

# Synthesis and Characterization of Aniline-Doped Mixed Copolymer Resins. II

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## SYNOPSIS

Copolymer resins were synthesized by the mixed condensation of resorcinol-CH<sub>2</sub>O, resorcinol-aniline-CH<sub>2</sub>O, resorcinol-aniline-urea-CH<sub>2</sub>O, resorcinol-aniline-thiourea-CH<sub>2</sub>O, and resorcinol-aniline-urea-thiourea-CH<sub>2</sub>O with a view to develop synthetic resins having improved properties and performance like toughness, mechanical properties, thermal resistance, chemical inertness, and adhesion. The resins were characterized by IR and TG analyses. The thermal analysis showed that the mixed copolymer resins have significantly better thermal stability than that of the simple phenol-CH<sub>2</sub>O, aniline-CH<sub>2</sub>O, urea-CH<sub>2</sub>O, and thiourea-CH<sub>2</sub>O resins. At 600°C, only a 50% weight loss is observed, and even at 800°C, the weight loss is about 70%. The resins are insoluble in most of the organic solvents including DMSO-*d*<sub>6</sub>. They too are unaffected by diluted HNO<sub>3</sub>, but dissolve in concentrated HNO<sub>3</sub>. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Phenolic resins are perhaps the first synthetic resins to have acquired significant commercial success.<sup>1-3</sup> This is due to the design flexibility to make resins of widely varying properties by altering the catalysts and relative mol ratios of phenolics to aldehydes. These resins, because of their stability, heat resistance, electrical insulation, dimensional stability, chemical resistance, etc., find widespread commodity applications in appliances, business machines, electronic controls, insulation materials, plywood, protective adhesive, telecommunication, writing devices, housewares, machine parts,<sup>4,5</sup> microelectronics, optical lithography, etc.<sup>6-9</sup> In addition, phenolic resins find wide application as matrix materials in the fabrication of composites for high-temperature and high-strength applications in aircraft, aerospace research, automotive industries, railways, constructions, building industries, etc.<sup>10-14</sup>

Work on mixed condensation copolymer resins is scanty.<sup>15-19</sup> Mixed copolymer resins have been

patented that are superior in properties and performance over simple resins. So, we are currently synthesizing condensation copolymer resins comprising phenolics, aromatic amines, ethers, acids, hydroxy acids, aliphatic diamides, and thioamides, etc., and formaldehyde/furfural with a view to using these resins as matrix materials in developing lightweight low-cost composites of commercial success. The present communication is an aspect of our research on composites.

## EXPERIMENTAL

### Materials and Methods

Resorcinol, aniline, urea, and thiourea were from BDH Chemicals and were used after purification by standard methods. Formaldehyde used for the purpose was a 40% solution (formalin) (BDH) and used as such. Other reagents like acetone, benzene, toluene, hexane, methanol, *n*-propanol, DMSO, DMSO-*d*<sub>6</sub>, and DMF were of AR grade and used without purification.

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## Synthesis of Resins

### Resorcinol- $\text{CH}_2\text{O}$ (R-F) Copolymer Resin

An alkaline solution (25% w/v NaOH) of resorcinol (50 g) with formaldehyde (80 mL) was refluxed at 60°C for 1 h. The color of the solution changed from pink to red and a reddish black resin was formed. The resin was filtered, washed with methanol, acetone, and water, and vacuum-dried. The yield was 70%.

### Resorcinol-aniline- $\text{CH}_2\text{O}$ (R-A-F) Copolymer Resin

A mixture of resorcinol (37.5 g) and formaldehyde (70 mL) was stirred for 15 min. Aniline (20 mL) dissolved in 2N HCl was added to the mixture at room temperature maintaining vigorous stirring. A orange-colored polymer was precipitated within 5 min. It was isolated in an ice-cold water-methanol mixture. The polymer was filtered, washed with acetone and water, and vacuum-dried. The yield was 75%.

