Synthesis, Structural Characterization and Pyrolysis Studies of Poly-2-vinylpyridine Composites

U. RAFIQUE, M. MAZHAR*, M. M. BHATTI AND S. ALI
Department of Chemistry, Quaid-i-Azam University,
Islamabad 45320, Pakistan

(Received 30th January, 2002, revised 25th November, 2002)

Summary: Poly 2-vinylpyridine and its homogeneous composites using different alkali metal salts were synthesized and characterized by molecular weight determination, infrared spectroscopy, scanning electron micrography and thermogravimetry. Pyrolysis studies by TG, DTG and DTA under ambient conditions of static air or argon suggest decomposition of the polymer and composites in more than one step. Kinetic parameters i.e., order of reaction, rate of thermal decomposition of reaction and energy of activation were evaluated from TG isotherm using Horowitz and Redfern methods. It was found that the pair of composites having the same anions follows the same thermal and kinetic stability order.

Introduction

Polymer composites, a versatile domain of polymer science, keep on arousing a great deal of practical interest to be used them as conducting and semi-conducting materials. Because of this fact, it is of prime importance to synthesize new polymeric materials and then observe their degradation pattern in the presence of a dopant. Thermal properties of a styrenated polyester were studied by Anderson and Freeman [1]. TGA, DTA, infrared and mass spectrometry were used to study the thermal degradation of this polymer both in air and in argon. Anderson [2] studied the pyrolysis of polytetrafluoroethylene in vacuum by means of TGA techniques over the temperature range of 450 to 550°C. Employing the method of Freeman and Carroll [3] of estimating kinetic parameters, the values of Ea and n were found to be 74.8 ± 3.9 and 1.02 ± 0.07 kcal./mol. respectively. Light and co-workers reported TGA methods for the analysis of silica filled polytetrafluoroethylene [4]. Detailed studies of the physiochemical properties of polymer electrolytes based on poly(ethylene oxide) [5] have been extended to include their thermal and thermooxidative stability [6,7].

We report here synthesis, structural characterization and pyrolysis studies of poly-2-vinylpyridine and its composites with sodium thiocyanate, potassium thiocyanate, sodium iodide, and potassium iodide. The structural characterization was carried out by molecular weight determination, infrared spectroscopy, scanning electron micrography and thermogravimetry. Pyrolysis studies were carried out by TG, DTG, and DTA and kinetic parameters, such as order of reaction, rate constant and activation energy were evaluated from TG isotherms.

Results and Discussion

Characterization

The molecular weight of poly2-vinylpyridine as determined by vapour pressure osmometric method was 9755 with an error margin of ±5%. Glass transition temperature of the composites of metal-poly-2-vinylpyridine seems to be influenced by the nature of the salt as reported earlier for polypropyleneoxide salts [11]. We observed that larger the size of the anion of the dopant, higher the Tg of the composite and has no relationship with the melting point of the pure dopant (Table 1).

---

*To whom all correspondence should be addressed.

Table-1: Comparison of Melting Points of Salts with Glass Transition Temperature of Poly-2-vinylpyridine and Composites.

Salt	Melting Points	Composite	Glass Transition Temperature
		Poly2-Vinylpyridine	100-110^{0}C
NaSCN	287^{0}C	Poly2-Vinylpyridine-NaSCN	170-200^{0}C
KSCN	172.3^{0}C	Poly2-Vinylpyridine-KSCN	130-150^{0}C
NaI	651^{0}C	Poly2-Vinylpyridine-NaI	160-190^{0}C
KI	723^{0}C	Poly2-Vinylpyridine-KI	120-140^{0}C

The important infrared absorp-tion frequencies (in cm^{-1}) used to characterize poly2-vinylpyridine and its composites with sodium thiocyanate, potassium thiocyanate, sodium iodide, and potassium iodide are given below as 1, 2, 3, 4, and 5 respectively.

1. 3068, 3001, 293.18, 1588.7, 1472.4, 1433.7, 1296.5, 1147.5, 1090.9, 1046.1, 992.5, 783.3, 742.1, 622.9, 542.4.

2. 2078.2, 1479.8, 1433.4, 1144.6, 1084, 1047.7, 997.2, 779.1, 744.8, 623.7, 538.8, 478.3.

3. 2057.3, 1592.6, 1588.2, 1479.9, 1434, 1302.7, 1148.1, 1082.4, 1048, 787.49, 779.91, 747.54, 624.42, 546, 470.

