

Synthesis and thermal stability of xylene-formaldehyde resins

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Abstract. *o*-, *p*- and *m*-xylene have been condensed with formaldehyde using paratoluene sulphonic acid as a catalyst and acetic acid/acetic anhydride as a solvent. The xylene-formaldehyde resins thus obtained have been characterised by IR and NMR spectra. The average molecular weight of the resin samples was determined by vapour pressure osmometry. Kinetic parameters were determined by differential thermal analysis, thermogravimetry and differential scanning calorimetry.

Keywords. Xylene-formaldehyde resin; paratoluene sulphonic acid; differential thermal analysis; thermogravimetry; differential scanning calorimetry.

1. Introduction

Polymeric products can be obtained by the acid catalysed condensation of aromatic hydrocarbon with formaldehyde (Bayer 1872). Dixylene methane and its polymer containing 3 to 4 units are formed by the reaction between *p*-xylene and paraformaldehyde in the presence of aluminium chloride (Hustons and Ewing 1915). Reaction of xylene, paraformaldehyde and sulphuric acid in the proportion of 2: 1: 0.06 mol at 120° C gave good results (Ratnikova and Dushkina 1958). Ching-Yun-Huang (1959) have studied the reaction between formaldehyde with *m*-xylene and also with its intermediates. Polymers have also been prepared by the reaction of formaldehyde with naphthalene, anthracene, toluene, phenol, diaryl methans and *m*-xylene (Ghatge 1966). Kinetic parameters of the non-isothermal addition-condensation of *m*-xylene-formaldehyde system were studied by Lee (1970). The reaction is reported to be of the second order having an activation energy of 23.3 kcal/mol and a frequency factor 6.6×10^{13} 1/mole-min.

However, the physical properties of individual xylene and formaldehyde resin do not appear to have been studied and this paper reports results of our study.

2. Experimental

2.1. Condensation reaction

The chemicals used were of analytical grade. The reaction was carried out in a three-necked flask. Paraformaldehyde was depolymerised in the flask and xylene

was added to it. The reaction was carried out under reflux at constant temperature in an oil-bath ($\pm 0.2^\circ\text{C}$). The product was obtained by discharging the polymer solution into ice-cold water and the granular solid obtained was thoroughly washed to remove acid and formaldehyde. Xylene-formaldehyde (XF) resin was dissolved in toluene and insoluble fraction was separated. Petroleum ether (non-solvent) $40\text{--}60^\circ$ was added to the clear solution of resin. The precipitated resin thus obtained was dried in vacuum for 24 h at room temperature.

Preliminary studies on the concentration of catalysts, reaction temperature, solvent and monomer concentration, showed that the solid product could be obtained with the conditions mentioned in table 1. These samples of KF-resins were used for their characterisation and the study of thermal stability.

2.2. Characterisation

The IR absorption spectra of XF-resins were scanned on a Carl Zeiss model UR-10. The NMR data were obtained using the Varian A-60 D spectrophotometer operating at an applied radio-frequency (*rf*) of 60 megacycles/sec. The average molecular weight of the XF-resin samples was determined using Hewlett-Packard Model-302 B vapour pressure osmometer. The results are given in table 1. The thermal properties of the XF-resins were studied using differential thermal analysis (DTA) and thermogravimetry (TG) equipment. The differential scanning calorimetry (DSC) was studied with a Dupont model-900 Thermal Analyser-USA. The results are given in tables 2 and 3.

3. Results and discussion

The experimental conditions regarding the preparation of XF resins are given in table 1. When *p*-xylene is condensed with paraformaldehyde in the presence of paratoluenesulphonic acid as catalyst, it gives two types of product, one soluble (mp 105°C) and the other one insoluble (mp 210°). *o*-xylene and *m*-xylene gives soluble products having mp 113° and 100°C . The average molecular weight of the resin for *p*-, *o*-, and *m*-xylene-formaldehyde resin is 850, 1033 and 742 respectively. Indicating that as the molecular weight increases, mp also increases.

The IR spectra consider the important frequencies for the aromatic ring sketching, methylene bridge stretching, phenyl vibration and aromatic methyl group vibrations. In the region from $2800\text{--}3000\text{ cm}^{-1}$, the aromatic -CH stretching band appears at 3000 cm^{-1} and 2971 cm^{-1} . The asymmetric stretching of methyl group on aromatic ring -CH_2 bridge is reflected between 2905 cm^{-1} to 2950 cm^{-1} . The symmetrical stretching band is observed between 2858 cm^{-1} to 2870 cm^{-1} . The band in the region between 1374 cm^{-1} to 1386 cm^{-1} is only due to symmetric scissoring of methyl group on carbon atom. The methyl rocking is mass-sensitive and obtained at 1042 cm^{-1} . The distinct absorption band between 1444 cm^{-1} to 1458 cm^{-1} represents the bending modes of methylene groups in bridge which afford clear evidence for the existence of -CH_2 group in the resins. This is further evident from the band appearing between $1192\text{--}1362\text{ cm}^{-1}$ due to CH_2 bending.

NMR spectra of all the XF resins except *p*-xylene-formaldehyde (*p* · XF-insoluble) resin show aromatic proton multiplet at $7.0\text{--}7.6\delta$, methyl proton singlet at 2.7δ , and methylene proton singlet at 4.25δ .

