



Spectral, Thermal and Crystalline Properties of Substituted Aniline Conducting Polymers

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ABSTRACT

The synthesis of polymers based on anthranilic acid(o-amino benzoic acid) ,p-chloroaniline and o-methylaniline by aniline-initiated ammonium peroxydisulfate oxidation method has been attempted. Poly(anthranilic acid),poly(p-chloroaniline),and poly(orthomethylaniline) thus synthesized were characterized by using infrared spectroscopy (FTIR),¹H –nuclear magnetic resonance spectroscopy(¹H-NMR),X-ray diffraction (XRD) and thermo gravimetric analysis(TGA). The TGA analysis of the conducting polymers have been followed using a computer analysis method LOTUS PACKAGE, developed by us for assigning the degradation mechanism. The degradation pattern of the polymers has been explained on the basis of kinetic parameters .

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INTRODUCTION

In recent year, conducting polymers have attracted attention of many researcher because of their diverse applications, including electronics[1],energy storage[2], catalysis[3], chemical sensing[4], and biochemistry.[5] Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical, and optical properties, as well as good stability.[6] Polyaniline is typically synthesized by oxidizing aniline monomer either electrochemically [7,8] or chemically.[9-11]. Electrochemically synthesized polyaniline is difficult to process due to its low solubility, while chemically synthesized polyaniline suffers from low molecular weight, which results in low mechanical strength.[11] In recent years, considerable effort has been devoted to developing new methods to synthesize polyaniline to achieve better mechanical properties while maintaining high conductivity. The most common strategy that has been implemented is to change the oxidizing agent employed in the chemical polymerization reaction.[11-13]. For example, it has been shown that when (NH₄)₂S₂O₈ or K₂Cr₂O₇ is used, high molecular weights can be achieved by lowering the polymerization temperature to below 0 °C.[14] The highest weight-average molecular weights that have been reported using these approaches are on the order of 10⁵.

In addition to low mechanical strength, adhesion of polyaniline on solid substrates is another important factor that has limited its utility in applications such as in antistatic coatings.[15,16] For example, although polyaniline films cast from N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), or dimethylformamide (DMF) solutions adhere strongly to glass in dry atmospheres, adhesion quickly fails when the films are immersed in water. The conducting salt of polyaniline is insoluble. The undoped and base forms of polyaniline are soluble but only in a small number of polar solvents with high boiling points, such as N-methyl-2-pyrrolidinone (NMP),

dimethylsulfoxide (DMSO), and dimethylpropylene urea, which are not environmentally friendly.[17,18] One of the characteristics required of polyaniline, especially for technological applications, is solution processability. Intense effort has therefore been directed toward optimizing the processability, conductivity, and stability of polyaniline through modifications of the oxidation state, dopant, and polymerization conditions.[19–23]. These research efforts have led to the synthesis of a number of ring-substituted polyanilines such as polytoluidines, polyanisidines, polyphenetidines, polynitrosoanilines, polyhaloanilines, and polydihaloanilines with significantly improved solubility.[24–34]. These polyaniline derivatives show good solubility not only in NMP but also in less-polar solvents such as toluene. Manipulation of the acid dopants and processing conditions improved the conductivity up to 1 - 10² S/cm.[35,36]. However, the polymer derivatives are limited to some nonfunctional substituents that can improve only solubility in organic solvent. In present research programme, we wish to report the synthesis and characterization of some substituted polyanilines using,FTIR,¹H-NMR, XRD and TGA methods. The most remarkable part of the analysis is the use of computerized LOTUS PACKAGE method formulated by us for monitoring the degradation mechanism of these polymers[37,38,39,40].

