could be obtained by polycondensation of 5,5'- diformil 2,2'-bipyrrole with hydrazine, 1,4-diaminobenzene and 4,4'-diaminobiphenyl. Experimentally, the polymers were synthesized by oxidative coupling of monomers obtained by condensation of pyrrole 2-carboxaldehyde with the corresponding diamines.

Experimental

Materials

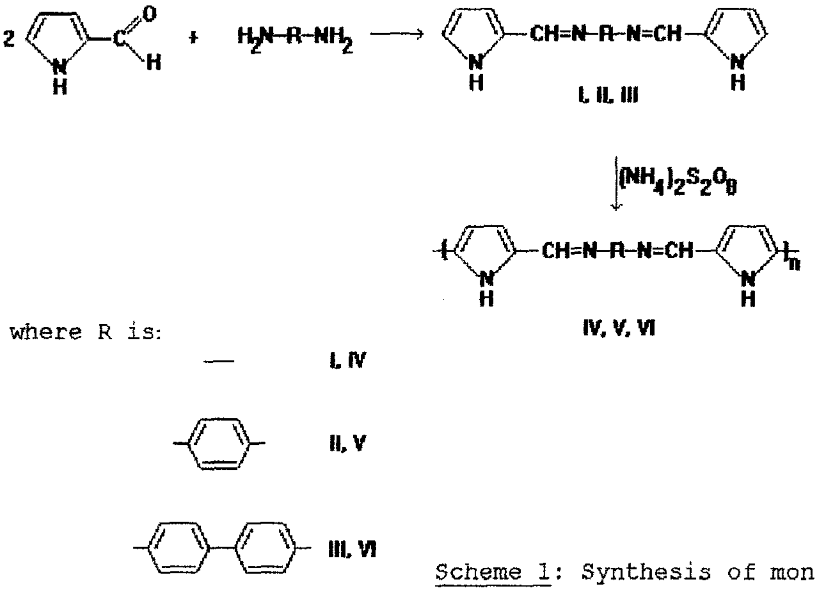
The chemicals used in the synthesis of the monomers were used as received or purified as described below. Pyrrole-2-carboxaldehyde (Aldrich, 99%),pyrrole (Carlo Erba, 98%) p-toluenesulfonic acid (Aldrich, 99%), hydrazine monohydrate (Fluka AG, 98%), 4,4'-diaminobiphenyl (Flucka AG, p.a.) and ammonium peroxidisulfate (Merck, p.a.) were used as recieved. p-Phenylenediamine (Schuchardt Munchen, p.a.) was twice recrystallized from methanol. Toluene was distilled from sodium before use.

Instrumentation

The melting points reported were determined on a Boetius Microscope. Infrared spectra were obtained on a Perkin Elmer 577 infrared spectrometer.Proton NMR spectral analyses were performed on a JNM-C60HL, 60MHz apparatus, at 20°C using DMSO-d_6 as solvent and tetramethylsilane, TMS, was used as an internal standard and chemical shifts (δ) are recorded in ppm from TMS. Thermogravimetric data were recorded with a Paulik-Paulik- Erdey (Budapest) apparatus, heating rate: 12°C/min. The UV spectra were registered using a Specord M80 Carl Zeiss Jena spectrophotometer. The conductivity measurements were performed on disc-shaped samples (13 mm diameter) prepared by pressing the polymer powder in mould under a pressure of 10^5 N/cm^2. The discs were provided with vacuum evaporated silver electrodes of circular form. In order to remove current leakages on the surface, the electrodes had a diameter of only 10mm and were centrally placed on both sides of the disc. The conductivity measurements were carried out in dry N_2 at normal pressure using an already described chamber [10].

Monomers

The synthesis of monomers is outlined in Scheme 1.



Scheme 1: Synthesis of monomers and polymers

Synthesis of I

A 250 ml 3-necks round bottom flask equipped with a Dean-Stark trap, nitrogen inlet-outlet, and magnetic stirrer was charged with pyrrole-2-carboxaldehyde (5.991g, 0.063 mol), hydrazine monohydrate (1.5g, 0.03 mol), p-toluenesulfonic acid (0.05g) and 100ml toluene. Nitrogen was sparged through the reaction mixture for 15 minutes, then the mixture was heated to reflux with stirring. The reaction was maintained at reflux for 4 hours removing continuously the eliminated water as a toluene- water azeotrope The reaction mixture was allowed to cool and the solid product was filtrated, dried, two times recristalized from 1.2-diclorethane. Yield 3.739g (67%) of yellow-green crystals with m.p. 158°C.

Analysis. Calculated for $C_{10}H_{10}N_4$ (M_w=186): C, 64.48%; H, 5.42%; N,30.10%. Found: C, 63.70%; H,6.48%; N:28.30%. UV absorptions (in methanol): 254 and 357nm. ^{1}H-NMR (in DMSO-d_6): 6.2(m, 2H from position 4 of pyrrole ring), 6.6(m, 2H, from position 3 of pyrrole ring), 7.0(m, 2H, from position 5 of pyrrole ring) and 8.4(s, 2H, -CH=N-). IR absorptions:

3250cm^{-1} (νNH), 1650 (ν C=N), 1555 cm^{-1} (νC=N), 1555, 1425 cm^{-1}, 1150 and 620 cm^{-1} (pyrrole ring), 1050 cm^{-1} (βCH) and 750 cm^{-1}(γCH).

