

Thermal behaviour of resorcinol-1,2-dichloroethane resin

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Abstract. Resorcinol-1,2-dichloroethane resin was prepared by Friedel-Craft polymerization from resorcinol and 1,2-dichloroethane. The resin sample was characterised by IR and UV spectra and the average molecular weight was determined by vapour pressure osmometry. Kinetic parameters from TG and DTA thermograms are reported.

Keywords. Resorcinol ; dichloroethane resin ; differential thermal analysis.

1. Introduction

Friedel-Craft's reaction of benzene or substituted benzene and 1,2-dichloroethane gives resins in which benzene nuclei are linked through ethylene bridges (Shinkle 1935; Towne 1937; Sisido and Kato 1940; Shishido and Nita 1945; Shishido and Miyoshi 1945; Shishido and Irie 1945). Anisolic and derivatives of anisolic resins with methylene bridges have been reported by Shah (1973). A literature survey revealed that resin having resorcinol with ethylene bridges has not been reported. This paper reports the synthesis and thermal behaviour of resorcinol-1,2-dichloroethane resin.

2. Experimental

2.1. Friedel-Craft polymerisation

The chemicals used were of analytical grade. The reaction was carried out in a three-necked flask. The preliminary experimental conditions of varying the monomer concentration, catalyst concentration, reaction period and temperature showed that the optimum condition for the preparation of the resin is as follows. Resorcinol (0.10 mol), 1,2-dichloroethane (DCE) (0.25 mol) and aluminium chloride (0.20 mol) as catalyst were mixed and heated at 115°C for 2.5 hr. The reaction mixture was poured in ice and hydrochloric acid followed by repeated washing with distilled water. The resin obtained was further purified using methyl ethyl ketone as solvent and petroleum ether (40°-60° C) as nonsolvent.

2.2. Characterisation

The IR-absorption spectra of resorcinol-1,2-dichloroethane (resorcinol-1,2-DCE) resin were scanned on a Carl Zeiss model UR-10. DK-2A Beckman quartz spectrophotometer was used for light absorption measurements in the ultraviolet regions. The number of average molecular weight (M_n) of the resin sample was determined using a Hewlett-Packard Model-302B vapour pressure osmometer. The differential thermal analysis (TGA) and the thermogravimetry (TG) equipment were used to study the thermal property. The kinetic parameters were evaluated from TG-study (Chatterjee 1965; Anderson and Freeman 1961; Broido 1969; Flynn and Wall 1966). The data obtained are given in table 1. Table 2 shows the kinetic parameters obtained from DTA using Reich (1969) and Kissinger (1956) methods.

3. Results and discussion

Resorcinol-1,2-DCE resin was amorphous in nature and did not soften upto 280° C. The M_n of resin was 827. The resin was soluble in diethylether, acetone and methyl ethyl ketone. The IR spectra of resin showed a band in the region from 2800 – 2975 cm^{-1} ascribed to aromatic C-H stretching and methylene group. The bands were obtained in the range of 1220 to 1250 cm^{-1} and 1350 to 1390 cm^{-1} due to aromatic hydroxyl group. A band at 282 nm in the UV-spectra of this resin sample indicated that the growth of polymeric chain through ethylene bridge did not significantly alter the resonance system of the individual phenolic unit.

DTA and TG analyses of the resorcinol-1,2-DCE have been carried out at 1°, 2·5°, 4·0° and 6·5° C min^{-1} in static air. The TG-thermogram of the resin sample showed a single-step degradation corresponding to 100% weight loss. The temperature ranges for the decomposition at the different RH respectively were: (a) 290° to 500°, (b) 255° to 465°, (c) 295° to 515° and (d) 280° to 585° C.

The DTA thermograms were exothermic in nature, and all peaks were associated with humps (h). The decomposition reaction as revealed from TG is assumed to take place at the hump temperature for all the heating rates. The temperature for the humps and the peak maxima at different RH respectively are: (a) 275°, 390°, (b) 290°, 405°, (c) 290°, 415° and (d) 300°, 440° C.