Work-Up Procedure

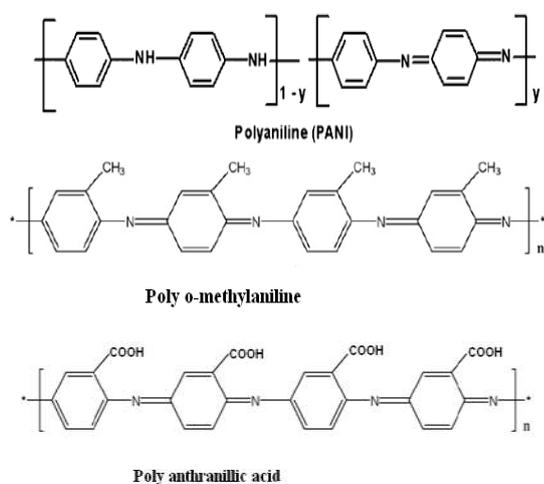
Materials

Aniline, anthranilic acid, p-chloroaniline,o-methylaniline and ammonium peroxydisulfate from Merck(Germany) were used. Aniline was doubly distilled prior to polymerization and others were recrystallised in suitable solvents.

Synthesis

Polymers were synthesized by ammonium peroxydisulfate oxidation in a method similar to polyaniline preparation[41]. The individuals do

not form homopolymers even if the reactants are kept for 48 h at room temperature. By addition of few drops of aniline (15%) to the system, polymerization took place at different temperatures [42]. A component to be polymerized is taken 14.49 mmol and aniline is 15 mol% of component, were dissolved in 150 ml of 1M HCl. A solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (2.89 gm, 12.67 mmol) in 50 ml of 1M HCl was added dropwise with constant stirring over a period of 30-40 min. A dark brownish black color developed and polymerized products precipitated in the solutions. The reaction mixture was stirred at room temperature for 48 hrs, the polymer was collected by filtration, washed with 1M HCl until the filtrate was colorless and then dried in vacuum at 20°C to constant weight. Under the same condition, Polyanthranilic acid (PAA), poly(p-chloroaniline) (PPCA), poly(methylaniline) (POMA) were prepared. Apart of the polymer was transferred into a conical flask containing 100 ml of 1M HCl and was stirred for about 4 h at room temperature. The resulting materials were filtered and dried in vacuum desiccators in the presence of P_2O_5 (48 h) to yield the HCl-doped polymers. The general structures of substituted polyaniline have been represented schematically as shown in scheme 1.



Scheme-1

Measurements

Conductivity

The dc electrical measurement has been taken by using a four-probe technique considering the thickness and diameter of the pellets at room temperature where the four points in the sample surface were in line at an equal spacing of 1 mm [43]. During the measurement, an appropriate constant current in the range of 0.01–50 mA was applied to the two outer probes and the voltage drop across the two inner probes was measured to determine the conductivity.

FTIR spectra

Fourier transform infrared (FTIR) spectra of the samples were measured by the KBr pellet technique in the range of 4000–400 cm^{-1} with a Bruker IFS 55 instrument.

NMR

NMR spectra were taken using a 300 MHz spectrophotometer with Tetra Methyl Silane (TMS) as a reference compound.

XRD

The X-ray diffraction (XRD) graphs were recorded for the powdered materials with a Siemens D5005 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The solubility of the copolymers in their salt form was tested in the solvent DMSO.

TGA

The thermograms were analyzed by a computerized Lotus package method, for the study of degradation mechanism and energy of activation.

RESULTS AND DISCUSSION

Conductivity

The conductivities data of homopolymers synthesized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ salt are demonstrated in Table 1. It is seen that the highest conductivity corresponds to Poly(p-chloroaniline) (PPCA) with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as 1.2×10^{-6} S/cm and the conductivity of poly(o-methyl aniline) (POMA) is 1.2×10^{-6} s/cm and the conductivity poly anthranilic acid (PAA) is 1.8×10^{-8} s/cm. The conductivities of polymers have changed due to different substituent bonded to aromatic ring. Both the conjugation length and the redox potential are affected by nature and the position of the substituent on the ring [44]. Thus, the conductivities of polymers are found different from each other. The polymerization of substituted anilines by ammonium peroxydisulfate oxidation using aniline initiator was carried out at room temperature. Table-2 lists the solubility characteristics of the polymers. In general all polymers were completely soluble in DMSO, DMF and NMP and also these are completely soluble in 96% H_2SO_4 .

