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2-Hydroxyacetophenone–thiourea–trioxane resins and their thermal studies

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Abstract

Resins have been synthesised by the condensation of 2-hydroxyacetophenone (HA) with thiourea (T) and trioxane (T′) in the presence of 2 M HCl/H_2SO_4 as a catalyst, with varying molar proportions of the reactants. The resins were characterised by elemental analyses, IR spectral study, number-average molecular weights and viscosity. Thermal studies of the resins have been carried out to determine their mode of decomposition, apparent activation energy and the order of each thermal reaction.

INTRODUCTION

2-Hydroxyacetophenone and its substituted derivatives have been condensed with formaldehyde to produce heat and light stabilisers [1,2]. Parmar et al. [3,4] have synthesised chelating ion-exchange resins by condensation of hydroxyacetophenone derivatives with formaldehyde. Manavalan and Patel [5] have synthesised salicylic acid–thiourea–trioxane resins. We report here the synthesis and characterisation of 2-hydroxyacetophenone (HA)–thiourea (T)–trioxane (T′) resins and their thermal studies.

EXPERIMENTAL

Chemicals

All the chemicals used were either AR grade or chemically pure grade. DMF was used after distillation. Pyridine and methanol were purified by conventional chemical methods. 2-Hydroxyacetophenone (b.p. 91°C) was prepared by a known method [6].

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Synthesis of resins

A mixture of 2-hydroxyacetophenone (0.1 mol), thiourea (0.1 mol) and trioxane (0.2 mol) in the presence of 2 M HCl/H_2SO_4 as a catalyst, was heated in an oil bath at 100 °C for 4 hours. The separated yellow resin product (HATT′) was washed with hot water and methanol to remove unreacted monomers. The resin was purified by dissolving in 8% NaOH and reprecipitating by dropwise addition of 1:1 (v/v) HCl. The precipitated resin product was filtered, washed with hot water until it was free of chloride ions and dried at 60 °C. Different resin samples were prepared employing different molar ratios of reactants (Table 1).

Analytical methods

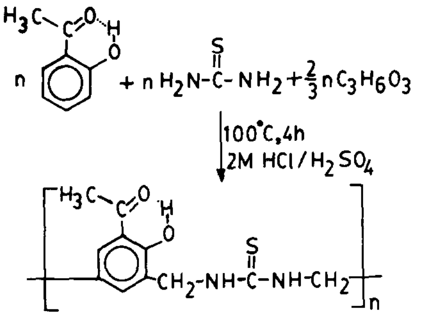
Microanalyses for carbon and hydrogen contents were carried out on a Carlo Erba elemental analyser. Nitrogen was estimated by the Kjeldahl method and sulphur was determined by the Carius method. Molecular weights of the resins were determined by non-aqueous conductimetric titrations in pyridine against standard sodium methoxide (CH_3ONa) dissolved in pyridine [7] and by vapour pressure osmometry (VPO) using DMF as a solvent and benzil as a calibrant. The viscosity measurements were carried out in DMF at 35 °C using an Ubbelohde viscometer. The infrared spectra in the region 4000–400 cm^{-1} were recorded in the solid state (KBr pellets) on a Perkin–Elmer 983 spectrophotometer. Thermal studies were done on a Du Pont 951 thermal analyser at a heating rate of 10 °C min^{-1} in air, using 5–10 mg samples.

RESULTS AND DISCUSSION

Characterisation of resins

The analytical data, resin composition, intrinsic viscosity and molecular weights are given in Table 1. All the resins are in powder form, yellow in colour and soluble in DMF, DMSO, pyridine, and aqueous NaOH. The resin compositions were calculated using the S% of the resins. From the known S%, the percentage of the thiourea repeating unit ($-CH_2-NH-CS-NH-$) (A) is given by ($\%S \times 88)/32$ and the percentage of the 2-hydroxyacetophenone repeating unit ($-C_6H_2 \cdot COCH_3 \cdot OH-CH_2-$) ($B$) is given by (100-$A$).

The average molecular weights of the resins determined by non-aqueous conductimetric titrations and by VPO are in good agreement (Table 1). The resins with higher molecular weights in the series have higher intrinsic viscosity values.



