

Photoemission and Conductivity Measurement of Poly(*N*-methyl aniline) and Poly(*N*-ethyl aniline) Films

ANJALI A. ATHAWALE,¹ BHAVANA DEORE,¹ MAHESH VEDPATHAK,² SULABHA K. KULKARNI²

¹ Department of Chemistry, University of Pune, Pune 411 007, India

² Centre for Advanced Studies in Material Science and Solid State Physics, Department of Physics, University of Pune, Pune 411 007, India

Received 24 November 1998; accepted 25 March 1999

ABSTRACT: The studies involve the X-ray photoelectron spectroscopy (XPS) and conductivity measurements of poly(*N*-methyl aniline) and poly(*N*-ethyl aniline) films deposited electrochemically at different pH values of -0.96, 2.22, and 3.78 for *N*-methyl aniline and 1.10, 2.22, and 3.78 for *N*-ethyl aniline. The results obtained reveal significant differences in the film properties of the two matrices as a function of pH of solution. These differences are explained on the basis of the competitive reaction products formed during polymerization in the two matrices along with the differences in the electron-donating ability of the methyl and ethyl groups present on the nitrogen (N) atom. These results are further supported by the UV-Visible and IR data. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1286–1292, 1999

Key words: poly(*N*-methyl aniline); poly(*N*-ethyl aniline); pH effect; XPS; conductivity

INTRODUCTION

Electroactive polymers have attracted a great deal of attention during the past decade because of their unusual electrical/electronic properties. A variety of these materials have been explored with a great potential for commercial applications.^{1,2} Among them, polyaniline is one of the most interesting materials because of its moderately high conductivity (10 S/cm) achieved on doping with some acids,^{3,4} possible processability, and good environmental stability. However, in recent investigations it has been observed that substituted derivatives of polyaniline could also serve as a good alternative for polyaniline with comparable conductivities.

In the present article, the influence of pH of solution on the properties of poly(*N*-methyl aniline) and poly(*N*-ethyl aniline) films deposited electrochemically has been investigated with the help of X-ray photoelectron spectroscopy (XPS) analysis and conductivity measurement. These results have been supplemented by UV-Visible (UV-Vis) and IR spectroscopic investigations.

MATERIALS AND METHODS

The monomers *N*-methyl aniline and *N*-ethyl aniline (Qualigen, Glaxo India Ltd., Bombay, India) were doubly distilled before use. Reagent-grade sodium chloride and sulfuric acid (Qualigen, Glaxo India Ltd., Bombay, India) were used as received. Electrolyte solution of pH (-0.96, 1.1, 2.22, and 3.78) were prepared in double-distilled water by adding an appropriate amount of sulfuric acid.

Correspondence to: A. A. Athawale.

Contract grant sponsor: CSIR, DST, and UGC.

Journal of Applied Polymer Science, Vol. 74, 1286–1292 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/051286-07

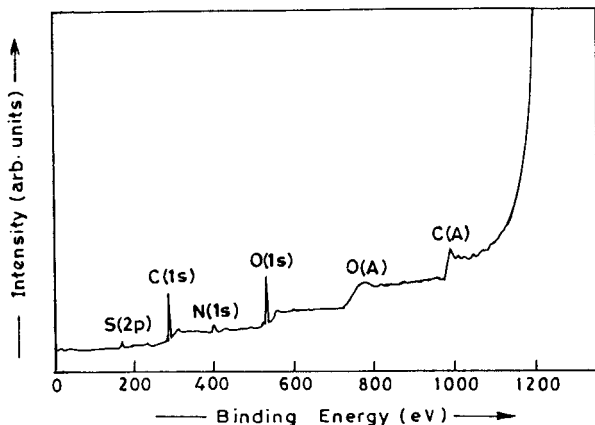


Figure 1 Typical survey scan of poly(*N*-methyl aniline) film obtained at -0.96 pH.

NaCl (5.89 g) was used as a supporting electrolyte at a solution pH of 2.22 and 3.78.