Table 1: Polymerization and conductivity of substituted polyaniline

Sample	Yield (%)	Reaction t_c	Conductivities S/cm
Poly(anthranilic acid) (PAA)	70	30-35	1.8×10^{-8}
Poly(p-chloroaniline) (PPCA)	76	30-35	3.5×10^{-6}
Poly(o-methylaniline) (POMA)	78	30-35	1.2×10^{-6}

Table 2: Solubility of conducting polymers

Solvent	PAA	PPCA	POMA
H_2O	i	I	i
$\text{C}_2\text{H}_5\text{OH}$	i	I	i
HCl (conc)	i	I	i
H_2SO_4	s	S	s
Benzene	i	I	i
Toluene	i	I	i
CHCl_3	i	I	i
CH_3CN	i	I	i
DMSO	s	S	s
DMF	s	S	s
NMP	s	S	s
THF	ss	Ss	ss

[i:insoluble; ss:slightly soluble; s:soluble; DMF:Dimethylformamide; DMSO:Dimethyl sulfoxide; NMP:N-methyl pyrrolidone.]

FTIR

The FTIR spectra used to characterize the structure of substituted polyaniline are presented in Fig. 2. The FTIR spectrum of PAA is shown in fig. 2a. A strong band for C=O stretching at 1683.2 cm^{-1} and C-N stretching at 1296.2 cm^{-1} . The vibration modes of the benzene ring appear between 1576.2 cm^{-1} and 1515.1 cm^{-1} . In addition, the band appear at 771.7 cm^{-1} corresponds to the C-H out of plane bending vibration 1,2,3-trisubstituted benzene ring. The FTIR spectrum PPCA and POMA are shown in the fig. (2b, 2c) which showed that 1566.1 cm^{-1} due to quinoid stretching. The presence of 1,2,3-trisubstitution is indicated by the bands in the region 715.7 – 1102.7 cm^{-1} (PPCA) and 817 – 1107.8 cm^{-1} (POMA) ascribed to the C-H in plane and out-of-plane bending modes. The characteristic amine vibration bands are presented at 3246.4 cm^{-1} (PPCA) and 3124.2 cm^{-1} (POMA). The C-Cl(s) bands appear at 715.7 cm^{-1} for PPCA. The FTIR spectral data confirms the predicted structures of the polymers.