IR spectral study

All the resins give rise to nearly similar IR spectra. The broad band in the region 3400–3300 cm^{-1} is due to –OH and –NH stretching vibrations. The strong ν(C=O) band at 1635 cm^{-1} and a weak band around 2700–2600 cm^{-1} indicate intramolecular hydrogen bonding [8]. The bands in the region of 2860, 1460 and 720 cm^{-1} suggest the presence of methylene bridges in the resins [8]. The bands at 1500, 1430 and 960 cm^{-1} may be considered as composite bands of $-NH_2$ bending, C–N stretching and C=S stretching [9]. The band at 900 cm^{-1} indicates penta-substituted phenyl ring.

Thermal studies

The use of thermogravimetric data to evaluate kinetic parameters of solid state reactions involving weight loss has been investigated by a number of workers [10–12]. We followed the method of Broido [13]. The kinetic parameters of each thermal decomposition step were calculated from the TG curves and are presented in Table 2. The reaction rate is dependent on the product of the frequency factor A, and $e^{-E/RT}$, where R is the molar gas constant, T is the absolute temperature, and E is the activation energy. Thus, the decomposition equation of a first-order reaction, i.e. $n = 1$, of the type $A(s) \rightarrow B(s) + C(g)$ will be $k = Ae^{-E/RT}$. This equation takes the form $\ln[\ln(1/y)] = -(E/R)(1/T) + \text{constant}$, where the fraction not yet decomposed, i.e. the residual weight fraction $y = (W_t - W_\infty)/(W_0 - W_\infty)$, where W_t is the weight of the substance at temperature t, W_0 is the initial weight of the substance and W_∞ is the residue at the end of the decomposition.

TG curves for selected resin samples are shown in Fig. 1. The thermal stability of the resins decreases in the order HATT′-III > -VII > -I > -V, -VIII > -IV > -II > -VI. This indicates that the thermal stability of the

TABLE 1

Synthesis and analytical data of resins

Resin sample	Mole ratio of reactants HA:T:T′ (% yield)	Catalyst (2 M) (ml)	Average molecular weight $\overline{Mn}$ by		Intrinsic viscosity $\eta \times 10^2$ (dl g^{-1})	Analyses (%) [a]				Resin composition [a]	
			VPO	Conductimetric titrations		C	H	N	S	*A* unit	*B* unit
HATT′-I	1:1:2 (51)	HCl (100)	2930	2950	8.20	55.66 (55.92)	5.10 (5.12)	11.69 (11.86)	13.31 (13.57)	36.60 (37.32)	63.40 (62.68)
HATT′-II	3:1:4 (59)	HCl (200)	2780	2710	7.88	61.53 (62.48)	5.22 (5.24)	6.88 (7.29)	7.86 (8.34)	21.62 (22.94)	78.38 (77.06)
HATT′-III	1:3:4 (37)	HCl (200)	2610	2660	7.45	47.52 (48.13)	4.91 (4.97)	17.07 (17.27)	19.48 (19.77)	53.57 (54.37)	46.43 (45.63)
HATT′-IV	1:1:1 (47)	HCl (50)	1990	1970	5.33	62.01 (62.48)	5.21 (5.24)	6.84 (7.29)	8.23 (8.34)	22.63 (22.94)	77.37 (77.06)
HATT′-V	1:1:2 (48)	H_2SO_4 (100)	2830	2850	8.08	59.11 (59.98)	5.15 (5.20)	8.73 (9.03)	9.70 (10.33)	26.68 (28.41)	73.32 (71.59)
HATT′-VI	3:1:4 (54)	H_2SO_4 (200)	2490	2530	7.03	63.88 (64.18)	5.22 (5.28)	5.42 (6.11)	6.73 (6.99)	18.51 (19.22)	81.49 (80.78)
HATT′-VII	1:3:4 (33)	H_2SO_4 (200)	2330	2270	6.60	50.48 (51.41)	4.98 (5.03)	14.64 (14.99)	16.77 (17.16)	46.12 (47.19)	53.88 (52.81)
HATT′-VIII	1:1:1 (44)	H_2SO_4 (50)	1930	1970	5.63	59.32 (59.98)	5.16 (5.20)	8.52 (9.03)	9.81 (10.33)	26.98 (28.41)	73.02 (71.59)

[a] Values in parentheses are calculated.