Electrochemical polymerization was carried out in a single compartment cell equipped with three electrodes, SnO_2 : F-coated glass ($2.5 \times 1 \text{ cm}^2$), sheet resistance $10 \Omega/\square$ served as working electrode⁵; platinum as the auxiliary; and a saturated calomel electrode (SCE) as a reference electrode. The polymer films were deposited at a current strength of 0.25 mA at -0.96 and 1.10 pH and 3 mA at 2.22 and 3.78 pH by using a potentiostat/galvanostat (CL 95, Elico Pvt. Ltd., India) at room temperature. The substituted polymer films were washed with distilled water to remove soluble oligomers, excess monomer molecules, and Cl^- anions before characterization. The XPS analysis was carried out using an Escalab MK II (V.G. Scientific, UK) spectrophotometer with an AlK_α and MgK_α twin-anode X-ray radiation source. The concentric hemispherical analyzer (CHA) with 50 eV was used. Serving as an external reference was $\text{Au } 4f_{7/2}$ at 84.0 ± 0.1 eV. Graphitic C 1S at 284.0 eV was used as an internal reference. The conductivity measurement of the sample was measured at room temperature ($\sim 25^\circ\text{C}$) using a two-probe method. A Hitachi (Japan) 220 double-beam spectrophotometer was used to record the absorption spectra of poly(*N*-methyl aniline) and poly(*N*-ethyl aniline) films in the range of 300–900 nm. A Perkin–Elmer 1600 (USA) FTIR spectrophotometer was used to record IR spectra in the range of 400–4000 cm^{-1} . KBr pellets of polymer were prepared in the ratio of 200 : 1 mg.

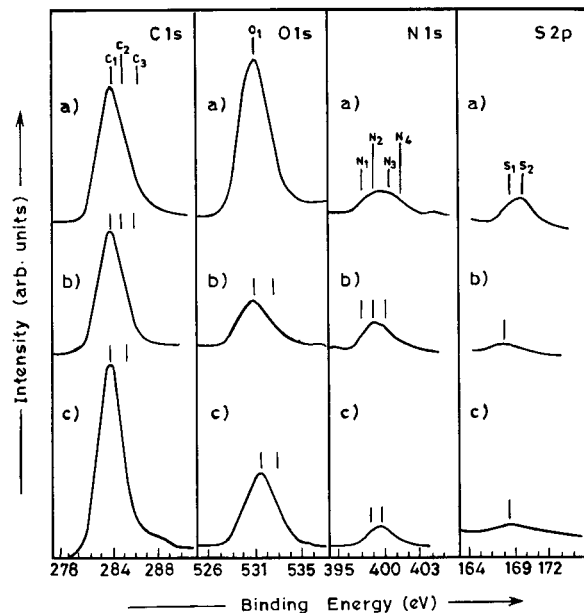


Figure 2 C, O, N, and S core-level spectra of poly(*N*-methyl aniline) films deposited as a function of pH of solution. (a) -0.96 , (b) 2.22, and (c) 3.78.

RESULTS AND DISCUSSION

XPS Studies

Typical XPS survey scan of poly(*N*-methyl aniline) film obtained at -0.96 pH is depicted in

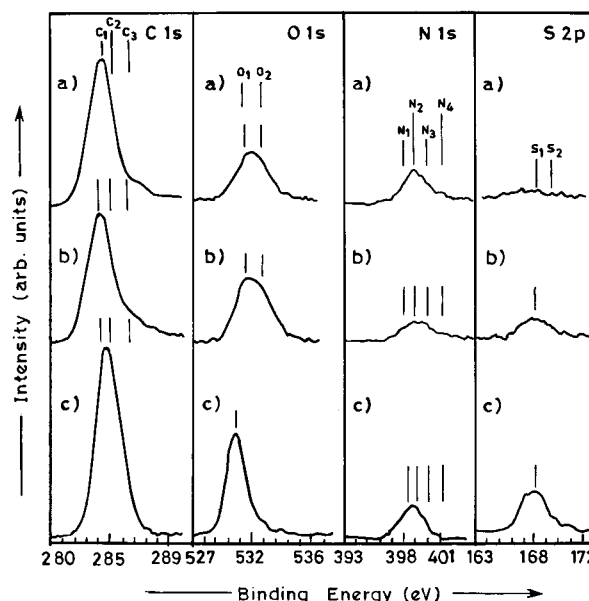


Figure 3 C, O, N, and S core-level spectra of poly(*N*-ethyl aniline) films deposited as a function of pH of solution. (a) 1.10, (b) 2.22, and (c) 3.78.

