Synthesis and characterization of poly(2,5-dimethoxyaniline) and poly(aniline-Co-2,5-dimethoxyaniline): The processable conducting polymers

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Abstract. Poly(2,5-dimethoxyaniline) (PDMOA) and its copolymers with aniline (PADMOA), which exhibit remarkably improved solubility in common organic solvents, were obtained by chemical polymerization, and characterized by a host of physical techniques. The lowering of the quinoid absorption in the IR spectra and the upshifting of the N_{1s} envelope in the XPS spectra indicate residual doping in the XPS polymers and thermal characteristic of the polymers provide evidence for hydrogen bonding, which appear to enhance the thermal stability of the homopolymer. These polymers are highly planar and conjugated, with well-developed polaronic features, shown by the XRD, ESR and UV-spectral data. The conductivity, however, is not high and apparently may be due to localization of polaronic charges at the hydrogen-bonding sites and the increased proportion of the insulating methoxy component in the polymer matrix.

Keywords. Poly(2,5-dimethoxyaniline); poly(aniline-Co-2,5-dimethoxyaniline); conducting polymer.

1. Introduction

Conducting polymer with polyaromatic back bone including polypyrrole, polythiophene, polyaniline etc has received a great deal of attention in the last two decades. Polyaniline has attracted attention because of its electronic, electrochemical and optical properties and environmental and thermal stability (Stotheim 1987; Macdiarmid *et al* 1989; Genies *et al* 1990; Olinga *et al* 2000; Ruckenstein and Yin 2000). Polyaniline, however, is severely limited in view of its insolubility in common organic solvents making its characterization rather intricate. Recently, synthesis of some substituted polyanilines which are soluble in organic solvents as well as in water beside being thermally and environmentally stable have been achieved (Watanabe *et al* 1987; Aurian-Blajeni *et al* 1988; Somasiri and MacDiarmid 1988). In order to obtain materials with superior electrical and optical properties we have selected dimethoxy aniline derivative in this investigation, which is polymerized to get more regular and processable conducting polymer. In this paper, we report here the chemical synthesis and characterization of homopolymer of 2,5-dimethoxy aniline and its copolymer with aniline (PADMOA) (figure 1). A better rationalization of structure, property correlation should be possible in case of dimethoxy substituted polyaniline systems where steric, electronic and other effects generated by

substituents are expected to enhance their potentiality as novel materials (Wei and Hsuch 1989; Chan *et al* 1992, 1993, 1995; Leclerc *et al* 1993; Ray *et al* 1995, 1999).

2. Experimental

Aniline was doubly distilled and 2,5-dimethoxy aniline was sublimed at reduced pressure prior to polymerization and commercial ammonium persulfate was used without purification. Polyaniline (PAN) and poly(2,5-dimethoxyaniline) (PDMOA) were synthesized by chemical oxidation of their respective monomer using $(NH_4)_2S_2O_8$ as initiator (Focke *et al* 1987; Cromack *et al* 1991).

In a 100 ml-conical flask required amount of 2,5-dimethoxyaniline was dissolved in 1 M HCl and the solution was cooled to 0–5°C. To this, prechilled solution of ammonium persulfate dissolved in 1 M HCl was added drop wise over a period of 25 min under vigorous stirring. During addition of ammonium persulfate solution deep blue colour developed rapidly. The resultant reaction mixture was stirred at that temperature for another 4 h, when a blue precipitate gradually separated which was subsequently collected in a buchner funnel, washed with 1 M HCl until the filtrate became colourless.

Emeraldine bases were prepared by suspending a part of the virgin polymer in 0·1 M NH_4OH solution. The HCl doped polymer was prepared by suspending virgin polymer in 1 M HCl solution. The elemental analysis of the HCl doped emeraldine gave C = 55·46%, H = 5·12%, N = 7·82%, Cl = 9·21%.

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Table 1. Experimental details for the polymerization of 2,5-dimethoxyaniline.