4. 3478, 1597.6, 1478.4, 1439.6, 1156.4, 1083.5, 1058.1, 1001.4, 795.8, 751.1, 637.8, 560.3, 542.4, 475.3.

5. 2931.8, 1591.6, 1561.8, 1475.4, 1438.6, 1299.5, 1147.5, 1082.6, 1052.1, 992.5, 786.6, 748.1, 625.9, 545.4, 470.9.

The assignment of the infrared spectrum of pyridine is well established [12-14]. Gill and co-workers [15] have found that the spectrum of complexed pyridine is little changed from that of the free base, the minor shifts or splittings are significant and are related to the stereochemistry of the complexes. The two lowest frequency bands of pyridine, 605 and 405 cm^{-1}, both suffers significant shifts (50-80 cm^{-1}) to higher frequencies upon complex formation. Clarke and Williams [16] found that the 605 cm^{-1} band is more sensitive to stereochemistry. A shift of about 65-73 cm^{-1} is noted in our synthesized composites.

Pyridine [14,17] shows C-H stretching absorption in region 3100-3000 cm^{-1} characteristic in carbocyclic compounds and can be extended to the heterocyclic systems [18]. The peak at 2931 cm^{-1} is of asymmetric $-CH_2$ vibration in poly-2-vinylpyridine whereas at 3068 and 3001 cm^{-1} are ring –CH vibrations. Peaks at 1588-1561 cm^{-1}, 1440-1433 cm^{-1}, 1156-1147 cm^{-1}, and 751-742 cm^{-1} for poly-2-vinylpyridine and its composites are assigned to C=C ring (conjugated) stretching, $CH=CH_2$ deformation, -CH in-plane deformation, and -CH out-of-plane deformation vibrations, respectively.

In crystalline of poly-2-vinylpyridine bands were observed by infrared spectroscopy at 928 and 1180 cm^{-1} [19]. Absence of both peaks in the sample indicates that the material has changed from crystalline to amorphous. In addition, the appearance of new and intense peaks at 2078.2, 2057.3, 3478, and 2931.8 cm^{-1} for composites with sodium thiocyanate, potassium thiocyanate, sodium iodide and potassium iodide, respectively, suggests interaction between the polymer and the added salts through nitrogen atom of the pyridine ring.

Scanning electron microphoto-graphs for poly-2-vinylpyridine, added salts, and composites indicate that the morphology of poly-2-vinylpyridine changes as salt is added to it. Composites exhibit more compact, heterogeneous and irregularly shaped particles dispersed in the matrix suggesting interaction of salt with poly-2-vinylpyridine. The particle size ranges from 60-400 um, 4-60 um, and 40-220 um for poly-2-vinylpyridine, salts and composites respectively. It may be speculated that a coherent material emerges due to coherence of two different components indicating the formation of some molecular aggregates in the composites possibly due to the presence of non-bonding part of the dopant. Microphotograph of a representative sample is presented in Figure 1.

Thermogravimetry (TG)

The thermogravimetric curve for poly-2-vinylpyridine in argon shows that poly2-vinylpyridine decomposes in two steps (Figure 2). In

Fig. 1 Scanning Electron Micrograph for poly-2-vinylpyridine-NaI composite.

Table-2: Pyrolysis Results of Poly-2-vinylpyridine and Composites.