The activation energies (E_a) obtained from the TG-thermograms using the method of Chatterjee (1965) for 25 and 50 mg of the sample heated at various heating rates were fairly constant, i.e., ~ 20 kcal mol^{-1} and the decomposition of the resin followed nearly first order kinetics (table 1).

The Anderson-Freeman method yielded activation energies for the decomposition of resorcinol-1,2-DCE resin, viz., (a) ~ 16, (b) ~ 16, (c) ~ 15 and (d) ~ 14 kcal mol^{-1} following the first order kinetics for all the RH and for 25 and 50 mg sample, respectively.

The activation energies from Broido method for 25 and 50 mg of the resin sample were (a) ~ 16, (b) ~ 16, (c) ~ 14 and (d) ~ 13 kcal mol^{-1} respectively at the RH mentioned above having a reaction order of 1·00.

The activation energy from Flynn-Wall method for 25 and 50 mg of the resin sample was 29·0 and 28·0 kcal mol^{-1} , considered to be fairly constant.

Table 1. Kinetic parameter from TG curve for the resorcinol-1,2-dichloroethane resin system.

Rate of heating °C/min	Amount of resin in mg	Temperature range °C	Decomposition range $\Delta T^\circ C$	E_A (kcal mole ⁻¹) methods						Order of reaction		
				Chatterjee	Anderson-Freeman	Broido	Flynn-Wall	Chatterjee	Anderson-Freeman	Broido		
6.5	25	280-585	305	20.2	13.8	12.6	29.0	1.00	0.95	1.00	1.00	
	50	280-585		20.1	13.8	12.9	28.0	1.00	0.90	1.00	1.00	
4.0	25	295-515	220	20.5	15.3	14.0	..	1.19	0.90	1.00	1.00	
	50	295-515		20.9	14.9	14.3	..	1.19	0.95	1.00	1.00	
2.5	25	255-465	210	19.9	16.8	16.4	..	1.04	0.90	1.00	1.00	
	50	255-465		20.7	16.4	16.1	..	1.04	1.00	1.00	1.00	
1.0	25	290-500	210	20.5	16.3	16.6	..	1.08	1.00	1.00	1.00	
	50	290-500		19.9	16.2	16.1	..	1.08	1.00	1.00	1.00	

Table 2. Kinetic parameter from DTA curve for the resorcinol-1,2-dichloroethane resin system.

Rate of heating °C min ⁻¹	Peak temperature °C	E_A kcal. mole ⁻¹		Order of reaction n'	
		Reich method	Kissinger method	Reich	Kissinger
6.5	300 (h) 440	53.4	32.0	0.92	0.80
4.0	290 (h) 415	53.1	..	0.72	..
2.5	290 (h) 405	54.2	..	0.75	..
1.0	275 (h) 390	55.3	..	0.77	..

The E_A values given in table 1 and evaluated by various methods show considerable variation among one another. But those calculated by the Chatterjee method are nearly constant at all the RH involved in the study. Further it is noted that E_A evaluated using the Anderson-Freeman and the Broido method showed decreasing trend with increasing RH. This may be ascribed to the utilisation of the heat energy required for the molecular rearrangements depending on the relaxation time τ . At high heating rate, the rearrangement of molecules is less likely and the heat is directly utilised for the breaking of bonds and there is a decrease in the heat capacity of the sample.

The E_A values evaluated from the DTA-thermogram using the Reich and the Kissinger method given in table 2 show that they have a decreasing trend with increasing RH. Once again this behaviour agrees with that mentioned above. The molecular rearrangement assumed to take place at low heating rate may indicate the flexible nature of the molecules.

The activation energy evaluated using the Kissinger method is ~ 32 kcal mol⁻¹. The Reich method deals with the activation energy for a single thermogram obtained at a single heating rate, whereas the Kissinger method involves many thermograms at different heating rates by keeping other experimental conditions constant. Maintaining the experimental conditions except R H are difficult and so the results are subject to reasonable variations.

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