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THERMAL DEGRADATION STUDIES OF SUBSTITUTED CONDUCTING POLYANILINES

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The synthesis of conducting polymers based on *m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol by aniline initiated ammonium peroxydisulfate oxidation, has been attempted. The IR spectra of the polymers have been studied. Thermogravimetric analysis of the conducting polymers has been followed using a computer analysis method LOTUS PACKAGE, developed by us for assigning the degradation mechanism. A number of equations have been used to evaluate the kinetic parameters. The mechanism of degradation of the conducting polymers has been explained on the basis of their kinetic parameters.

Keywords: *conducting, degradation, polyanilines*

Introduction

In recent years conducting polymers have attracted great attention due to their electrochemical, optical and environmental stability [1–4]. Among the organic conducting polymers, polyaniline is one of the most important classes of conjugated polymers studied with typical, chemical and mechanical properties along with major electronic characteristic of metals as well as semiconductors [5–7]. Further these types of polymers are stable under ambient conditions with readily available procedure of sample synthesis. These polymers are widely employed in the fabrication of rechargeable batteries, electronic windows, biosensors and antistatic materials but like the other polymers in this class, it is severely limited by its intractable & non-processable nature [8–11]. The non-conducting form of substituted polyanilines (alkyl, alkoxy and halide subsistent) which is soluble in several common aprotic organic solvents has been used to circumvent this limitation [12, 13]. These materials can be processed in the non-conducting form and then converted to conducting form when in their final physical configuration. The substituted polymers retain the electrochemical and electrochromic properties but have much lower electrical conductivities (10^{-3}–10^{-7} S cm^{-1}) than the parent polyaniline polymer [8]. Polyanilines are unique since they are soluble in aqueous solution and can be processed in water. Thus, avoiding the environmental concern associated with the use of organic solvents, it has been shown by various workers that substituted polyanilines with sulfonic acid or carboxylic acid side chains are soluble in aqueous alkaline solution [14].

A survey of literature reveals that the thermal degradation pattern of conducting polymers has not been seriously dealt with involving the various kinetic equations and the related parameters. The study of this particular aspect of the conducting polymers might throw light regarding the processability of conducting polymers.

In the present research program the thermal degradation pattern of some substituted polyanilines have been studied by using a LOTUS package developed by us and various kinetic parameters have been evaluated and the plausible degradation mechanism has been discussed.

Experimental

Materials and instrumentation

Aniline, *m*-nitroaniline, *m*-chloroaniline, *m*-aminophenol, ammonium peroxydisulfate were purchased from Merck (Germany). Aniline was doubly distilled prior to polymerization and others were re-crystallized in suitable solvent. Ammonium peroxydisulfate was used as the oxidant in polymerization.

Synthesis

Polymers were prepared by ammonium peroxydisulfate oxidation in a method similar to polyaniline preparation [15]. The individuals do not form a homopolymer even if the reactants are kept for 48 h at room temperature. By

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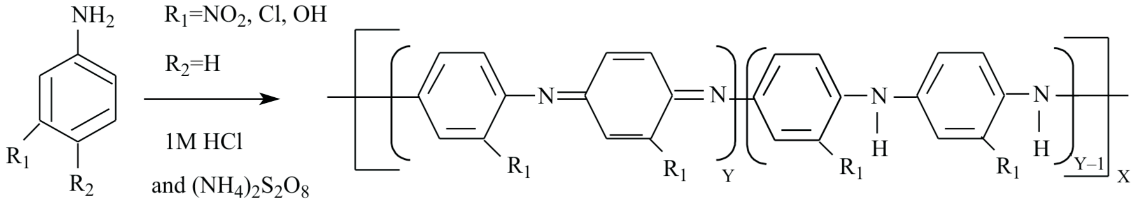

Scheme 1 Shematic respresentation of *m*-substituted polyanilin; 1 – Poly(*m*-nitro aniline) PMNA if R_1=NO$_2$, 2 – Poly(*m*-chloro aniline) PMCA if R_1=Cl, 3 – Poly(*m*-amino phenol) PMAP if R_1=OH

addition of a few drops of aniline (15 mol%) to the system, polymerization took place at different temperatures. A component to be polymerised is taken 14.49 mmol and aniline is 15 mol% of component were dissolved in 150 mL of 1M HCl. A solution of $(NH_4)_2S_2O_8$ (2.89 g, 12.67 mmol) in 50 mL of 1M HCl was added drop-wise with stirring over a period of 30–40 min. A dark brownish black color developed and the polymerised product precipitated in the solution. The reaction mixture was stirred at room temperature for 48 h. 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 mass. Under the same condition poly (*m*-nitro aniline) (PMNA), poly (*m*-chloroaniline) (PMCA), poly (*m*-aminophenol) (PMAP) were prepared.