### Resorcinol-aniline-urea- $\text{CH}_2\text{O}$ (R-A-U-F) Copolymer Resin

Resorcinol, 37.5 g, urea, 17 g, and formaldehyde, 120 mL, were well mixed in a round-bottomed flask. The

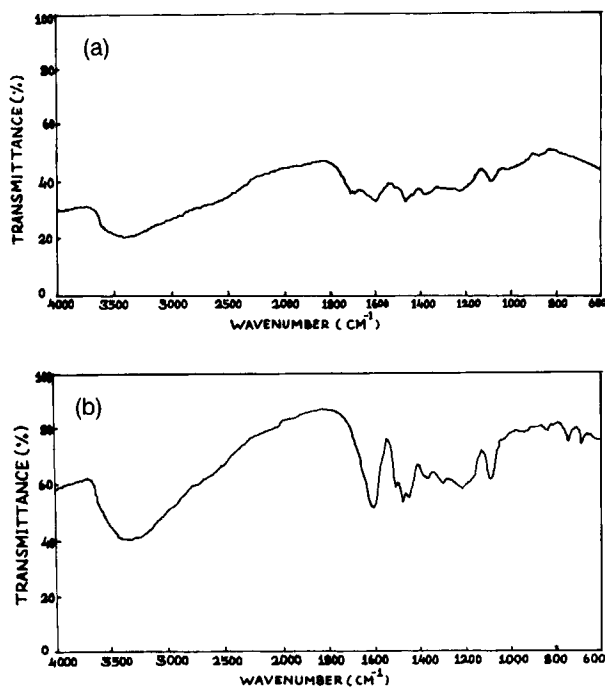


Figure 1 IR spectra of copolymer resins: (a) R-F; (b) R-A-F; (c) R-A-U-F; (d) R-A-T-F; (e) R-A-U-T-F.

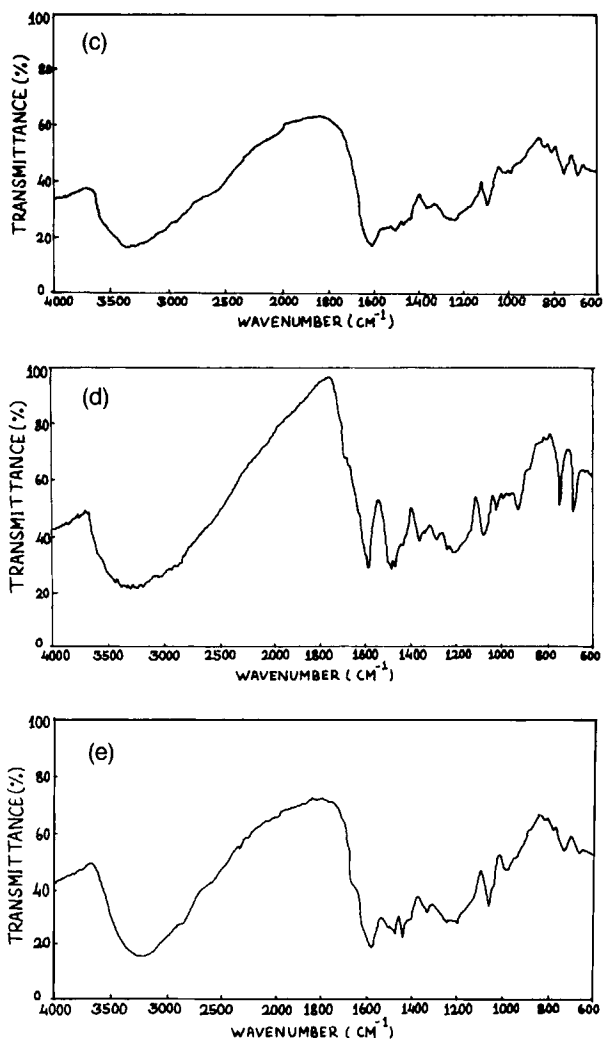
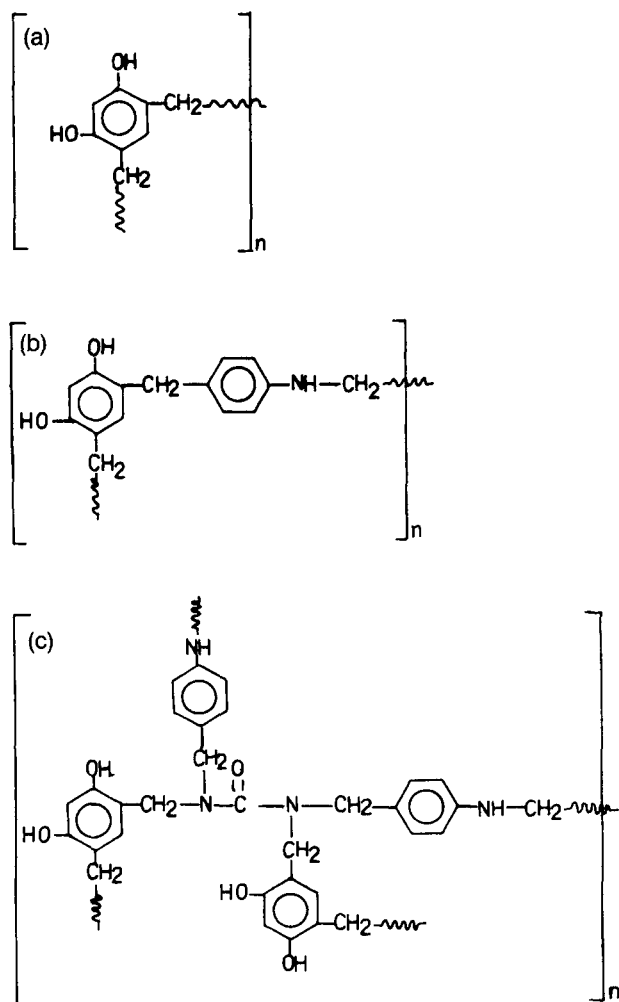