Sample (abbr.)	f_1	Time (h)	Yield (%)	Conductivity (S/cm)
Poly(aniline-Co-2,5-dimethoxyaniline) (PADMOA-16)	0·16	5	85	$9·7 \times 10^{-3}$
Poly(aniline-Co-2,5-dimethoxyaniline) (PADMOA-23)	0·23	6	82	$6·2 \times 10^{-3}$
Poly(aniline-Co-2,5-dimethoxyaniline) (PADMOA-30)	0·30	6	80	$4·7 \times 10^{-3}$
Poly(aniline-Co-2,5-dimethoxyaniline) (PADMOA-37)	0·37	5	80	$3·5 \times 10^{-3}$
Poly(aniline-Co-2,5-dimethoxyaniline) (PADMOA-60)	0·60	5	70	$1·7 \times 10^{-3}$
Poly(2,5-dimethoxyaniline) (PDMOA)	1·00	4	75	$3·6 \times 10^{-4}$

Table 2. Solubility and viscosity of polymers.

Solvent	PDMOA	h_{int} at 30°C	PADMOA-37	h_{int} at 30°C
NH$_4$OH	SS		IS	
H$_2$O	IS		IS	
C$_6$H$_6$	SS		IS	
C$_2$H$_5$OH	MS		IS	
CH$_3$OH	MS		IS	
CH$_2$Cl$_2$	S		IS	
CH$_3$COCH$_3$	SS		IS	
CHCl$_3$	S		SS	
CH$_3$CN	MS		SS	
THF	SS		IS	
DMF	MS		SS	
DMSO	MS		MS	
NMP	S		MS	
H$_2$SO$_4$	S	0·12	S	0·35
HCl	SS		S	

IS, Insoluble; S, Soluble; MS, medium soluble; SS, slightly soluble.

$R = H$ or OMe

Figure 1. General structure of polymers.

The copolymer (PADMOA) is mainly soluble in NMP and moderately soluble in DMF and DMSO. Both the copolymers are completely soluble in conc. H$_2$SO$_4$ (96%). For improved comparison viscosity measurements were carried out in conc.H$_2$SO$_4$. The viscosity data qualitatively suggests that the molecular weight of new polymer ($h_{\text{inst}} = 0·12$ dl/g at 30°C) are low as compared to polymer (PAN) ($h_{\text{inst}} = 0·74$ dl/g at 30°C). The molecular weight of copolymer (PADMOA) ($h_{\text{inst}} = 0·35$ dl/g at 30°C) is shown to be about three times higher than homopolymer (Zeng *et al* 1994).
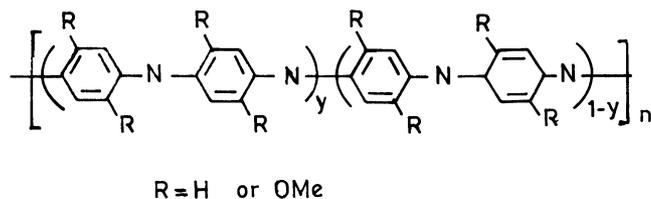
2.1 *Copolymerization*

Poly(aniline-Co-2,5-dimethoxyaniline) (PADMOA) were synthesized by oxidative coupling of aniline with various molar fractions of 2,5-dimethoxyaniline in the feed using ammonium persulfate as oxidant, in an aqueous acid medium at 0–5°C. Emeraldine bases and salts were prepared in the same manner (table 1).

3. Results and discussion

Poly(2,5-dimethoxyaniline) and its copolymer were obtained as finely powdered material by increasing the mol. fraction of the aniline in the feed.

3.1 *Solubility and viscosity*

The homopolymer base, however, is quite soluble in most organic solvents including CHCl$_3$, CH$_2$Cl$_2$ and moderately soluble in EtOH, MeOH, THF DMSO and DMF (table 2).

3.2 *IR spectra*

IR spectra of polymer are shown in figure 2. The benzoid and quinoid stretching appear at 1575–1587 cm^{-1} (1387 cm^{-1} in PAN) and 1503–1816 cm^{-1} (1496 cm^{-1}) (Salaneck *et al* 1985; Chiang and Macdiarmid 1986; Wang *et al* 1986; Tang *et al* 1988; Nguyen and Diaz 1994; Nguyen *et al* 1994). The lowering of benzoid stretching vibration (7–20 cm^{-1}) is due to substituent effect, which increases the level of oxidation especially in homopolymer. The UV-vis absorption spectra (figures 3, 4) of the polymers mainly consist of two absorption bands at 286–336 nm and 556–627 nm attributed to *p–p** transition in the benzoid rings and exciton absorption of the quinoid rings, respectively (Gupta and Umare 1992). The partially soluble HCl-doped polymers show *p–p** absorption at 286–336 nm and exciton transition at 557–597 nm. Concomitant to higher doping level is observed in PADMOA-37 copolymer. The reflectance spectra of the (figure 5) polymer films show large reflection (strong absorption) above 600 nm taken as evidence of improved conjugation and metallic behaviour (Diaz and KanaZawa 1983).