Infrared spectra of the polymers were recorded using Perkin-Elmer 1720 spectrophotometer. Thermal degradation pattern of the polymers were studied using thermogravimetric analyser (TGA-7; Perkin-Elmer, Norwalk, CT) in atmospheric condition at 3°C min^{-1} from room temperature to 650°C.

FTIR studies

The FTIR studies of the polymers have been undertaken in order to ascertain the structure of the polymers. The quinonoid stretching are present at 1586.4 cm^{-1} (PMNA), 1576.2 cm^{-1} (PMCA) and the benzonoid stretching present at 1520 cm^{-1} for PMAP. The presence of 1,2,4-tri-substitution is indicated by the bands in the region 746.3–1174 cm^{-1} (PMNA) and 787–1158.7 cm^{-1} (PMCA) and band around 848 cm^{-1} (PMAP) is ascribed to the C–H in-plane and out of plane bending modes. The symmetric N=0 stretch in the PMNA polymer is at 1352.2 cm^{-1}. The characteristic amine vibration bands are present at 3231 cm^{-1} appears for both PMNA and PMCA. The PMAP based polymer shows a broad peak at 3368.6 cm^{-1} for –OH bond, an amine vibration at 3205.7 cm^{-1}. A peak at 848.1 cm^{-1} confirms the presence of isolated –H of benzene ring. The C–Cl (S) bonds appear at 787 cm^{-1} for PMCA [1–2]. The plausible schematic representation of conducting polymer is given in Scheme 1.

Models used

The calculation of kinetic data from the TG curve is based on various kinetic equations [16–18]. All probable forms of ‘$g(\alpha)$’ are used for identification of the reaction mechanism [19–21]. A differential method was used to identify the most suitable reaction mechanism for identification of steps involved in a given thermal reaction. Hence for a single TG curve, one can use all ‘$g(\alpha)$’ functions and the one which has the best linearity would be considered as the most probable mechanism. The correlation coefficient ‘R^2‘, error in estimation of intercept and slope are used to test the linearity. The smaller error in estimation of intercept and slope, the better is the linearity. In the present investigation, a program has been developed using LOTUS macros to calculate these kinetic parameters from the non-isothermal TG curves [22]. After feed-

Table 1 Kinetic parameters of substituted conducting polyanilines

Sample	Steps	Temperature/°C		Model	R^2	Slope	Intercept	Act. energy/ kJ mol^{-1}	Frequency factor
		Start	End						
PMNA	1	70.92	311.56	B1	0.994	–787.187	6.971	14.418	2559.634
	2	317.59	613.89	B1	0.985	–1582.245	7.810	28.980	11912.091
	3	616.8	622.64	B1	0.993	–4263.035	10.857	78.081	675139.950
PMCA	1	146.16	409.63	B1	0.980	–907.249	7.071	16.617	3260.734
	2	415.64	594.25	B1	0.987	–2430.904	8.834	44.524	50921.660
	3	600.12	650.30	B1	0.952	–6304.475	12.939	115.870	8009856.100
PMAP	1	71.37	348.45	B1	0.992	–697.886	6.769	12.982	1854.241
	2	354.49	568.84	B1	0.984	–1859.950	8.211	34.066	20891.462
	3	574.77	616.26	B1	0.966	–7246.900	14.227	132.732	33381515.000

Table 2 Thermal decomposition data of substituted polyanilines (mass loss/% at various temperatures)

Sample	Temperature/°C					
	100	200	300	400	500	600
PMNA	2	9	17	33	59	95
PMCA		5.5	13	25	51	92
PMAP	4	11	19	39	74	97

ing the values of a corresponding temperatures and number of data points, the program calculates $\lg(\alpha)/T^2$, I/T, slope, intercept, R^2 and error values for all the thirty reaction mechanisms [19] and prepares corresponding charts.