Table I Relative Composition of C, N, O, and S in Poly(*N*-methyl aniline) and Poly(*N*-ethyl aniline) Films

	pH	C (%)	O (%)	N (%)	S (%)	C : N	S : N
Poly(<i>N</i> -methyl aniline)	-0.96	62.3	24.5	6.5	6.5	9 : 1	0.99 : 1
	2.22	75.7	11.4	8.6	2.6	9 : 1	0.30 : 1
	3.78	81.1	12.4	5.6	0.8	14 : 1	0.14 : 1
Poly(<i>N</i> -ethyl aniline)	1.10	79.2	10.2	7.9	2.5	10 : 1	0.31 : 1
	2.22	74.6	15.5	7.0	2.8	10 : 1	0.40 : 1
	3.78	52.5	36.8	6.8	3.7	8 : 1	0.55 : 1

Figure 1. The spectrum shows the presence of the elements C, N, O, and S, which are the main constituents of the polymer. C and N form the main polymer chain, whereas the S and O in the form of SO_4^{2-} is a dopant anion attached to the polymer chain at N atom. Figures 2 and 3 demonstrate the core-level spectra of C, N, O, and S of poly(*N*-methyl aniline) and poly(*N*-ethyl aniline) films deposited as a function of pH of solution.

From the spectra one can note that the intensity of the peaks of the individual elements vary with the pH of solution. This is observed in terms of varying percent yield of the individual elements together with C : N and S : N ratio. The C : N ratio shows a jump at 3.78 pH in comparison with that at lower pH, whereas the S : N ratio (Table I) exhibits a downward trend in the case of poly(*N*-methyl aniline). On the other hand, poly(*N*-ethyl aniline) shows a reversed sequence.

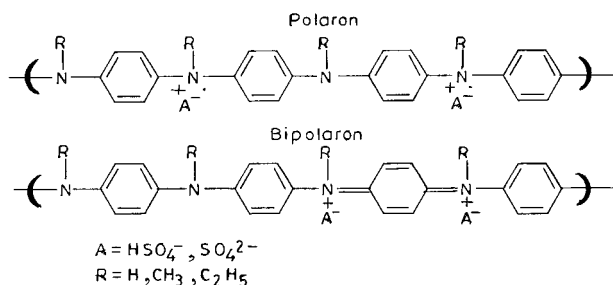
The binding energies for each element are given in Table II. In general, it is revealed that the nitrogen exhibits the presence of four species, whereas for carbon three species are observed together with two each for oxygen and sulfur. Among the four energies for nitrogen, $1s$ the lowest energy peak and $\text{N}_1 \sim 398.5$ eV corresponds to the neutral imine nitrogen present in the polymer network. The neutral amine with different basicity is identified as the N_2 (~ 399.4 eV) peak. The higher binding energy peaks $\text{N}_3 \sim 400.4$ eV and $\text{N}_4 \sim 401.5$ eV may be attributed to the nitrogen atoms with increasing positive charge, ignoring any shift induced by polymerization defects.⁶⁻⁸ The N_3 peak is attributed to the delocalized polaron-type structure (i.e., radical cation) that is derived from the oxidation of amine, whereas preferential protonation path of imine leads to the configuration of that of N_4 (bipolaron). Any delocalization of

Table II Binding Energies in Electronvolts and Line Widths of N 1s, C 1s, O 1s, and S 2p Lines

pH		Nitrogen				Carbon			Oxygen		Sulfur		
		N_1	N_2	N_3	N_4	C_1	C_2	C_3	O_1	O_2	S_1	S_2	
Poly(<i>N</i> -methyl aniline)	-0.96	B.E	398.3	399.4	400.5	401.3	284.1	285.0	286.4	531.1	—	168.4	169.5
		FWHM			4.4			3.2		2.9		2.8	
	2.22	B.E	398.3	399.4	400.5	—	284.0	285.1	286.5	531.3	532.7	168.1	—
		FWHM			3.2			3.0		3.3		2.7	
	3.78	B.E	398.6	399.5	—	—	284.0	285.2	—	531.3	532.8	168.3	—
		FWHM			3.0			2.4		3.4		2.3	
Poly(<i>N</i> -ethyl aniline)	1.10	B.E	398.5	399.3	400.4	401.3	284.1	285.2	286.6	531.2	532.6	168.2	169.4
		FWHM			2.9			2.6		3.3		2.4	
	2.22	B.E	398.3	399.2	400.3	401.5	284.1	285.2	286.3	531.2	532.6	168.2	—
		FWHM			3.0			2.6		3.1		2.8	
	3.78	B.E	398.5	399.3	400.3	401.3	284.2	285.0	286.4	530.9	—	168.1	—
		FWHM			2.9			2.6		2.4		2.4	