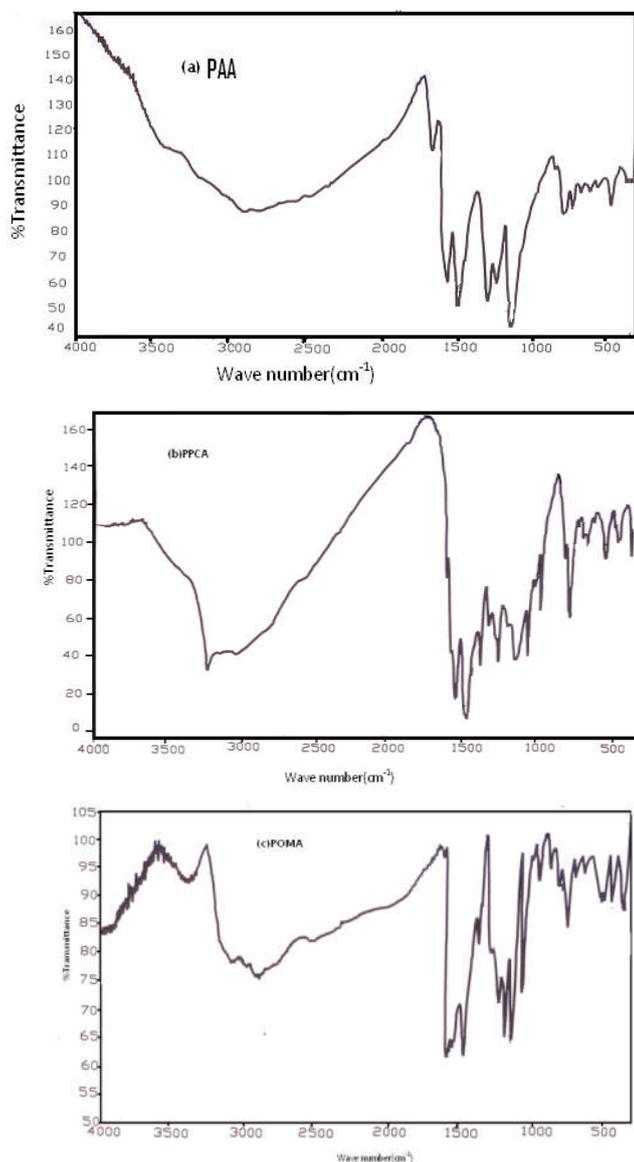


Fig. 2. FTIR. Spectra of (a) PAA (b) PPCA (c) POMA

¹H-NMR

The proton NMR spectra of PAA, PPCA and POMA are shown in the Fig.3. The ¹H-NMR spectrum of PAA is shown in the fig3a. The spectra presented a multiplet peak at 6.93-8ppm which has been assigned to aromatic protons [45,46]. A singlet peak at 10.8 ppm is due to the carboxylic acid protons arising due to resonance. The ¹H-NMR spectrum of PPCA and POMA are shown in figure (3b,3c). These spectra showed the multiple peak at 6.58-7.62ppm (PPCA) and 6.59-7.94ppm (POMA) are due to aromatic protons. Other singlet peaks are present at 9.4ppm which are due to amino protons.

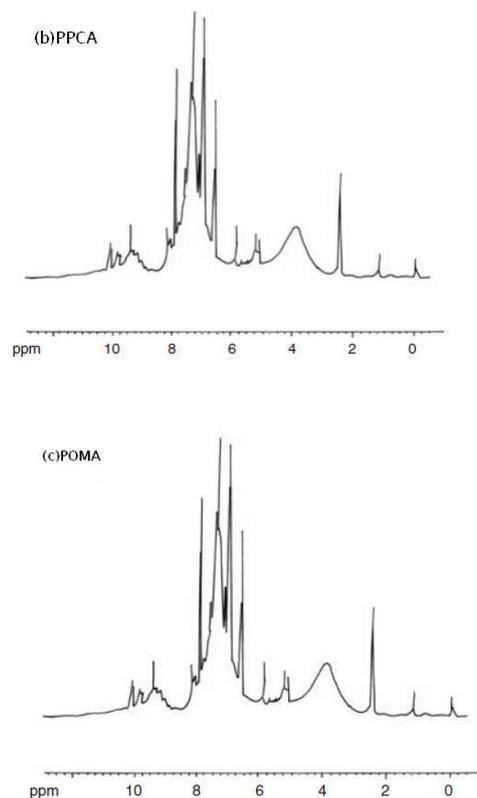
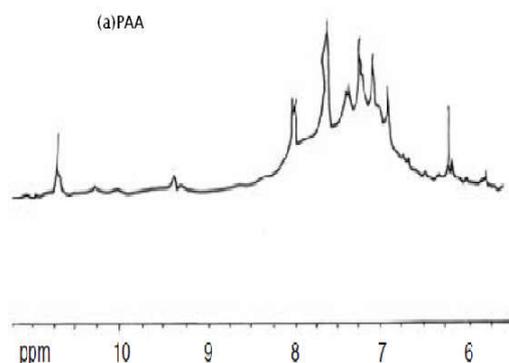
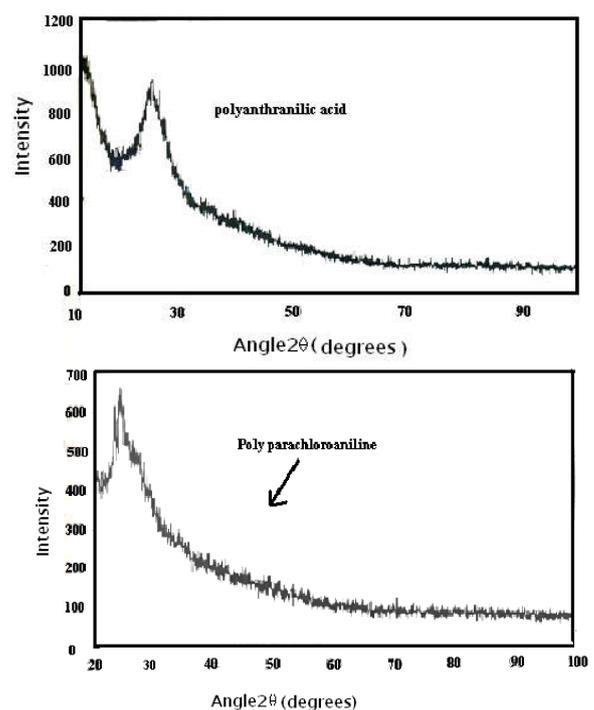