The kinetic parameters such as '*A*', and '*E*' etc. are calculated for all the synthesized products and the data are presented in Table 1.

TG data analysis

The data on temperature and percent weight loss have been subjected to differentiation to fix the actual number of stages involved in the process. Percentage mass loss was differentiated with respect to temperature and each time change in the sign of slope observed, it is presumed that there is a change in chemical reaction.

Results and discussion

The TG curve and derivative curve of the aniline initiated polymerisation of substituted anilines are presented in Figs 1–3 and the percent mass loss at a frequency of 100° temperature are shown in Table 2. The TG curve indicated three stages of degradation of the polymers. In case of the poly *m*-nitroaniline (PMNA), the first break takes place around 100°C having mass loss about 2%, the second break takes place around 317°C having mass loss about 19% and the third break takes place around 615°C having total mass loss about 97%. This can be explained by considering the structure of PMNA.

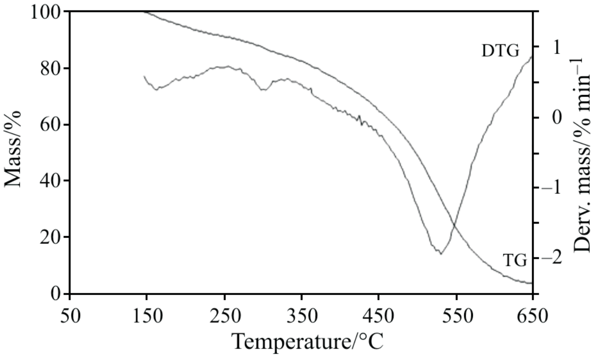

Fig. 2 TG and DTG curves for PMCA

The first break around 100°C is attributed to the elimination of water. The second break around 317°C is due the breakage of the side chain eliminating gases like N_2 and NO_2 etc. The third break around 615°C may be due to the breakage of the aromatic ring forming gases like CO_2 etc. Similar mechanism has also been observed in other two samples viz. PMCA and PMAP.

The perusal of the values of the activation energy for different stages of the degradation indicates that in case of all the polymers the degradation is very fast in the first stage and slows down gradually till the last stage of degradation. This is obvious since in the first step moisture absorbed in the polymer is eliminated. In the second step, the side chain breaks producing probably some gases like N_2 or NO_2. The third step is very slow since in this step the benzenoid ring is ruptured which is generally a very slow process.

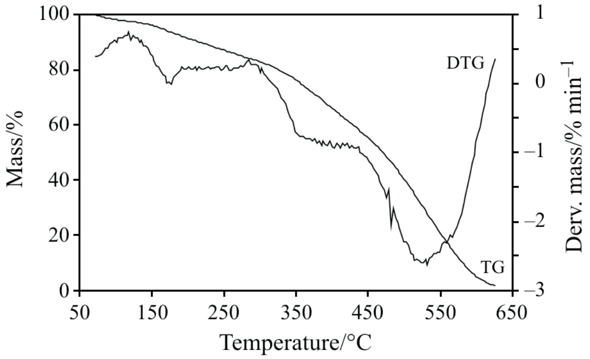

Fig. 1 TG and DTG curves for PMNA

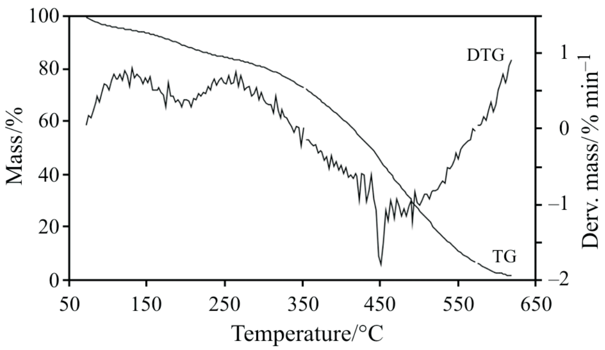

Fig. 3 TG and DTG curves for PMAP

Appendix

Where α is the fractional loss of the sample at temperature T and $g(\alpha)$ is a function of α and governs the type of mechanism that the reaction follows. A is the frequency factor and E is the energy of activation.

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