3.3 *Thermal analysis data*

Thermal analysis data (figure 6) for PDMOA-HCl and PADMOA-HCL 37 polymers are shown in table 3. The weight loss of polyaniline and its derivatives is comprised of three major stages (Hagiwara *et al* 1988; Wei and Hsuch 1989). The minimum weight loss (0–4%) (except 37) in the first stage can be attributed to release of free and bound water dopant which contribute to the endothermic peak in DSC (figure 7). Two endothermic peaks observed in the thermogram of copolymer at 220°C and 340°C may be assigned to morphological changes (Chan
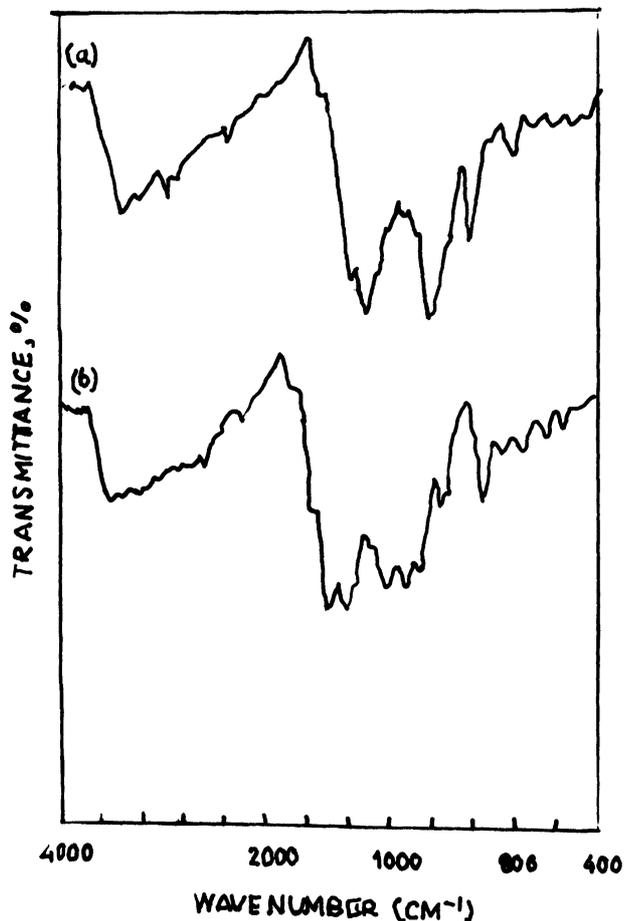
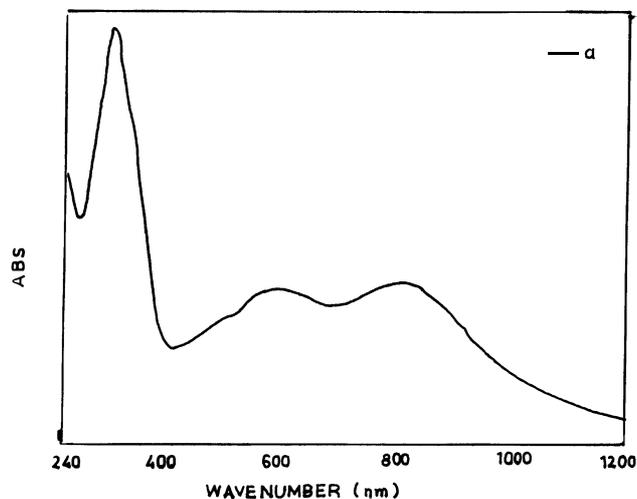**Figure 2.** Infrared spectra of (a) PDMOA and (b) PADMOA-37.

