*Thermochimica Acta*, 180 (1991) 219–224
Elsevier Science Publishers B.V., Amsterdam

# SYNTHESIS, CHARACTERISATION AND THERMAL STUDIES OF RESACETOPHENONEOXIME–THIOUREA–TRIOXANE RESINS

HEMENDRA B. PANCHOLI and MOHAN M. PATEL *

*Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat (India)*

(Received 21 August 1990)

## ABSTRACT

Resins have been synthesised by the condensation of resacetophenoneoxime with thiourea and trioxane in the presence of 2M $HCl/H_2SO_4$ as a catalyst and varying molar proportion of 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

Stanley [1] has synthesised several heat and light stabilisers by condensing *o*-hydroxyacetophenone and its substituted derivatives with formaldehyde to stabilise polyolefins. Sykora and Dubsky [2] have prepared a selective cation exchanger by condensing 2,4-dihydroxyacetophenoneoxime with resorcinol and formaldehyde in an alkaline media. Parmar et al. [3] have synthesised resacetophenoneoxime–formaldehyde resins in acidic media. Manavalan and Patel [4] have synthesised salicyclic acid–thiourea–trioxane resins. This inspired us to report the synthesis, characterisation and thermal study of resacetophenoneoxime (RO)–thiourea (T)–trioxane (T′) resins.

## EXPERIMENTAL

### *Chemicals*

All the chemicals used were of AR grade. Resacetophenone (m.p. 144 °C) was prepared by a known method [5]. Resacetophenoneoxime (m.p. 210 °C)

---

* Author to whom correspondence should be addressed.

0040-6031/91/$03.50

TABLE 1

Synthesis and analytical data of resins

| Resin sample | Mole ratio of reactants (RO:T:T′) [a] | Yield (%) | Average molecular weight $\overline{M}_n$ by | | Intrinsic viscosity $\eta \times 10^2$ (dl g$^{-1}$) | Analyses (%) [b] | | | | Resin composition [b] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | VPO | Conductometric titrations | | C | H | N | S | *A* unit | *B* unit |
| ROTT′-I | 1:1:2 | 61 | 2025 | 2058 | 5.73 | 48.92 | 4.88 | 14.87 | 11.11 | 30.55 | 69.45 |
| | | | | | | (49.43) | (4.90) | (15.72) | (12.00) | (33.00) | (67.00) |
| ROTT′-II | 3:1:4 | 68 | 2577 | 2572 | 7.38 | 51.46 | 4.87 | 12.81 | 8.41 | 23.13 | 76.87 |
| | | | | | | (52.16) | (4.94) | (13.74) | (8.98) | (24.70) | (75.30) |
| ROTT′-III | 1:3:4 | 50 | 2890 | 2818 | 8.20 | 43.21 | 4.78 | 19.21 | 17.89 | 49.20 | 50.80 |
| | | | | | | (43.93) | (4.82) | (19.70) | (18.04) | (49.61) | (50.39) |
| ROTT′-IV | 1:1:1 | 38 | 1668 | 1681 | 4.68 | 48.98 | 4.84 | 14.94 | 11.88 | 32.67 | 67.33 |
| | | | | | | (49.43) | (4.90) | (15.72) | (12.00) | (33.00) | (67.00) |
| ROTT′-V | 1:1:2 | 56 | 1365 | 1426 | 3.88 | 52.48 | 4.82 | 12.07 | 6.77 | 18.62 | 81.38 |
| | | | | | | (53.80) | (4.97) | (12.55) | (7.18) | (19.75) | (80.25) |
| ROTT′-VI | 3:1:4 | 62 | 1591 | 1573 | 4.50 | 55.12 | 4.93 | 10.47 | 4.68 | 12.87 | 87.13 |
| | | | | | | (55.67) | (4.99) | (11.19) | (5.12) | (14.08) | (85.92) |
| ROTT′-VII | 1:3:4 | 48 | 1454 | 1423 | 4.05 | 45.91 | 4.81 | 17.27 | 14.78 | 40.65 | 59.35 |
| | | | | | | (46.29) | (4.86) | (17.99) | (15.45) | (42.49) | (57.51) |
| ROTT′-VIII | 1:1:1 | 32 | 2244 | 2213 | 6.23 | 48.23 | 4.88 | 15.24 | 11.24 | 30.91 | 69.09 |
| | | | | | | (49.43) | (4.90) | (15.72) | (12.00) | (33.00) | (67.00) |

[a] Catalyst: 2 M HCl for ROTT′-I–IV and 2M $H_2SO_4$ for ROTT′-V–VIII.