Table 1. Preparation of xylene-formaldehyde resin using acetic acid (5 ml) and acetic anhydride (5 ml) as solvent and paratoluenesulphonic acid (PTS) as catalyst.

Mole of xylene	Mole of paraformaldehyde	Reaction time hr.	Reaction temp. °C	PTS in g	State of product	Solubility in CHCl ₃ , CCl ₄ , C ₆ H ₆	Melting point* °C	Yield in g	Average molecular weight \bar{M}_n
0.1 M <i>p</i> -xylene	0.1	3	120	2.0	yellow amorphous solid	Soluble Insoluble	105 210	4.5 3.0	850
0.1 M <i>o</i> -xylene	0.1	3	120	1.0	„	Soluble	113	8.0	1033
0.1 M <i>m</i> -xylene	0.1	3	120	1.0	„	Soluble	100	8.0	742

* Value of melting point is obtained from DSC curve.

Table 2. Kinetic parameters from thermogravimetry (TG). Method: Chatterjee (1965); System: Xylene-formaldehyde resin.

Resin	Rate of heating (° C/min)	Amount of resin (mg)	Decomposition temp. range (° C)	ΔT (° C)	Weight loss (%)	Energy of activation kcal/mole	Order of reaction n	Frequency factor $A \text{ min}^{-1}$
<i>p</i> -Xylene-formaldehyde resin (soluble)	6.5	50	165-395	455	45	18.4	1.14	6.58×10^6
			395-620		55	26.7	1.14	7.54×10^6
		25	160-395	470	45	18.0	1.14	4.93×10^6
			400-630		55	23.2	1.14	7.27×10^6
<i>p</i> -Xylene-formaldehyde resin (insoluble)	6.5	50	300-650	350	100	14.7	0.86	9.81×10^3
			25	305-650	345	100	13.7	0.86
<i>o</i> -Xylene-formaldehyde resin	6.5	50	320-645	325	100	31.9	1.30	8.86×10^7
			25	325-630	310	100	31.9	1.30
<i>m</i> -Xylene-formaldehyde resin	6.5	50	300-650	350	100	14.5	0.96	1.43×10^3
			25	305-655	350	100	14.0	0.98

Table 3. Kinetic parameters from differential thermal analysis (DTA) and differential scanning calorimeter (DSC). System: Xylene-formaldehyde resin.

Name of the resin	Rate of heating ° C/min	DTA data			DSC data			
		Peak temp. ° C	Energy of activation Kcal. mole ⁻¹	Order of reaction	Amount of resin (mg)	Rate of heating (° C/min)	γ -axis sensitivity (° C/min)	ΔH_f (Cal/mg)
<i>p</i> -Xylene-formaldehyde resin (soluble)	6.5	400 510	71.9	2.24	6.0	20	0.2	2.6
<i>p</i> -Xylene-formaldehyde resin (insoluble)	6.5	410 505	55.6	0.84	6.5	20	0.5	5.7
<i>o</i> -Xylene-formaldehyde resin	6.5	525	28.8	0.94	5.0	20	0.2	5.5
<i>m</i> -Xylene-formaldehyde resin	6.5	515	65.6	1.43	6.0	40	0.2	9.0

The NMR and IR spectra confirms that there is a methylene bridge between two aromatic ring. The DTA and TG analyses of XF resins have been carried out at a heating rate of $6.5^{\circ}\text{C}/\text{min}^{-1}$ in static air to study their thermal stability and kinetic parameters. Table 2 describes the kinetic parameters of XF resin obtained by Chatterjee (1965) from the TG-thermogram. *p*-xylene-formaldehyde (*p*·XF-soluble) resin showed two steps degradation corresponding to the weight loss of 45% and 55% in the temperature range of 165° to 395°C and 395° to 620°C . The energy of activation for both the steps was 18.4 and 26.7 kcal. mole⁻¹ respectively and the order of reaction 1.14.

p·XF-insoluble resin decomposed in the temperature range 300° to 650°C in one step. The energy of activation and the order of reaction was 14.7 kcal./mol and 0.86 respectively.

The decomposition of *o*-xylene-formaldehyde (*o*·XF) resin started at 300°C and ended at 650°C . The energy of activation was 31.9 and the order of reaction 1.30.

The decomposition of *m*-xylene-formaldehyde (*m*·XF) resin started at 300°C and ended at 650°C . The energy of activation for the reaction was 14.5 kcal. mole⁻¹ and the order of reaction 0.96.

Table 3 represents the kinetic parameter obtained by the Reich (1969) method from DTA studies. The kinetic parameters for *p*·XF (soluble), *p*·XF (insoluble), *o*·XF and *m*·XF resins were 71.9, 55.6, 28.8 and 65.6 kcal. mole⁻¹ and the corresponding order of reactions was 2.24, 0.84, 0.94 and 1.43 respectively.

The heat of fusion as revealed from the DSC-study for *p*·XF (soluble), *p*·XF (insoluble), *o*·XF and *m*·XF resins is 2.6, 5.7, 5.5 and 9.0 Cal/mg respectively.

The decomposition range of XF is resins but their order of reaction, energy of activation and heat of fusion are different. This clearly suggests that their mode of decomposition is different and structural-dependent.

The trend of decomposition followed for the XF-resins as revealed from the thermal studies is:



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