Fig. 3. ¹H-NMR spectra for (a) PAA (b) PPCA (c) POMA

XRD

The x-ray diffraction profiles of PAA, PPCA and POMA are shown in the Fig -4. All these polyanilines are characterized by the broad, amorphous scattering at $2\theta=30^\circ$. They however exhibit slight crystallinity and are not totally amorphous as indicated by the presence of peaks figure of $2\theta=25.5^\circ$ (PAA), $2\theta=24.75^\circ$ (PPCA), $2\theta=20.3^\circ, 24.1^\circ$ and 27.1° (POMA). The values of crystallinity (X_{cr}) presented in the Table -3 is calculated by conventional graphical method. The XRD pattern indicates that PAA polymer sample is somewhat more crystalline with peaks being more sharper than other conducting polymers.



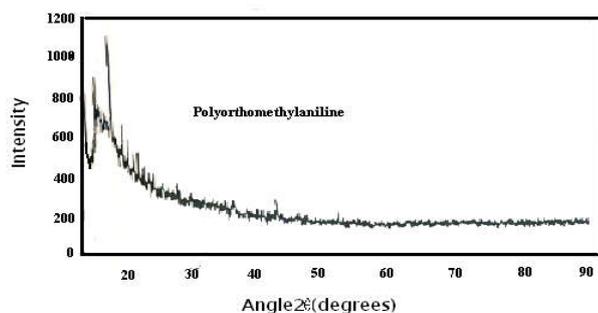


Fig. 4. XRD data of (a).PAA (b).PPCA (c) POMA

Table 3. Details of Crystallinity of polysubstituted anilines

Sample	Peaks	Σ AIUC	AUB	AAB	X _{cr}
PAA	1	7879.275	5562.0	2317.075	0.294072
PPCA	1	6408.6	4999.5	1409.1	0.219876
POMA	1	600.925	449.5	151.425	0.251987
	2	528.375	391.875	136.5	0.258339
	3	1833.075	1731	102.075	0.055685
	4	2212.95	1995.8	217.15	0.098127

*Crystallinity is somewhat responsible for tensile strength.

TGA

The thermogram of PAA, PPCA and POMA polymers are shown in the fig.5. The percent weight loss at various temperatures are shown in the Table. In case of polyanthranilic acid (PAA) (Fig5a), the first break takes place around 100⁰ C having weight loss about 2%, the second break takes place around 420⁰C having weight loss around 33% and the third break takes place around 605⁰C having total weight loss about 93%. This can be explained by considering the structure of PAA. The first break around 100⁰C is attributed to the elimination of water. The second break around 420⁰C is due to the breakage of the side chain eliminating gases like N₂ and NO₂ etc. The third break around 605⁰C may be due to the breakage of the aromatic ring forming gases like CO₂ etc. In case of poly (para chloroaniline) (PPCA)(Fig5b), there are four breaks in the thermogram. The first break takes place around 100⁰C having weight loss about 15% is due to elimination of water molecules present as free moisture. The second break takes place around 320⁰C having weight loss about 33% may be due to the breakage of side chain eliminating gases like Cl₂, etc. The third break takes place around 405⁰C having weight loss about 44%, may be due to the breakage of side ring eliminating gases like N₂, NO₂ etc. However, the fourth break takes place around 550⁰c having total weight loss about 86%, may be due to the breakage of aromatic ring forming gases like CO₂ etc.