[b] Values in parentheses are calculated.

was prepared by condensing resacetophenone with hydroxylamine-hydrochloride in 70% ethanol.

### *Synthesis of resins*

A mixture of resacetophenoneoxime (0.1 mol), thiourea (0.1 mol) and trioxane (0.2 mol) in the presence of 2M $HCl/H_2SO_4$ as a catalyst was heated in an oil bath at 120 °C for 4 hr. The separated yellow resin product (ROTT′) was washed with hot water and methanol to remove unreacted monomers. The resin was purified by dissolving in 8% NaOH and reprecipitating by drop-wise addition of 1 : 1 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 with 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 by the Carius method. Molecular weights of the resins were determined by non-aqueous conductometric titration in pyridine [6] and 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 thermal analyser-951 at a heating rate of 10 °C $min^{-1}$ in air, using 5–10 mg samples.

TABLE 2

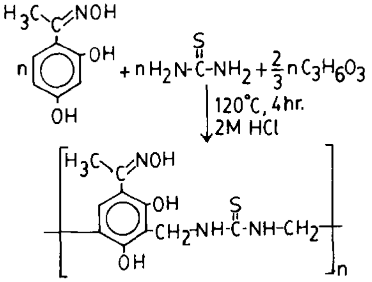
Kinetic parameters of resins

| Resin sample | Temperature (°C) ranges | | Wt. loss (%) | | Activation energy (kcal $mol^{-1}$) | |
|---|---|---|---|---|---|---|
| | First stage | Second stage | First stage | Second stage | First stage | Second stage |
| ROTT′-I | 150–444 | 440–515 | 58.6 | 31.2 | 8.100 | 16.698 |
| ROTT′-II | 150–320 | 320–465 | 21.5 | 72.0 | 8.751 | 15.792 |
| ROTT′-III | 150–510 | 510–590 | 70.5 | 27.2 | 5.669 | 21.056 |
| ROTT′-IV | 150–400 | 400–530 | 47.1 | 52.0 | 9.389 | 15.493 |
| ROTT′-V | 150–340 | 340–530 | 21.2 | 72.4 | 6.909 | 13.051 |
| ROTT′-VI | 150–315 | 315–550 | 14.6 | 81.9 | 5.758 | 12.591 |
| ROTT′-VII | 150–425 | 425–625 | 49.2 | 44.0 | 7.757 | 9.212 |
| ROTT′-VIII | 150–415 | 415–625 | 27.4 | 62.9 | 6.189 | 12.589 |

## RESULTS AND DISCUSSION

### *Characterization of resins*

The analytical data, resin composition and molecular weights are given in Table 1. All the resins are in powder form, yellow in colour and are soluble in DMF, DMSO, pyridine and aqueous NaOH. The resin compositions were calculated using the S% of the resins. From the known S%, the % of the thiourea repeating unit ($-CH_2-NH-CS-NH-$) ($A$) is given by $A = (\%S \times 88)/32$ and the % of the resacetophenoneoxime repeating unit ($-C_6H-C \cdot NOH \cdot CH_3 \cdot (OH)_2 \cdot CH_2-$) ($B$) is given by $(100 - A)$.



The average molecular weights of the resins determined by non-aqueous conductometric 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 strong $\nu_{C=N}$ band at 1635 $cm^{-1}$ and a weak band around 2720 $cm^{-1}$ indicate an intramolecular H-bond [7]. The bands at 2920, 1460 and 746 $cm^{-1}$ suggest the presence of methylene bridges in the resins [7]. The bands at 1500, 1430 and 940 $cm^{-1}$ may be considered as composite bands of $NH_2$ bending, C–N stretching and C=S stretching [8]. The band appearing at 1120 $cm^{-1}$ is attributed to N–O stretching [7].