Sample **W$_o$(mg)**	**Atmosphere**	**% Wt.Loss Ist Step**	**% Wt. Loss 2nd Step**	**% Wt. Loss 3rd Step**	**%Wt of Residue**
Poly-2-Vinylpyridine **20.9mg**	**Air**	54.79 315-482^{0}C Tr =405.5^{0}C	18.29 482-860^{0}C Tr =556^{0}C		26.92
Poly-2-Vinylpyridine **34.7mg**	**Argon**	3.07 140-310^{0}C Tr=200.2^{0}C	80.86 310-523^{0}C Tr=416.9^{0}C	6.10 523-920^{0}C Tr=1098^{0}C	9.97
Poly-2-Vinylpyridine-NaSCN **28.5mg**	**Argon**	9.93 342-514^{0}C Tr=415.3^{0}C	50.62 514-925^{0}C Tr=628^{0}C		39.45
Poly-2-Vinylpyridine-KSCN, 25.1mg	**Air**	45.05 352-496^{0}C Tr= 426.3^{0}C	10.66 496-776^{0}C Tr=628.6^{0}C		44.29
Poly-2-Vinylpyridine-KSCN, 9.2mg	**Argon**	41.96 363-496^{0}C Tr=413.2^{0}C	16.95 496-1108^{0}C Tr=983^{0}C		41.09
Poly-2-Vinylpyridine-NaI **24.0mg**	**Air**	10.69 90-320^{0}C Tr=123.2^{0}C	42.11 320-480^{0}C Tr=409^{0}C	32.71 480-993^{0}C Tr=936.6^{0}C	14.49
Poly-2-Vinylpyridine-NaI **34.1mg**	**Argon**	7.28 60-306^{0}C Tr=129.7^{0}C	49.53 306-483^{0}C Tr=403.4^{0}C	37.82 483-1126^{0}C Tr=1002.9^{0}C	5.37
Poly-2-Vinylpyridine-KI **25.6mg**	**Air**	47.91 341-491^{0}C Tr=411.9^{0}C	35.27 491-970^{0}C Tr=928.2^{0}C	9.2 970-1111^{0}C Tr=1065.9^{0}C	7.62
Poly-2-Vinylpyridine-KI **35.7mg**	**Argon**	3.10 100-289^{0}C Tr=140^{0}C	49.23 289-551^{0}C Tr=401.7^{0}C	43.45 551-1155^{0}C Tr=1040.6^{0}C	4.22

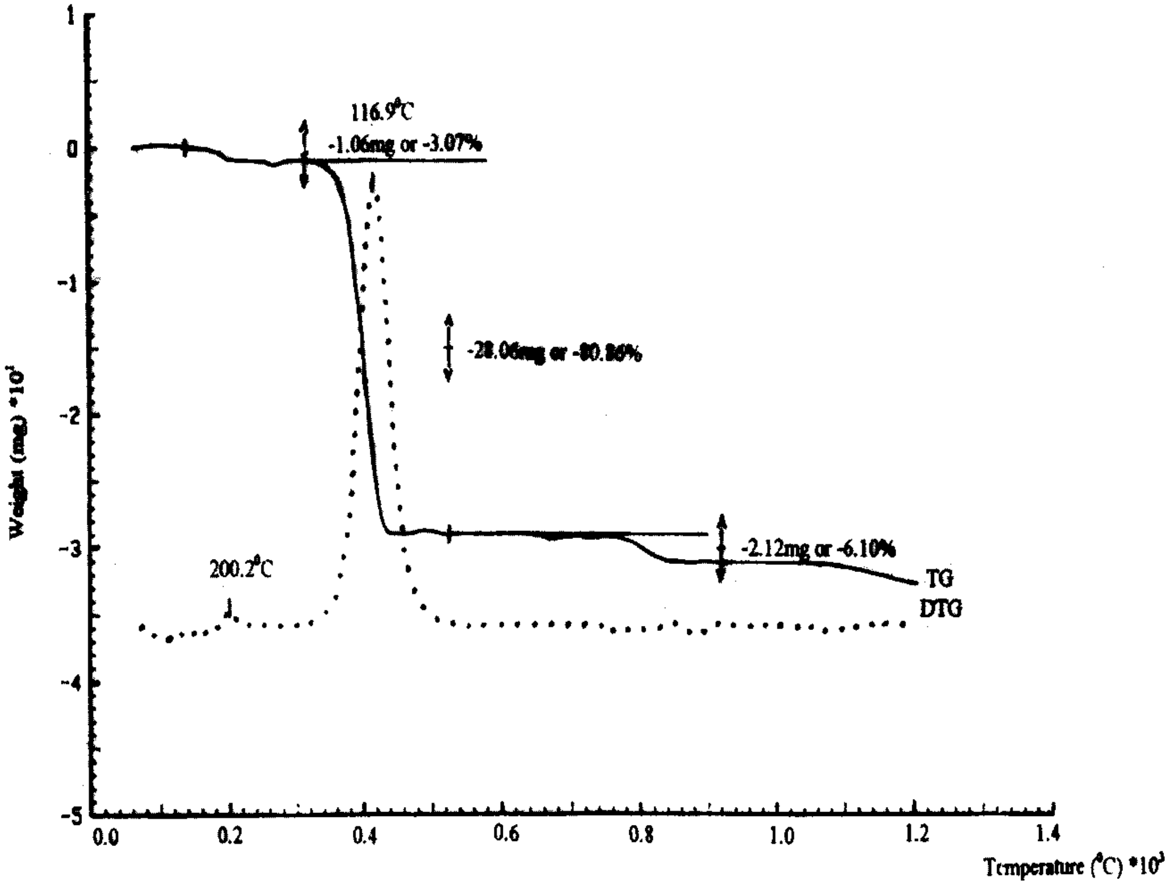

Fig. 2 Thermogram for poly-2-vinylpyridine in Argon.