In case of poly (orthomethylaniline)(POMA)(Fig5c), the first break takes place around 100⁰c having weight loss about 13% which is attributed to elimination of water present as apparent moisture. The second break takes place around 200⁰c having weight loss about 22% may be due to breakage of side chain eliminating gases like NO₂, N₂ etc. While third break takes place around 375⁰c having total weight loss about 40% may be due to the breakage of aromatic ring forming gases like CO₂ etc. The values of the activation energies were calculated by a Lotus Package method developed by us. (Ref) The perusal of the values of the activation energy for different stages of the degradation indicates that in case of all polymers, the degradation is very first in the initial stages and slows down gradually till the last stage of the degradation. This is obvious since in the first step moisture absorbed in the polymer is eliminated. In the middle step, the side chain breaks producing probably some gases like N₂ or NO₂ or Cl₂. The third step is very slow since in this step the aromatic ring is ruptured which is generally a very slow process. Hence the predicated mechanism is in full agreement with the calculated values of the energy activation. Our thermal degradation studies might help in processing these polymers for industrial applications.

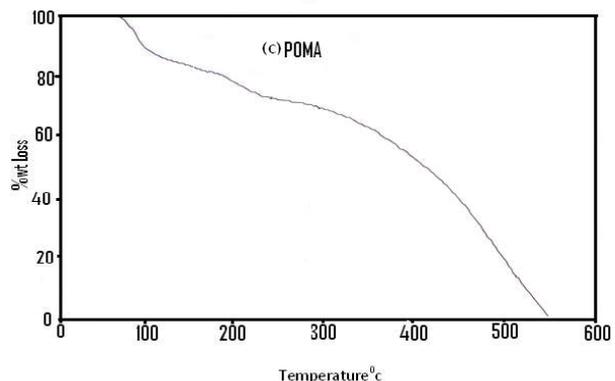
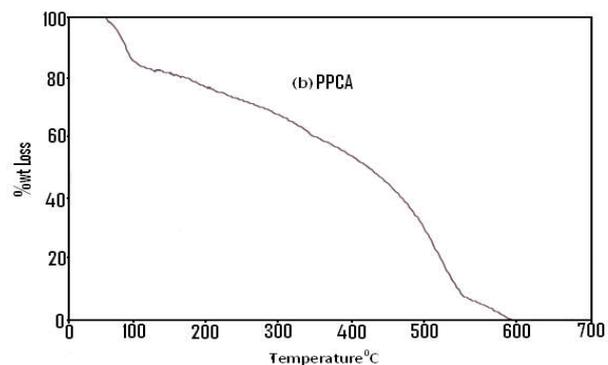
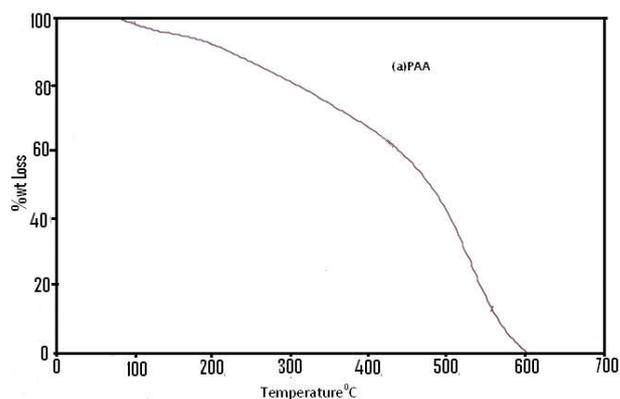


Fig. 5. TGA data of (a) PAA (b) PPCA (C) POMA

Table 4. Thermal Decomposition Data of substituted polyanilines

Sample Name	Temperature					
	100 ⁰ c	200 ⁰ c	300 ⁰ c	400 ⁰ c	500 ⁰ c	600 ⁰ c
PAA	1.5	7	17	30	56	93
PPCA	15	22	31	44	69	91
POMA	13	22	29	46	78	92

(% wt. loss of various temperatures.)