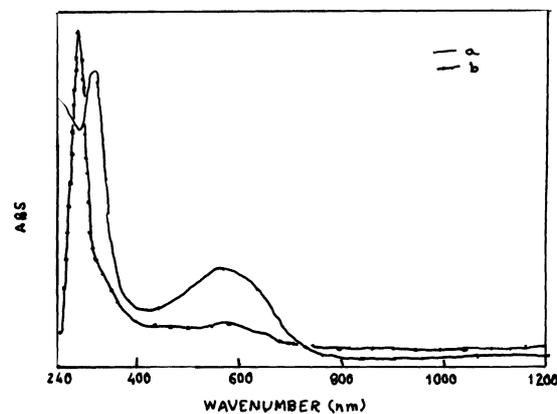**Figure 3.** UV-vis spectra of PDMOA base in a. CHCl₃.

Figure 4. UV-vis spectra of PADMOA-37 in a. THF and b. PADMOA-37 in DMSO.
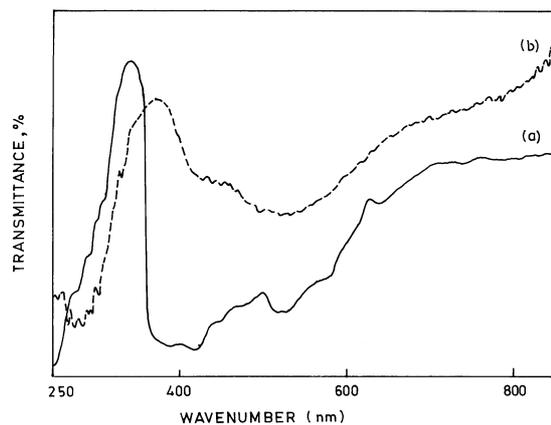
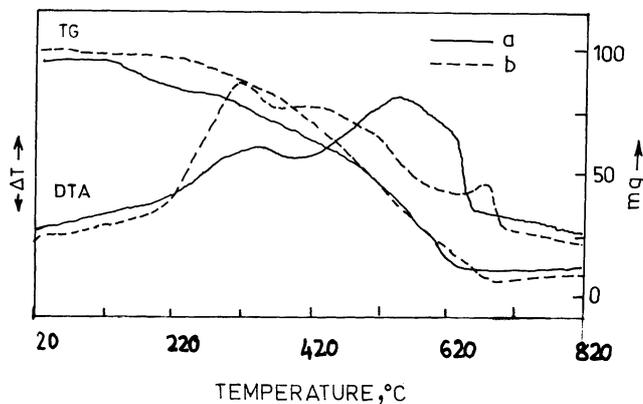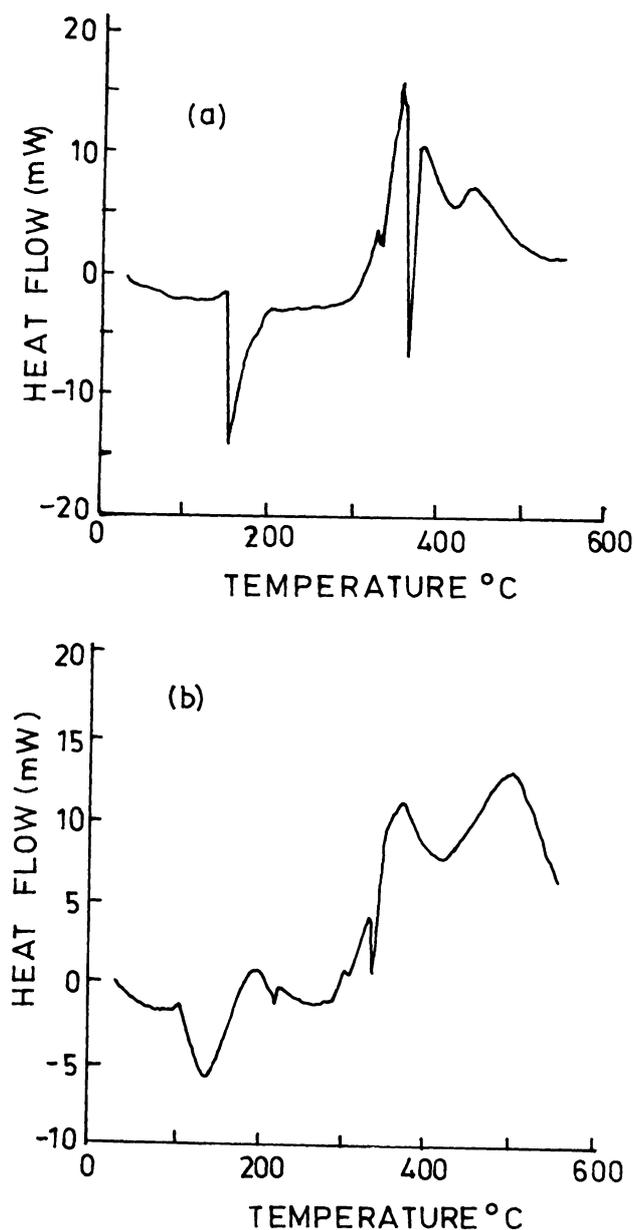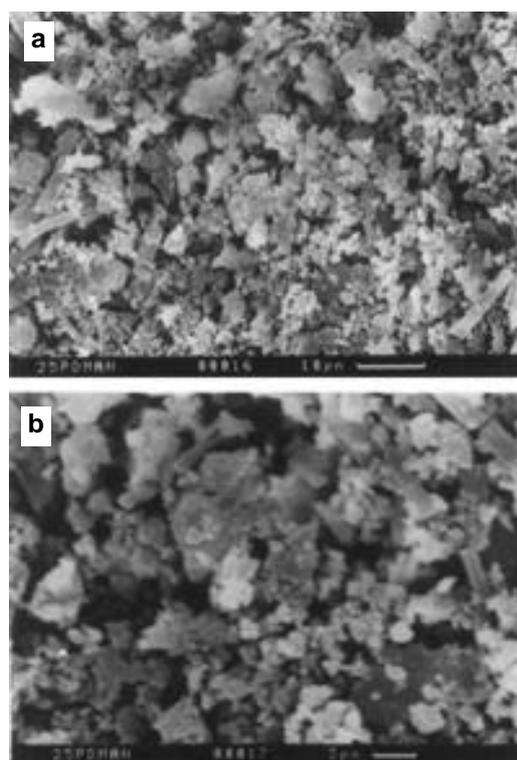**Figure 5.** UV-reflectance spectra of (a) PDMOA film and (b) PADMOA-30 film.