the first step, 80.86% weight loss was observed till 454°C. In the second step, there was relatively less weight loss (6.10%) and this loss continued to a maximum of 86.96% at 846°C. Two stage decomposition is typical of the polymethylmethacrylate [20]. The first stage at lower temperature is initiated at unsaturated chain ends (resulting from disproportionation in the termination step of polymerization) and the second stage by random scission of the backbone.

The thermograms for the representative composites of poly-2-vinylpyridine are illustrated in Figures 3 and 4. Pyrolysis results, total percent weight loss, and 50% decomposition temperatures are summarized in Tables 2-4, from where it can be found that poly2-vinylpyridine and its composites follow the stability order: Poly-2-vinylpyridine-KSCN > poly-2-vinylpyri-dine-NaSCN > poly2-vinylpyridine > poly-2-vinylpyridine-NaI > poly-2-vinylpyridine-KI. The thermal stability of poly-2-vinylpyridine is affected by the nature of the dopant. It is evident (Table 2) that addition of potassium thiocyanate and sodium thiocyanate has a stabilizing effect on poly-2-vinylpyridine whereas additives like potassium iodide and sodium iodide accelerate thermal decomposition, making it relatively unstable. It also appears that a change in ambient from air to argon exhibits no change in the order of thermal stability of the composites.

The larger residues obtained from poly-2-vinylpyridine-KSCN and poly-2-vinylpyridine-NaSCN indicate that continued heating of the composites generate cyclic rather than volatile products as noted in case of iodide samples. The process of cyclization seems to continue with constant heating causing a change in structure as

Table 3: Total Percent Weight Loss of Poly-2-vinylpyridine and Composites

Sample	Dopant	% Wt. Loss	
		In Air	In Argon
Poly-2-Vinylpyridine	-	73.08	90.03
Poly-2-Vinylpyridine-NaSCN	NaSCN	-	60.55
Poly-2-Vinylpyridine-KSCN	KSCN	55.71	58.91
Poly-2-Vinylpyridine-NaI	NaI	85.51	94.63
Poly-2-Vinylpyridine-KI	KI	92.38	95.78

Table 4: 50% Decomposition Temperature of Poly-2-Vinylpyridine and Composites.

Sample	Atmosphere	50% decomposition temperature
Poly-2-Vinylpyridine	Air	475.00°C
Poly-2-Vinylpyridine	Argon	389.01°C
Poly-2-Vinylpyridine-NaSCN	Argon	1097.52°C
Poly-2-Vinylpyridine-KSCN	Air	520.12°C
Poly-2-Vinylpyridine-KSCN	Argon	522.40°C
Poly-2-Vinylpyridine-NaI	Air	858.47°C
Poly-2-Vinylpyridine-NaI	Argon	1708.29°C
Poly-2-Vinylpyridine-KI	Air	517.61°C
Poly-2-Vinylpyridine-KI	Argon	578.46°C

noted earlier [21] in degradation study of cuprous cyanide, $Cu(CN)_2$.

Kinetic Study

Kinetic parameters such as energy of activation (E_a), reaction rate (k) and order of reaction (n) for the pyrolysis of poly2-vinylpyridine and its composites are determined according to Coats and Redfern [22] method using the following equation for n = 1.

$$\log[-\log(1-\alpha)/T^2] = \log AR/\alpha E_a\,[1-2RT/E_a] - E_a/2.3RT$$

and for n values other than 1

$$\log\{1-(1-\alpha)^{1-n}/T^2(1-n)\} = \log AR/\alpha E_a\,[1-2RT/E_a\} - E_a/2.3RT$$

where α is fraction decomposed at time t, n is order of reaction and k is the rate constant. Different