BE, Binding energy; FWHM, full width at half maximum.

electrons over nitrogen of N_4 -type structure to adjacent quinonic ring to give the polaron lattice would lead to its conversion to N_3 type of structure. Among the four structures, the N_3 peak ascribed to polaron lattice plays an important role in the electrical conductivity in polymers.⁹ It has a net spin of $\frac{1}{2}$, whereas the N_4 peak represents the bipolaron with a net spin of 0 leading to a decrease in conductivity. The structures are as follows.



In the case of C 1s, the C_1 (~ 284 eV) is attributed to the neutral C—C and C—H bonds,¹⁰ whereas $C_2 \sim 285$ eV and $C_3 \sim 286.5$ eV are assigned to the carbon bonded with polaronic and bipolaronic type of nitrogen atoms. O 1s peak observed at 531.1 eV is due to the most negatively charged component, and its position agrees well with that of oxygen in the sulfate group, whereas the additional peak of O 1s at 532.8 eV is attributed to the adsorbed water molecules.¹¹ Larger line width for this peak is indicative of the presence of water molecules in the polymer network that is responsible for hydrolysis reaction (i.e., formation of benzoquinone). The binding energy of S $2p_{3/2}$ and S $2p_{1/2}$ peaks at 168.3 and 169.3 eV indicate the presence of sulfate anion and adsorbed molecular H_2SO_4 on polymer surface, respectively. It is worth noting that Na^+ is also observed in a very small amount of $\sim 0.5\%$ in the films deposited at a pH of 2.22 and 3.78, respectively. From Table II

Table III pH Dependent Conductivity Values

Species	pH of Solution	Conductivity (S/cm)
Poly(<i>N</i> -methyl aniline)	−0.96	5.91×10^{-6}
	2.22	9.00×10^{-7}
	3.78	7.35×10^{-8}
Poly(<i>N</i> -ethyl aniline)	1.1	8.00×10^{-5}
	2.22	7.40×10^{-4}
	3.78	1.34×10^{-3}