Figure 6. TG-DTA thermogram of (a) PDMOA film and (b) PADMOA-37 film.

Table 3.   Thermal parameter of polymers.

Sample	Weight loss			Maximum decomp. temp.	Range of decomposition temp.
	25–100°C	200–300°C	400–550°C		
PAN	6–7	7–8	58–60	430, 545	100–560
PDMOA	0–1	2–3	55–56	403, 590	235–630
PADMOA-37	0–1	28–30	37–39	295, 480, 556	200–588

Figure 8.   SEM micrographs of PDMOA at magnifications: **a.** 1500 × and **b.** 3000 ×.

could be due to the increased hydrogen bonding between methoxy oxygen and NH^+ radical cation.

### 3.4   *Scanning electron micrograph*

In the SEM micrographs (figure 8) at 3000× magnification, a tubular morphology expected of substitute polymers could be recognized. The randomly oriented tubular forms appear to be characteristically different from that of PAN, which has a fibrillar microstructure.

Figure 7.   DSC thermogram of (a) PDMOA base and (b) PADMOA-37 base.

3.5   *ESR spectra*

The ESR spectra (figure 9) of HCl-doped polymer powders indicate that the polymers are strongly paramagnetic with G values of 2·0022 and 2·0011 and the peak to peak line width ΔH_{pp} of 5·5 and 2·0 G for PDMOA-HCl and

et al 1992). Thermal analysis data also suggest that homopolymer is more stable compared to the copolymer PADMOA-37. The extra stability of the homopolymer

Table 4. XPS binding energy data of polymers.