Table 5. Kinetic parameters of substituted conducting polymers

Sample No.	Steps	Temperature range		Model	R ²	Activation Energy: E(Kj/mol)
PAA		Start	End			
	1	73.95	413.34	B1	0.959	13.20
	2	416.36	601.06	B1	0.985	44.30
PPCA	3	604.01	636.49	B1	0.976	178.20
	1	38.50	82.02	B1	0.902	39.40
	2	85.41	316.03	B1	0.995	44.40
	3	319.05	401.07	B1	0.966	42.60
POMA	4	404.11	548.50	B1	0.980	50.90
	5	550.84	665.77	B1	0.988	71.70
	1	50.82	92.18	B1	0.867	42.30
	2	95.20	371.62	B1	0.991	53.70
	3	374.62	560.20	B1	0.986	68.50

Conclusion

Synthesis of conducting polymers from substituted anilines like ortho aminobenzoic acid, p-chloroaniline and o-methylaniline has been attempted. The aniline molecule having three different substituent like -COOH group, -Cl group and -CH₃ groups have been polymerized to know the polymerization characteristics. The polymers were characterized by using FTIR, SEM and XRD and TGA methods. The structure of the polymer has been ascertained from the FTIR and NMR spectra. The morphology of the polymers has been predicted from the SEM and XRD data. The thermal degradation mechanism has been monitored by LOTUS PACKAGE method using various kinetics models developed by us. The energy activation of the degradation mechanism of the various stages of the degradation polymer have been evaluated. Best on the values of the energy activation of the polymers the mechanism degradation has depicted.