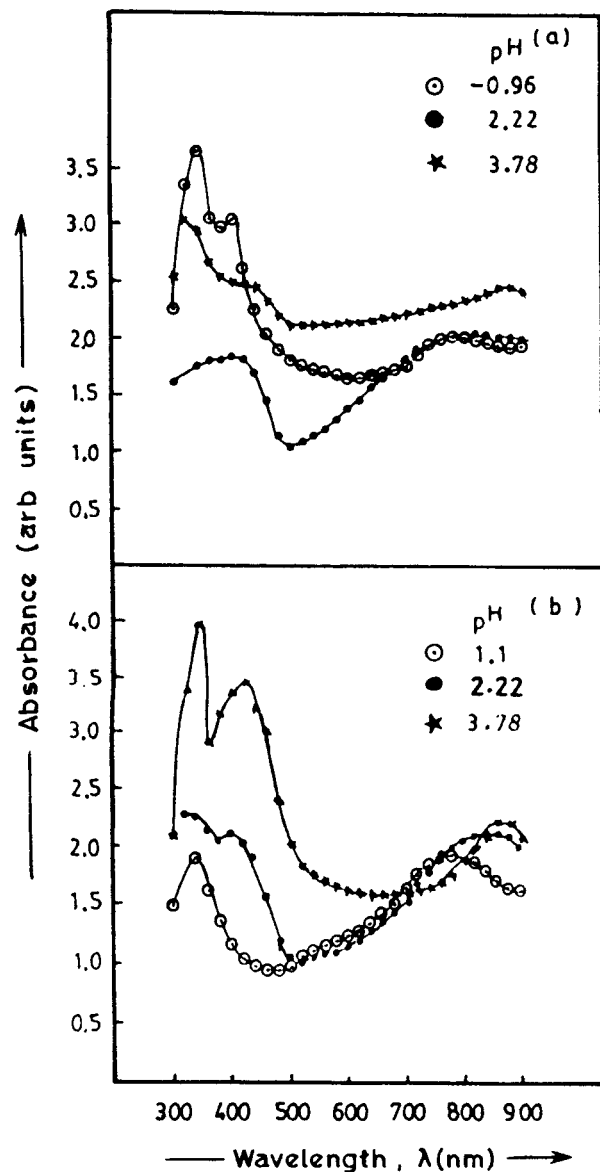


Figure 4 UV-Vis absorption spectra of (a) poly(*N*-methyl aniline) and (b) poly(*N*-ethyl aniline) films deposited as a function of pH of solution [pH −0.96 and 1.10; current strength, 3.00 mA; pH 2.22 and 3.78; current strength, 0.25 mA].

it appears that mixed phases of the polymer are formed during polymer deposition. However, it is worth noting that the predominance of the conducting emeraldine salt [ES] phase or the insulating phases such as pernigraniline and leucoemeraldine varies with pH of solution together with the soluble products such as benzidines and benzoquinones.

The above results depict the significant role played by the pH of solution on the film proper-

ties. In the case of poly(*N*-methyl aniline), the varying C : N and S : N ratio (Table I) leads us to conclude that the extent of formation of the conducting phase decreases with increasing pH of solution, whereas the formation of insulating phases is enhanced at higher pH values. This is further supported by the less intense C₂ and N₃ binding energy peaks corresponding to the polarons that represent the conducting phase. Apart from this, it is observed that the competitive reaction product (i.e., benzoquinone formation) is accelerated at a higher pH of solution as demonstrated by Table I observed at pH of 2.22 and 3.78. In agreement with this, the full width at half maximum (FWHM) values observed for oxygen also show an increasing trend in Table II.

In contrast with this, in poly(*N*-ethyl aniline), exactly the opposite sequence is observed. The intensity of the C₂ and N₃ peak increases with pH of solution in hand with the S : N ratio. Also, the absence of O₂ peak at higher pH of solution indicates that benzoquinone formation is suppressed in this system.

It is worth noting that the differences could be due to the electron-donating ability of the *N*-methyl and *N*-ethyl groups. The *N*-ethyl group would be a stronger electron donor than the *N*-methyl group, hence the radical cations of *N*-ethyl aniline are expected to have higher stability. Due to this, the dimer formation in *N*-ethyl aniline via para-aminodiphenylamine (PADPA) would occur at a lower rate leading to enhanced selectivity in the product formation. Further, the increase in selectivity in the formation of conducting phase with pH of solution in poly(*N*-ethyl aniline) can be attributed to the less-favored hydrolysis reaction resulting in the formation of benzoquinone at higher pH of 2.22 and 3.78.

Electrical Conductivity

These results are well supported by the conductivity data (Table III) obtained for both polymers at different pH values. The conductivity in poly(*N*-methyl aniline) is seen to decrease with an increase in pH of solution. In contrast, in poly(*N*-ethyl aniline), it is observed to increase with pH of solution which is obviously due to the enhancement in the fraction of conducting phase formed during polymerization.

Optical Properties

UV-Vis Spectra

Similarly, the UV-Vis spectra (Fig. 4) show sequential changes as discussed above for the two

polymers deposited as a function of pH of solution. A relatively sharp conducting phase peak is observed at ~ 780 nm in poly(*N*-methyl aniline) film deposited at a solution pH of -0.96 . In contrast with this, poly(*N*-ethyl aniline) displays a sharp peak for conducting phase ~ 840 nm (red-shifted) for the films deposited at 3.78 pH. Other species that are observed in the optical spectra are radical cation and leucoemeraldine absorbing ~ 420 and 320 nm, respectively. It is worth noting that the selectivity in the formation of each of these species is found to be greater in poly(*N*-ethyl aniline) than that observed in poly(*N*-methyl aniline). This can be attributed to the less-favored hydrolysis reaction taking place during polymerization leading to the formation of benzoquinone derivatives at pH of 2.22 and 3.78 in poly(*N*-ethyl aniline).