Polymer	Element	Range, eV	Centre, eV	FWHM, eV
PDMOA	C_{1s}	280·7–290·5	285·0	3·35
	N_{1s}	394·5–402·2	398·8	2·70
	O_{1s}	527·0–537·5	532·6	2·93
PADMOA-30F	C_{1s}	280·6–291·2	285·0	3·31
	N_{1s}	396·1–403·8	399·3	2·96
	O_{1s}	528·0–537·4	531·8	3·19
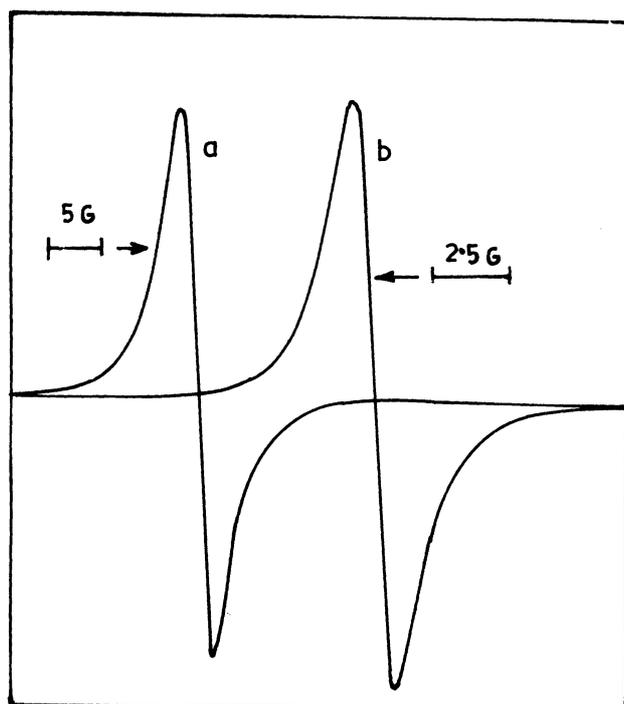
Figure 9. ESR spectra of HCl doped (a) PADMOA-30 and (b) PDMOA.
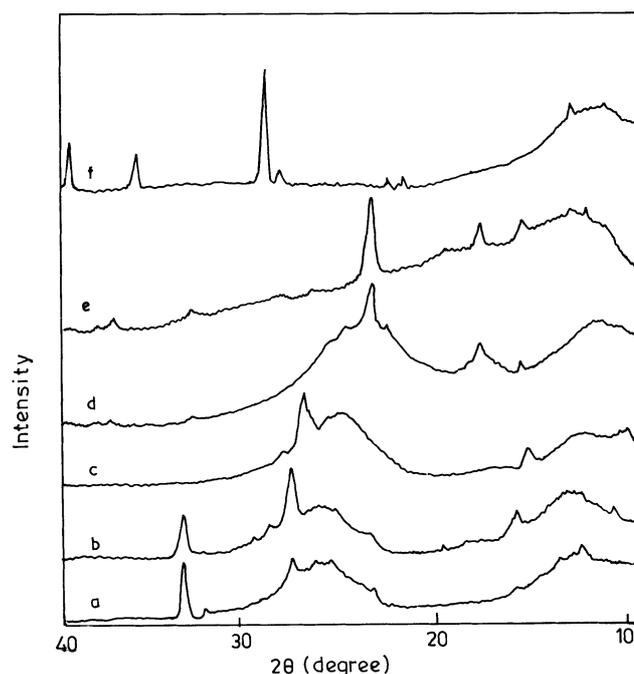
Figure 10. XRD spectra of a. virgin PDMOA, b. PDMOA, c. PDMOA base doped by HCl, d. PDMOA base, e. PADMOA-16 base and f. PADMOA-037 base.

PADMOA-HCL-37, respectively (Yue *et al* 1991; Nguyen *et al* 1994).

3.6 *X-ray diffraction*

X-ray diffraction profile (figure 10) of the polymer indicates substantial degree of crystallinity in the doped forms. The base form of the homopolymer is found to have less crystallinity, compared to the doped form. Unit cell parameters, *a*, *b*, *c*, defined as in the work of Josefowiez *et al* (1989), and deduced from observed 2*q* and *d* values are summarized in table 5 along with the index planes for the orthorhombic crystal cell (Gupta and Umare 1992).