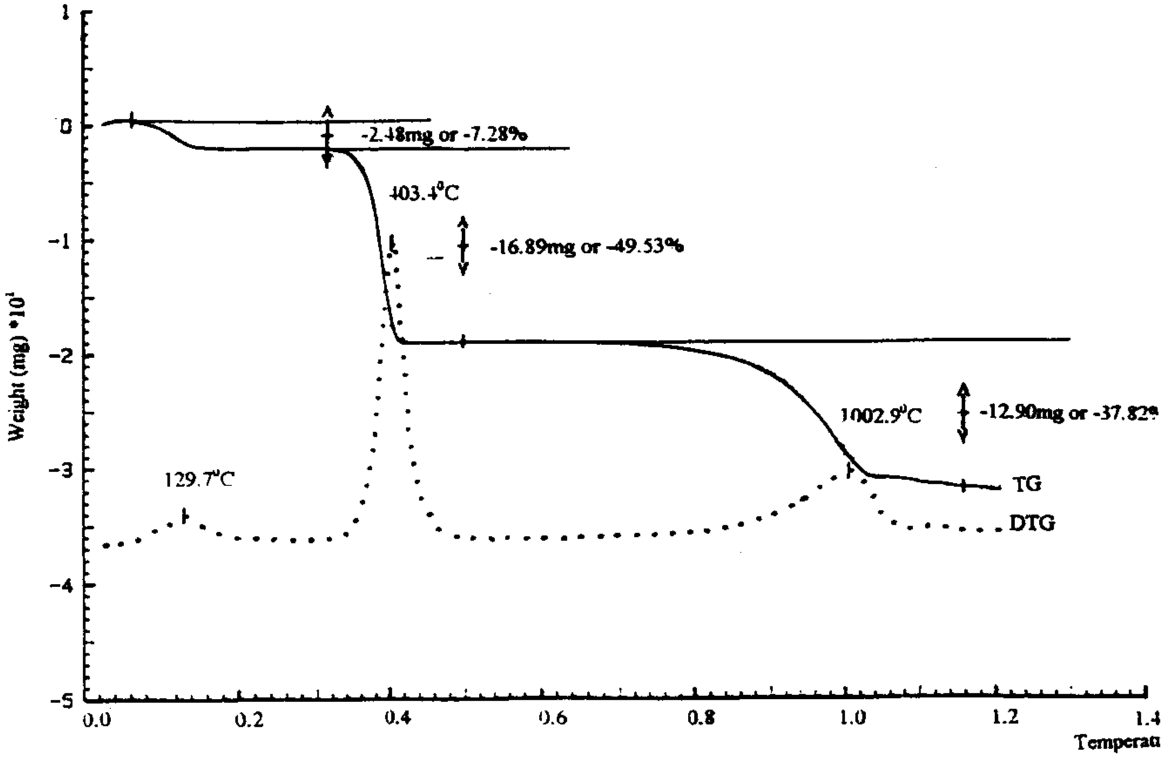

Fig. 3 Thermogram for poly-2-vinylpyridine-NaI in Argon.

Table 5: Energy of Activation (Ea) And Order of Reaction (n) for Poly-2- vinylpyridine and Composites

Sample	Decomposition Stage	Atmosphere	Order of Reaction (n)	E_a (kJ/mol) Redfern	E_a (kJ/mol) Horowitz
Poly-2-vinylpyridine	1	Air	0.8	60.82	61.01
	2		0.5	39.69	40.96
Poly-2-vinylpyridine	1	Argon	1.7	54.83	54.28
	2		3.3	101.34	100.04
Poly-2-vinylpyridine-KSCN	1	Argon	0.5	53.11	53.33
	2		0.7	32.60	31.65
Poly-2-vinylpyridine-NaSCN	1	Air	0.6	58.52	59.21
	2		0.4	45.75	46.85
Poly-2-vinylpyridine-NaSCN	1	Argon	0.4	58.83	58.92
	2		1.0	36.64	38.03
Poly-2-vinylpyridine-NaI	1	Air	0.4	13.74	13.36
	2		0.9	58.91	57.73
	3		1.8	46.73	47.88
Poly-2-vinylpyridine-NaI	1	Argon	1.0	12.40	12.61
	2		0.8	48.94	47.85
	3		1.3	56.67	56.47
Poly-2-vinylpyridine-KI	1	Air	0.5	51.80	51.11
	2		1.9	58.18	58.96
	3		0.5	206.16	210.17
Poly-2-vinylpyridine-KI	1	Argon	0.6	30.81	30.58
	2		1.5	66.57	65.60