IR Spectra

The IR data exhibits the presence of the usual absorption bands observed for polyaniline (Table IV). The position of the $820\text{--}870$ cm⁻¹ peak is characteristic of paradisubstituted aromatic rings that indicate the polymer formation. The bands ~ 1220 and $620\text{--}680$ cm⁻¹ are assigned to the in-plane and out-of-plane bending motions of the aromatic ring, whereas the bands $\sim 1160\text{--}1010$ cm⁻¹ correspond to the dopant ions HSO₄⁻ and SO₄²⁻. A band appearing near about 1260 cm⁻¹ represents the C—N stretching vibration. A major contribution of the quinoid ring units is represented by the band ~ 1580 cm⁻¹, whereas the presence of the benzenoid ring is depicted by the band ~ 1470 cm⁻¹. However, comparison of the ratio of relative intensities of the imine to amine rings shows opposite trends in poly(*N*-methyl aniline) and poly(*N*-ethyl aniline) with increasing pH of solution.

CONCLUSION

XPS studies of poly(*N*-methyl aniline) and poly(*N*-ethyl aniline) films shows varying C : N and S : N ratios as a function of pH of solution, which lead us to conclude that the predominance of the conducting-phase formation is enhanced with increasing pH of solution in poly(*N*-ethyl aniline). A reverse trend is observed in the case of poly(*N*-methyl aniline).

Bhavana Deore and Mahesh Vedpathak are thankful to CSIR for providing financial assistance. A. A. Athawale

Table IV Characteristic Frequencies of Poly(*N*-methyl aniline) and Poly(*N*-ethyl aniline)

pH	Nonsymmetric C ₆ Ring Symmetry		Out-of-Plane (C-H) Bending (cm ⁻¹)	In-Plane (C-H) Bending (cm ⁻¹)	<i>Para</i> - & Disubstituted Benzene Ring (cm ⁻¹)	(C-H) Stretching Vibration (cm ⁻¹)	(C-N) Stretching Vibration (cm ⁻¹)	Ph-H ^a (cm ⁻¹)	SO ₄ ²⁻ /HSO ₄ ⁻ (cm ⁻¹)
	Quinoid (cm ⁻¹)	Benzenoid (cm ⁻¹)							
Poly(<i>N</i> -methyl aniline) -0.96	1562	1400	638	1220	850	2928	1220	2364	1008
		1474				3124	1234		1168
	1542	1460	616	1240	876	2926	1378	2364	1108
2.22	1552	1508							
	1588								
3.78	1562	1474	670		802	2924	1240	2362	1152
		1494			892		1256		
Poly(<i>N</i> -ethyl aniline) 1.10	1508	1400	689		864	3006	1230	2364	1016
						3126	1278		1170
	1562	1502	618	1278	831	2900	1306	2364	1110
2.22						3186			
	1564	1496	620	1208	818	2933	1242	2364	1112
3.78					856		1306		

^a Ph-H: phenyl hydrogen.

acknowledges DST and S. K. Kulkarni is thankful to UGC, India for financial support.

REFERENCES

1. Nagaoka, T.; Kakuno, K.; Fujimoto, M.; Nakao, H.; Yano, J.; Ogura, K. *J Electroanal Chem* 1994, 368, 315.
2. Rose, T. L.; D'Antonio, T. S.; Jillson, M. H.; Kon, A. B.; Suresh, R.; Wang, F. *Synth Met* 1997, 85 (1-3), 1439.
3. Duic, Lj.; Mandic, Z.; Kovacicsek, F. *J Polym Sci Part A* 1994, 32, 105.
4. Dao, L. H.; Leclerc, M.; Guay, J.; Chevalier, J. W. *Synth Met* 1989, 29, E377.
5. Agashe, C.; Takwale, M. G.; Marathe, B. R.; Bhide, V. G. *Sol Energy Mater* 1989, 17, 99.
6. Neoh, K. G.; Kang, E. T. *Synth Met* 1991, 40, 341.
7. Aldssi, M.; Armes, S. P. *Macromolecules* 1992, 25, 2963.
8. Demaret, X.; Cristallo, G.; Snauwaert, P.; Riga, J.; Verbist, J. J. *Synth Met* 1993, 55-57, 1051.
9. Nakajima, T.; Harada, M.; Osawa, R.; Kawagoe, T.; Furukawa, Y.; Harada, I. *Macromolecules* 1989, 22, 2644.
10. Kumar, S.; Gaillard, F.; Bouyssoux, G. *Synth Metal* 1990, 36, 111.
11. Dziembas, R.; Piwowarska, Z. *Synth Met* 1994, 63, 225.