3.7 *X-ray photoelectron spectroscopy*

XPS-core level spectra of C_{1s}, N_{1s} and O_{1s} are shown in figures 11–13. The C and oxygen content appears to

be exceedingly high due to contamination (Aldissi and Armes 1992). The C_{1s} spectra (table 4) are asymmetric and wide (284·6–295·1 eV) due to the loss of charge to the dopant as a result of protonation. According to the finding energy distribution in the C_{1s} components can be assigned to C–C, C–H, C–N, C=N, =C–O, C–O, C=N$^+$ and C–N$^+$ etc. In the homopolymer the N_{1s} peak shows dissymmetry towards lower binding energy which can be attributed to decrease in positive charge on the nitrogen due to delocalisation of **p**-electron cloud from the adjoining aryl rings with electron donating methoxy substituents and lower residual doping level compared to copolymer. The O_{1s} envelope in the homopolymer shows an overall shift to higher BE primarily due to the C–O–C (methoxy) component at 532·5 eV (Chan *et al* 1993). It also indicates that the oxygen component is associated with positive charge, possibly as a result of being hydrogen bonded to positively charged NH sites.
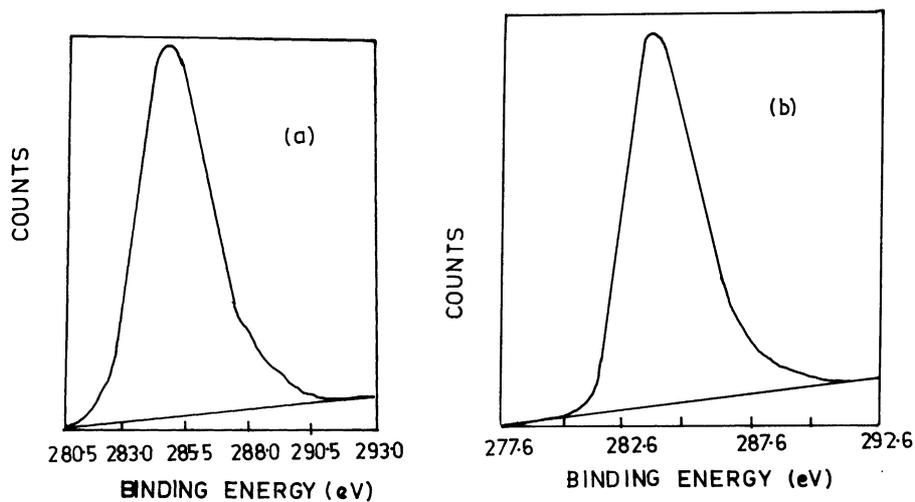
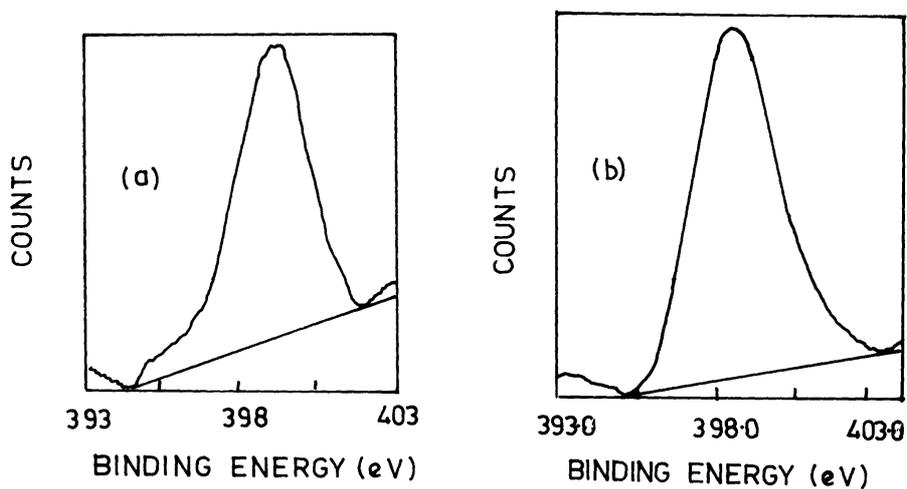**Figure 11.** XPS C_{1s} spectra of (**a**) PDMOA and (**b**) PADMOA-37 base film.