Synthesis of II

II was synthesized using a similar procedure to that employed for the synthesis of I except that 1.4-diaminobenzene was used instead of hydrazine hydrate. Yield: 89%, yellow -brown crystals with m.p. 201-202°C.

Analysis. Calculated for $C_{16}H_{14}N_4$ (MW=262): C, 7.25%; H, 5.38%; N,21.36%. Found: C, 74.02%; H, 4.90%; N, 19.62%. UV absorptions (in methanol): 241, 297 and 367nm. ^{1}H-NMR (DMSO-d_6): 6.35(m, 2H from position 4 of pyrrole ring), 6.85(m, 2H, from position 3 of pyrrole ring), 7.15 (m, 2H, from position 5 of pyrrole ring), 7.40 (m 4H, for phenylene ring) and 8.4 (s, 2H, -CH=N-). IR absorptions: 3250cm^{-1} (νNH), 1630 cm^{-1} (νC=N + νCC from C_6H_6), 1500cm^{-1} (νCC from C_6H_6), 1425 and 1145 cm^{-1} (pyrrole ring), 1050 cm^{-1} (βCH from pyrrole), 830 cm^{-1} (γCH from p-C_6H_4-) and 750cm^{-1} (γCH from pyrrole).

Synthesis of III

III was synthesized by using 4.4'-diaminobiphenyl in the same manner as described above. Yield 82%, orange crystals with m.p. 245°C.

Analysis. Calculated for $C_{22}H_{18}N_4$ (MW=338): C, 78.08%; H, 5.36%; N,16.56%. Found: C, 78.68%; H, 4.50%; N, 17.10%. UV absorptions (in methanol): 239, 294 and 361nm. ^{1}H-NMR (DMSO-d_6): 6.35(m, 2H from position 4 of pyrrole ring), 6.85(m, 2H, from position 3 of pyrrole ring), 7.15 (m, 2H, from position 5 of pyrrole ring), 7.4- 8.0 (m 4H, for phenylene ring) and 8.55 (s, 2H, -CH=N-). IR absorptions: 3250cm^{-1} (νNH), 1630 cm^{-1} (νC=N), 1600 cm^{-1} and 1500cm^{-1} (νCC from C_6H_6),1550, 1415, 1130 and 640 cm^{-1} (pyrrole ring), 1050 cm^{-1} (βCH from pyrrole), 830 cm^{-1} (γCH from p-C_6H_4-) and 750cm^{-1} (γCH from pyrrole).

Polymerization

Into a 100 ml 3-necked round bottom flask equipped with a condenser and a magnetic stirrer, were introduced 0.05 mol of monomer and 200 ml methanol. 0.1 mol $(NH_4)_2S_2O_8$ was dropped as an 1M aqueous solution during 15 minutes. The reaction mixture was stirred and maintained for 24h at room temperature. The black or dark-brown precipitate was filtered and washed with water, methanol and acetone to remove the unreacted oxidant, monomer and oligomers. Polymers were dried under vacuum. The structures of the polymers generated by the chemical polymerization are presented in Scheme 1.

Results and Discussion

The reaction sequence of Scheme 1 outlines the synthetic route applied for preparing Schiff base-type monomers I-III carrying two pyrrole groups. More particularly, pyrrole 2-carboxaldehide was reacted with half molar amount of diamine (more exactly 2.1:1 molar ratio) in toluene, at reflux temperature and presence of p-toluenesulfonic acid. The monomers are crystalline and colored products having IR characteristic absorptions at 1630-1660 cm^{-1} assigned to the νC=N bands, 1600 and 1500 cm^{-1} assigned to νC=C from phenyl rings, 1418 cm^{-1} (pyrrole ring vibration), 1040 cm^{-1} assigned to the aromatic in plan stretching from pyrrole ring and characteristic absorption (830 cm^{-1}) of p- substituted phenyl ring. The solubility of the monomers in toluene and 1,2-diclorethane decreases from I to III.

The polymerization of these monomers and pyrrole(for comparison) was performed by an oxidative coupling reaction with $(NH_4)_2S_2O_8$ in methanol at room temperature. The incatenation is probably a result of a coupling reaction of two pyrrole rings through their α-positions. The polymers had separated from the solution as black or dark-brown powders, partially soluble in polar organic solvents (DMF, DMSO). The yields and thermal degradation of these polymers are presented in Table I. The IR spectra of polymers present the same characteristic vibrations as their monomers, but the bands are broader and flatter (Figure 1).