REFERENCES

- Burroughes, J. H.; Jones, C. A.; Friend, R. H. (1988) *Nature*, 335:137.
- Conway, B. E. J. (1991) *Electrochem. Soc.*, 138:1539
- Andrieux, C. P.; Dumasbouchiat, J. M.; Save'ant, J. M. (1982) *J. Electroanal. Chem.*, 131:1
- Hsueh, C.; Brajter-Toth, A. *Anal. (1994)Chem.*, 66: 15.
- Miller, L. L. (1988) *Mol. Cryst. Liq. Cryst.*, 160:297.
- Chinn, D.; Dubow, J.; Liess, M.; Josowicz, M.; Janata. (1995) *J. Chem. Mater.*, 7: 1504.
- Rozsnyai, L. F.; Wrighton, M. S. (1996) *Chem. Mater.*, 8:309.
- Liu, G.; Freund, M. S. (1996) *Chem. Mater.*, 8: 1164.
- Yasuda, A.; Shimidzu, T. (1993) *Polymer J.*, 25, 329.
- Hand, R. L.; Nelson, R. F. (1978) *J. Electrochem. Soc.*, 125:1059.
- Abe, M.; Ohtani, A.; Umamoto, Y.; Akizuki, S.; Ezoe, M.; Higuchi, H.; Nakamoto, K.; Okuno, A.; Noda, Y. J. (1989) *Chem. Soc., Chem. Commun.*, 1736.
- MacDiarmid, A. G.; Chiang, J. C.; Halpen, M.; Huang, W. S.; Mu, S. L.; Somasli, N. L.; Wu, W.; Yaniger, S. I. *Mol. (1985)Cryst. Liq. Cryst.*, 121: 173.
- Pron, A.; Genoud, F.; Menardo, C.; Nechtschein, M. (1988) *Synth.Met.*, 24:193.
- Cao, Y.; Andretta, A.; Heeger, A. J.; Smith P. (1989) *Polymer*, 30: 230
- Trivedi, D. C.; Dhawan, S. K. (1993) *Polym. Adv. Technol.* 5:335.
- Ohtani, A.; Abe, M.; Ezoe, N.; Doi, T.; Miyata, T.; Miyake, A. (1993) *Synth. Met.* 1:3696.
- Angelopoulos, M.; Asturias, G. E.; Ermer, S. P.; Ray, A.; Scherr, E. M.; MacDiarmid, A. G. (1988) *Mol Cryst Liq Cryst*, 160:145.
- Tzou, K. T.; Gregory, R. V. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1994, 1.
- MacDiarmid, A. G.; Epstein, A. J. (1989) *Faraday Discuss Chem Soc*, 88:317.
- Wei, Y.; Hariharan, R.; Patel, S. A. (1990) *Macromolecules*, 23:3.
- Yue, J.; Epstein, A. J. (1990) *J Am Chem Soc*, 112:1990.
- Angelopoulos, M.; Patel, N.; Saraf, R. (1993) *Synth Met*, 55:1552.
- Cao, Y.; Smith, P.; Heeger, A. J. (1992) *Synth Met*, 48:91.
- Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J Phys Chem* 1989, 495.
- Leclerc, M.; Guay, J.; Dao, L. H. (1989) *Macromolecules*, 22:649.
- Dhawan, S. K.; Trivedi, D. C. (1993) *Synth Met*, 60:67.
- Pauget, J. P.; Laridjani, M.; Jozefowicz, M. E.; Epstein, A. J.; Scherr, E. M.; MacDiarmid, A. G. (1992) *Mater Res Soc Symp Proc*, 247:589.
- Jozefowicz, M. E.; Epstein, A. J.; Pauguet, J. P.; Masters, J. G. (1991) *Macromolecules*, 24:5863.
- Snauwaert, P. H.; Lazzaroni, R.; Riga, J.; Verbist, J. J. (1986) *Synth Met*, 16:245.
- Diaz, F. R.; Sanchez, C. O.; del Valle, M. A.; Tagle, L. H.; Bernede, J. C.; Tregouet, Y. (1998) *Synth Met* 92: 96.
- Anjoli, A. A.; Patil, S. F.; Deore, B.; Patil, R. C.; Vijayamohan, K. (1997) *Polym J*, 29:787.
- Kwon, A. H.; Conklin, J. A.; Makhinson, M.; Kaner, R. B. (1997) *Synth Met*, 84:95.
- Cihaner, A.; Onal, A. M. (2001) *Eur Polym J*, 37:1767.
- Sharma, A. L.; Annapoorni, S.; Malhotra, B. D. (2001) *Polymer*, 42: 8307.
- MacDiarmid, A. G.; Epstein, A. J. (1994) *Synth Met*, 65:103.
- Angelopoulos, M.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. (1987) *Synth Met*, 21: 21.
- Dash, D.K., Sahu, S.K., Nayak, P.L, (2006) *J. Therm. Anal. Cal.*, 86:2
- Swain, S.N., Rao, K.K., Nayak, P.L, (2004) *J. Therm. Anal. Cal.*, 79:33
- Swain, S.N., Rao, K.K., Nayak, P.L, (2004) *J. Appl. Polym. Sci.*, 93:2590.
- Pattanaik, T., Nayak, P.L., Lenka, S., Mohanty, S., K.K. Rao, (1994) *Thermochim. Acta*, 240:235
- J. STEJSKAL, R. G. GILBERT *Pure Appl. Chem.*, Vol. 74, No. 5, pp. 857-867, 2002.
- Roy BC, Gupta MD, Ray JK (1995) *Macromolecules* 28:1727
- Li, W. and Man, M. (1998). *Porus Polyaniline Films with High Conductivity*, *Synth. Met.*, 92: 121, 126
- Leclerc, M.; D'aprano G.; Zotti, G., *Synth. Met.* 1993, 1527, 55.
- Chan, S. A.; Lee, H.T. *Macromolecules*. 1993, 26, 3254.
- Cao, Y.; Li, S.; Xue, Z.; Guo, D., *Synth Met.* 1986, 16, 57.