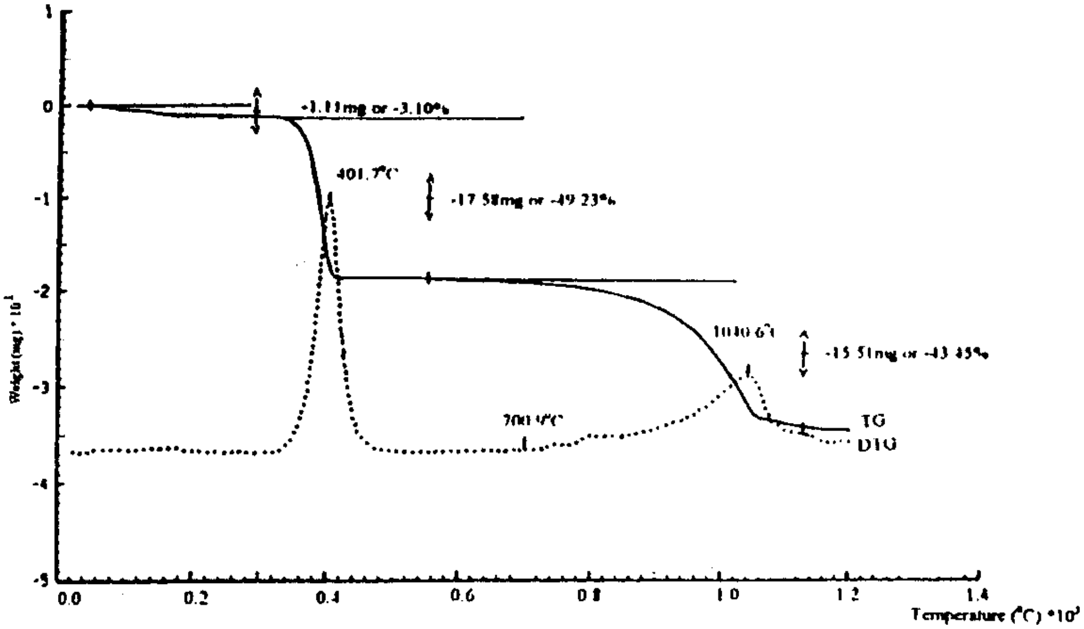

Fig. 4 Thermogram for poly-2-vinylpyridine-KI in Argon.

values of n are tried in order to obtain the best linear fitting of the experimental results. Energies of activation for poly-2-vinylpyridine and its composites are also calculated by Horowitz and Metzger [23] method using the equation:

$$\ln\ln W_0/W = E_a * \theta/RTr^2$$

As is clear from the data given in Table 5, energies of activation calculated for poly-2-vinylpyridine and its composites by two different methods [22,23] are found to be comparable. However, a slight discrepancy may be attributed to the mathematical treatment of pyrolysis data following different computing methods [24]. It is also apparent that pair of composites having the same anions follows the similar activation energy sequence. It is also observed that composites with thiocyanates are more stable than iodides. Hence, we concluded that the composites following the same thermal stability order experience the same kinetic stability order.

Experimental

Materials

2-Vinylpyridine (97%) obtained from Aldrich Chemical Company was dried over anhydrous sodium carbonate for 48 hours and distilled under vacuum at 60^0C. Tetrahydrofuran (THF) used as solvent for polymerization and composite formation was dried over sodium benzophenoate and distilled immediately before use. All other chemicals were of A.R. grade.

Polymerization of 2-vinylpyridine

40 ml (0.36 mol) of distilled 2-vinylpyridine was stirred with azoisobutyronitrile AIBN (0.1-2% wt./vol.) in a round bottom flask fitted with water condenser at 60^0C for 10 hours under helium gas. Poly-2-vinylpyridine obtained was purified by dissolving in THF and precipitating with dry n-hexane. The polymer was dried under vacuum for several hours.

Preparation of polymer composites

The following general procedure was adopted for the preparation of polymer composites.

0.526 g of poly-2-vinylpyridine was dissolved in 20 ml of dry THF in a 3-necked round bottom flask fitted with a magnetic stirrer and cold water condenser under inert atmosphere. 0.25 g of salt was dissolved in 20 ml of THF and added dropwise to the stirring solution of poly-2-vinylpyridine over a period of two hours. The solvent was removed on rotary evaporator followed by vacuum drying for several hours. In all the preparations 1:3 stoichiometry of salt to monomer was assumed as prescribed by Armand [8-10].