Figure 12. XPS N_{1s} spectra of (**a**) PDMOA base and (**b**) PADMOA-37 base film.
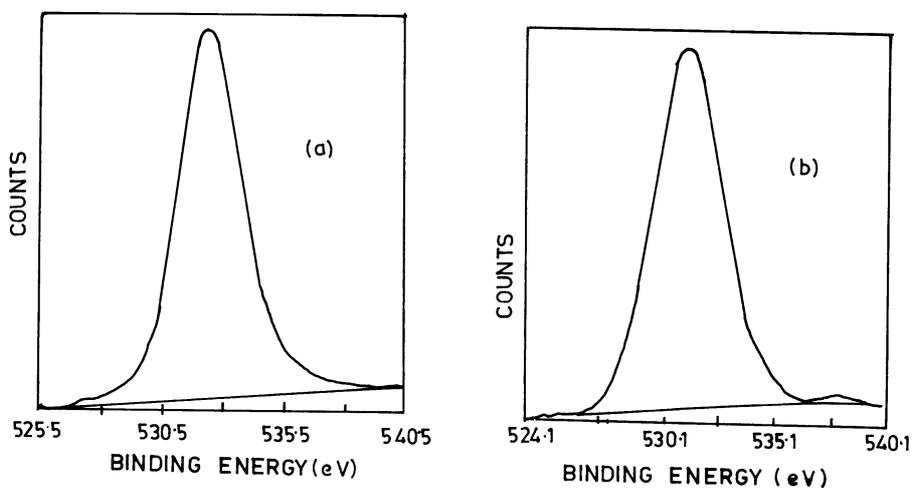

Figure 13. XPS O_{1s} spectra of (**a**) PDMOA base and (**b**) PADMOA-37 base film.

Table 5. Crystal structure, lattice parameters and 2*q* values of poly(2,5-dimethoxy aniline).

Sample	2*q* (observed deg.)	*d* value (obs.) (Å)	*d*-value (cal.) (Å)	*hkl*	Remarks
PDMOA–HCL	10·68	8·2737	8·2397	010	Orthorhombic unit cell dimensions
	12·15	7·2737	7·2266	011	$a = 7·7221$
	13·05	6·7759	6·8698	101	$b = 8·2397$
	15·60	5·6736	5·6345	110	$c = 15·0428$
	23·00	3·8622	3·8611	200	
	25·05	3·5505	3·5332	121	
	27·20	3·2746	3·2728	122	
	32·70	2·7353	2·7466	030	
PDMOA–Base	11·30	7·8211	7·9614	002	Orthorhombic unit cell dimensions
	13·45	6·5802	6·3993	100	$a = 6·3993$
	16·50	5·3661	5·3076	003	$b = 8·5686$
	18·60	4·7647	4·8805	111	$c = 15·9227$
	23·40	3·7971	3·7727	022	
	24·18	3·6763	3·6876	113	
	25·60	3·4755	3·4743	121	

3.8 *Electrical conductivity*

The poly(aniline-Co-2,5-dimethoxyaniline) copolymer as expected shows higher conductivity with increasing PAN content.

The homopolymer (PDMOA), however, exhibits rather low electrical conductivity ($10^4 s$/cm) inspite of (i) being more planar and having greater condition compared to PAN (UV and XRD results), (ii) high doping level (chemical analysis) and (iii) well developed polaronic features (UV, ESR results).

4. Conclusions

Poly(2,5-dimethoxyaniline) and its copolymers with aniline were synthesized by oxidative coupling in aqueous protic acid using ammonium persulfate as oxidant. Film casting of polymer bases in NMP solution was obtained. The polymer bases show enhanced solubility in common organic solvents like $CHCl_3$ and CH_2Cl_2 and their solutions in concentrated H_2SO_4 register moderately high viscosity. These polymers show resistance to thermal changes possibly due to cross-linking reactions taking place involving participation of methoxy groups along with visual imine/amine components. The relative lowering of N_{1s} binding energy in the XPS spectra of the homopolymer illustrates the effect of electron donating feature of methoxy substituent. The dimethoxy substituted polyanilines exhibit tubular morphology. The base form exhibits lesser planar deformation and hence increased planarity according to XRD results. The doped forms with substantially higher crystallinity are however less planar. The PDMOA polymers thus show fairly developed planarity and conjugation compared with PAN and achieve high doping levels. They are endowed with a well-developed polaronic structure, which is a sequel to the strong paramagnetism, manifested in their ESR spectra. The electrical conductivity nevertheless does not show significant improvement possibly due to the presence of insulating methoxy component, in addition to charge localization through the agency for H-bonding, the occurrence of which is suggested by the results of XPS and thermal analysis.

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