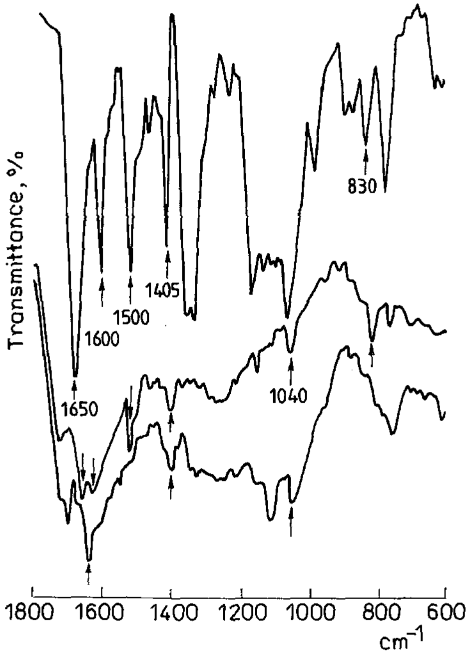


Figure 1: IR spectra of polymers IV-VI

Polymers V and VI containing the aryl group are thermally more stable. The thermostability is up to about 175°C (polypyrrole) and polymer IV), 195°C (polymer V) and 250°C (polymer VI) when they start to lose weight gradually. Therefore, as expected, the thermal stability of the polymers increases the in the order IV<V<VI.

Table 1 Chemical polymerization of pyrrole based monomers

Monomer[a]	Polymerization yield(%)[b]	Thermal stability of polymers		
			weight loss(%)	
		T, °C[c]	400°C	600°C
I	47	175	45	94
II	56	195	35	85
III	52	250	27	75
Pyrrole	67	175	53	86

a) Polymerization conditions: solvent, methanol; temperature, 20°C; time, 24 hours; monomer concentration, 0.05 mol/l; initiator concentration $(NH_4)_2S_2O_8$, 0.1mol/l.

b) After washing with water, methanol and acetone.

c) The begining of thermal decomposition.

Table 2 Electrical properties of polymers

Polymer	mol I_2[a]/ monomer unit	S_{20}, $(\Omega^{-1}.cm^{-1})$	E_a[b], (eV)
IV	0	$4.83\cdot10^{-13}$	0.53
	0.071	$4.5\cdot10^{-10}$	0.28
	0.163	$9.3\cdot10^{-8}$	
	0.243	$8.31\cdot10^{-6}$	
	0.315	$3.45\cdot10^{-4}$	
V	0	$1.67\cdot10^{-12}$	0.52
	0.142	$2.2\cdot10^{-7}$	0.225
	0.247	$7.2\cdot10^{-5}$	
	0.351	$8.04\cdot10^{-4}$	
	0.601	$2.97\cdot10^{-3}$	
VI	0	$8.7\cdot10^{-13}$	0.57
	0.092	$3.16\cdot10^{-10}$	0.355
	0.172	$3.38\cdot10^{-8}$	
	0.253	$2.06\cdot10^{-6}$	
	0.479	$5.667\cdot10^{-4}$	
Polypyrrole	0	$1.25\cdot10^{-12}$	0.85
	0.006	$4.87\cdot10^{-10}$	0.115
	0.033	$5.87\cdot10^{-6}$	
	0.079	$2.07\cdot10^{-4}$	
	0.142	$9.09\cdot10^{-4}$	

a) Doped state.

b) Conduction activation energy.

Some conduction measurements were performed in the doped state of polymer (oxidated form).

The chemical doping of polymers was carried out by exposing the polymer powders to iodine vapors at room temperature and removing the excess of dopant in vacuum. The doping process is slower for polymers IV, V and VI than for polypyrrole. Their d.c. conductivities were monitored by using a standard four-probe technique on pressed pellets and the results are presented in Table 2 and Figure 2. The best values for electrical conductivity and activation energy are shown by polymer V, comparable to polypyrrole (Table II). From Figure 2 it can see that polypyrrole attains the same conductivities as polymers IV-VI, at smaller doping levels.

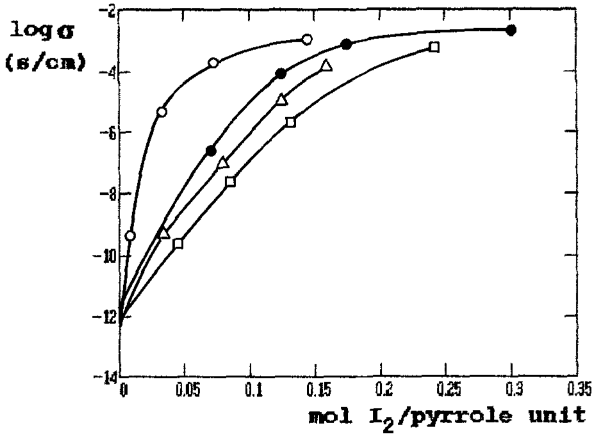


Figure 2 Doping level influence on the electrical conductivities

(△)- IV;
(●)- V
(□)- VI;
(○)- polypyrrole

The results on the pyrrole-based polymer conductivities and that of polypyrrole allow some observations. At low doping level (~0.05 mol I_2/pyrrole unit) the polypyrrole conductivity is higher. When the doping level is increased the electrical conductivity of polypyrrole is comparable with that of polymers IV-VI.

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