TABLE 2

Kinetic parameters of resins

Resin sample	Stage	Temperature ranges (°C)	Weight loss (%)	Activation energy (kJ mol^{-1})
HATT′-I	First	175–320	23.87	38.5
	Second	320–530	29.57	14.6
	Third	530–675	43.97	99.8
HATT′-II	First	160–320	16.75	44.1
	Second	320–515	47.02	16.9
	Third	515–690	23.79	86.6
HATT′-III	First	205–295	24.54	51.4
	Second	295–515	23.64	13.2
	Third	515–700	43.62	69.9
HATT′-IV	First	165–275	18.58	44.2
	Second	275–510	31.71	18.8
	Third	510–625	39.87	77.5
HATT′-V	First	170–310	21.08	43.4
	Second	310–560	24.28	13.9
	Third	560–725	45.34	85.2
HATT′-VI	First	155–315	23.18	27.2
	Second	315–515	24.67	14.4
	Third	515–650	51.09	85.0
HATT′-VII	First	180–295	24.39	50.6
	Second	295–545	31.06	9.8
	Third	545–700	44.00	79.9
HATT′-VIII	First	170–330	23.42	33.3
	Second	330–545	28.54	14.3
	Third	545–720	46.88	80.2

resins increases with increasing percentages of the thiourea repeating unit. The thermal degradation of all the resins started at about 150–205 °C and ended at about 625–725 °C, with 87–99% weight loss being observed. The TG curves show three decomposition stages in all the resin samples. The thermal degradation range and % weight loss during decomposition are presented in Table 2. The thermal degradation may be proposed as described earlier for phenolic resins [14,15]. The first stage may be due to thermal degradation of the hydroxyl and ketonic groups; the second stage may be due to degradation of the methyl groups and methylene bridges; and the third stage may be due to aromatic ring cleavage.

The plot of $\ln(\ln(1/y))$ against $(1/T)$ gives a straight line of slope $-E/R$ (Fig. 2). The order of reaction was assumed to be one in all cases. The plots made according to the Broido method were found to be linear over the entire range of decomposition and this strengthens the assumption regarding the overall order of the thermal decomposition reaction. The apparent activation energy was calculated for all three decomposition stages and is reported in Table 2.

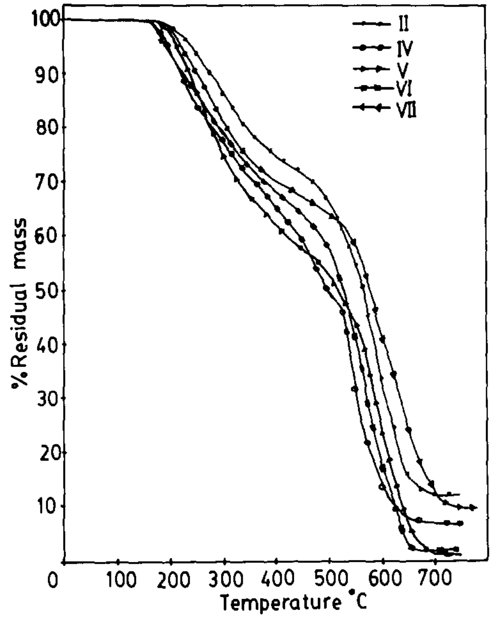


Fig. 1. TG curves for HATT′ resins.

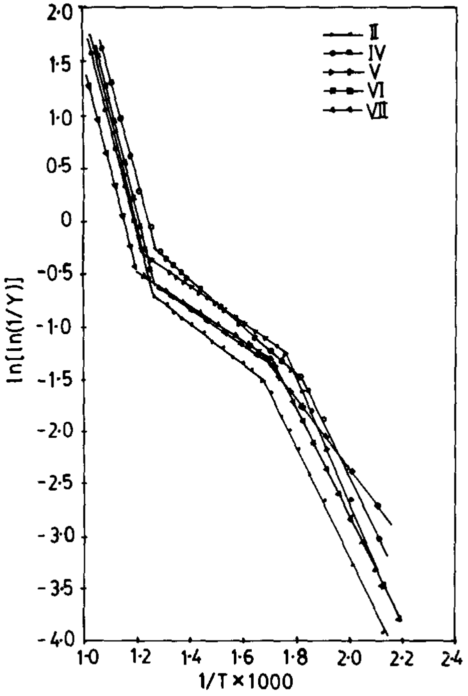


Fig. 2. Plots of ln(ln(1/y)) vs. 1/T for HATT′ resins.

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