Molar mass of poly-2-vinyl-pyridine was estimated by vapour pressure osmometry. Infrared spectra of samples were recorded on Hitachi model 270-50 Japan with data processor. Scanning electron micro-photographs for poly-2-vinylpyridine and its composites were obtained by dispersing the samples on a brass support and fixed with a double face 3M™ tape. The material was then coated with gold/ palladium alloy using the sputtering technique with the Sputter Low Voltage LVC76 from Plasma Science Inc. The scanning electron microscope (JEOL JSM T-300) was connected to a secondary electron image and x-ray dispersive detectors were used. Thermogravimetric analysis was conducted on a NETZSCH Simultaneous Thermal Analyzer STA 429 using the ambient conditions of static air or argon.

Conclusions

The following conclusions are drawn:

1. The route adopted to synthesize poly-2-vinylpyridine (molar mass 9755) and its metal complexes provides a convenient and efficient method of preparation, which also excludes the possibility of getting impurities or, moisture in the materials.

2. Infrared spectra indicate the occurrence of structural changes on addition of salts to poly-2-vinylpyridine that may be attributed to the formation of composite involving interaction between the two.

3. Poly-2-vinylpyridine is thermally stable and doping with alkali metal salts further increase its stability due to resonance effect of nitrogen in pyridine ring, which acts to stabilize a carbenium ion on the polymer chain.

4. Addition of thiocyanates of sodium and potassium as dopant have stabilizing effect whereas iodides of sodium and potassium facilitate thermal decomposition.

References

1. D. A. Anderson and E. S. Freeman, *J. Appl. Polymer Sci.*, **1**, 192 (1959).
2. H. C. Anderson, *Makromol. Chem.*, **51**, 233 (1962).
3. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
4. T. S. Light, L. F. Fitzpatrick and J. P. Phaneuf, *Anal. Chem.*, **37**, 79 (1965).
5. C. Robitaille, S. Marques, D. Boils and J. Prud'homme, *Macromolecules*, **20**, 3023(1987); G. G. Cameron, J. L. Harvie, M. D. Ingram and G. A. Sorrie, *Br. Polym. J.*, **20**, 199 (1988).
6. G. G. Cameron, M. D. Ingram, M. Y. Qureshi, H. M. Gearing, L. Costa and G. Camino, *Eur. Polym. J.*, **25**, 779 (1989).
7. L. Costa, A. M. Gad, G. Camino, G. G. Cameron, M. D. Ingram, and M. Y. Qureshi.

Second International Symposium on Polymer Electrolytes; B. Scrosati, Elsevier, Applied Science, London, (1990).
8. M. Armand, *Solid State Ionics*, **9&10**, 745 (1983).
9. T. Hibma, *Solid State Ionics*, **9&10**, 1101 (1983).
10. A. Okamura and J. Turkevitch, *Polym.*, **28**, 1815 (1987).
11. D. B. James, R. E. Wetton, and D. S. Brown, *Polym.*, **20**, 187 (1979).
12. C. H. Kline and J. Turkevitch, *J. Chem. Phys.*, **12**, 300 (1944).
13. L. Corsin, B. J. Fax and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953).
14. J. K. Wilmshurst and H. J. Bernstein, *Canad. J. Chem.*, **35**, 1185 (1957).
15. N. S. Gill, R. H. Nuttal, D. E. Scaife and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, **18**, 79 (1961).
16. R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).
17. L. Marion, D. A. Ramsay and R. N. Jones, *J. Am. Chem. Soc.*, **73**, 305 (1951).
18. W. H. Tallent and I. J. Siewers, *Anal. Chem.*, **28**, 953 (1956).
19. S. Arichi, *Bull. Chem. Soc. Jap.*, **41**, 244 (1968).
20. H. H. G. Jellinek, *Aspects of Degradation and Stabilization of Polymers*, Elsevier, Amsterdam, (1978).
21. M. Mazhar, N. A. Khan, N. Baber and M. Z. Iqbal, *Chem. Mater.*, **5**, 1283 (1993).
22. A. W. Coats and J. P. Redfern, *Nature*, **68**, 201 (1964).
23. H. H. Horowitz and G. Metzger, *Anal. Chem.*, **35**(10) 1464. (1963)
24. F. Carrasco, *Thermochim. Acta*, **213**, 114 (1993).