### *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 [9–11]. We followed the method of Broido [12]. The kinetic parameters of each decomposition step were calculated from the TG curves, and are presented in Table 2. The probability of a molecule possessing energy in

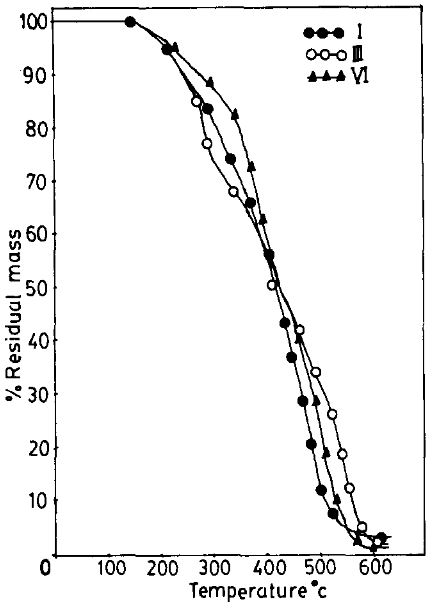


Fig. 1. TG curves for ROTT′ resins.

excess of an amount $E$ per mole at a temperature $T$ is related to the Boltzman factor, $e^{-E/RT}$, where $R$ is the molar gas constant. The reaction rate is dependent on the product of $A$, the frequency factor, and $e^{-E/RT}$.

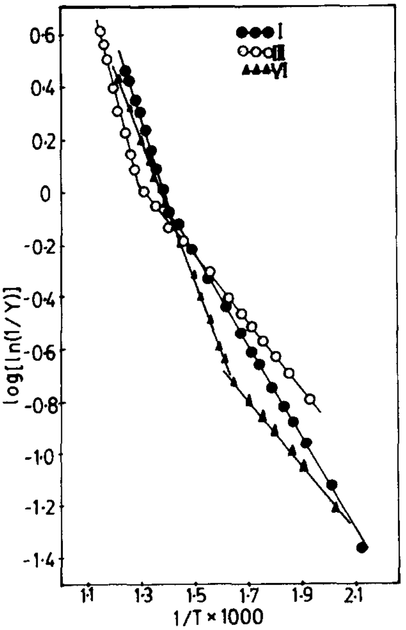


Fig. 2. Plots of log[ln(1/$y$)] vs. 1/$T$ for ROTT′ resins.

Thus the decomposition equation of a first-order reaction of the type A(s) → B(s) + C(g) will be $K = A\ \mathrm{e}^{-E/RT}$ for a first-order reaction, i.e. $n = 1$. This equation takes the form $\log[\ln(1/y)] = (\mathrm{E}/2.303\mathrm{R})(1/T) + \text{constant}$, where the fraction not yet decomposed, i.e. the residual weight fraction, $y = (W_\mathrm{t} - W_\alpha)/(W_0 - W_\alpha)$, $W_\mathrm{t}$ is the weight of the substance at temperature $t$, $W_0$ is the initial weight of the substance and $W_\alpha$ is the residue at the end of the decomposition.

TG curves are shown for selected resin samples in Fig. 1. The TG curves show two decomposition stages in all resin samples. The thermal degradation of the resins may follow that described for phenolic resins [13,14]: in the first stage, carbonyl, oxime and hydroxyl groups, and methylene bridges degrade; in the second stage, the aromatic ring cleaves and the remaining resin fragments degrade. The thermal decomposition ranges and the % weight loss during decomposition are presented in Table 2.

The plot of $\log[\ln(1/y)]$ against $(1/T)$ results in a straight line of slope E/2.303R (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 both stages of decomposition (Table 2).

## REFERENCES

1 T. Stanley, U.S. Patent 3,288,180 (1967); Chem. Abstr., 66 (1967) 29601.
2 V. Sykora and F. Dubsky, Collect. Czech. Chem. Commun., 32 (1967) 3342.
3 J.S. Parmar, M.R. Patel and M.M. Patel, Angew. Makromol. Chem., 105 (1982) 75.
4 R. Manavalan and M.M. Patel, Indian J. Chem., 22A (1983) 117.
5 R. Robinson and R.C. Shah, J. Chem. Soc., (1934) 1494.
6 B.K. Patel and M.M. Patel, Angew. Makromol. Chem., 165 (1989) 47.
7 K. Nakanishi, Infrared Absorption Spectroscopy, Nankodo Co. Ltd., Tokyo, Japan, 1964.
8 E. Spinner, Spectrochim. Acta, 15 (1959) 95.
9 E.S. Freeman and B. Caroll, J. Phys. Chem., 62 (1958) 394.
10 A. Berlin and R.J. Robinson, Anal. Chim. Acta, 27 (1962) 50.
11 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
12 A. Broido, J. Polym. Sci. Part A-2, 7 (1969) 1761.
13 R.T. Conley, I.F. Bierum and P. Perch, J. Am. Chem. Soc., 20 (1960) 244.
14 R.T. Conley, I.F. Bierum and P. Perch, J. Appl. Polym. Sci., 7 (1963) 103.