Figure 1 (Continued)

mixture was stirred vigorously for 15 min. Aniline, 20 mL, dissolved in 2N HCl was added to the mixture while stirring was maintained. An orange-yellow-colored polymer precipitated within 5 min. The polymer was filtered, washed with acetone, methanol, and water, and vacuum-dried. The yield was 70%.

### Resorcinol-aniline-thiourea- $\text{CH}_2\text{O}$ (R-A-T-F) Copolymer Resin

Resorcinol, 37.5 g, thiourea, 17 g, and formaldehyde, 120 mL, were well mixed in a round-bottomed flask. The contents were stirred vigorously while 20 mL of aniline dissolved in 2N HCl was added. After 5 min, a deep orange-colored polymer precipitated. The polymer was filtered, washed with methanol and acetone followed by water, and vacuum-dried. The yield was 85%.



**Figure 2** Structures of copolymer resins: (a) R-F; (b) R-A-F; (c) R-A-U-F; (d) R-A-T-F; (e) R-A-U-T-F.

#### Resorcinol-aniline-urea-thiourea-CH<sub>2</sub>O (R-A-T-F) Copolymer Resin

Resorcinol, 37.5 g, Urea, 8.5 g, thiourea, 8.5 g, and formaldehyde, 120 mL, were well mixed. To it, 20 mL of aniline dissolved in 2N HCl was added while vigorously stirring the mixture. A yellow-colored polymer precipitated after 15 min. It was filtered, washed with methanol and acetone followed by water, and vacuum-dried. The yield was 80%.

#### Element Detection

Lassaigne's test<sup>20</sup> for nitrogen was positive for all the resins except for the resorcinol-CH<sub>2</sub>O resin. This confirms the presence of nitrogen in these mixed copolymer resins.

#### Characterization

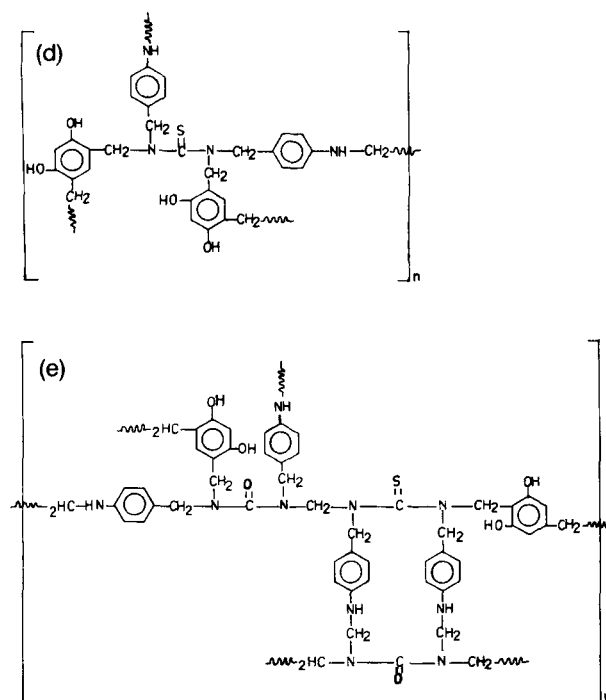
TG analysis was carried out on a DuPont 9900 thermal analyzer. The TG thermograms were obtained at a constant heating rate of 10°C per min in a nitrogen atmosphere.

#### IR Study

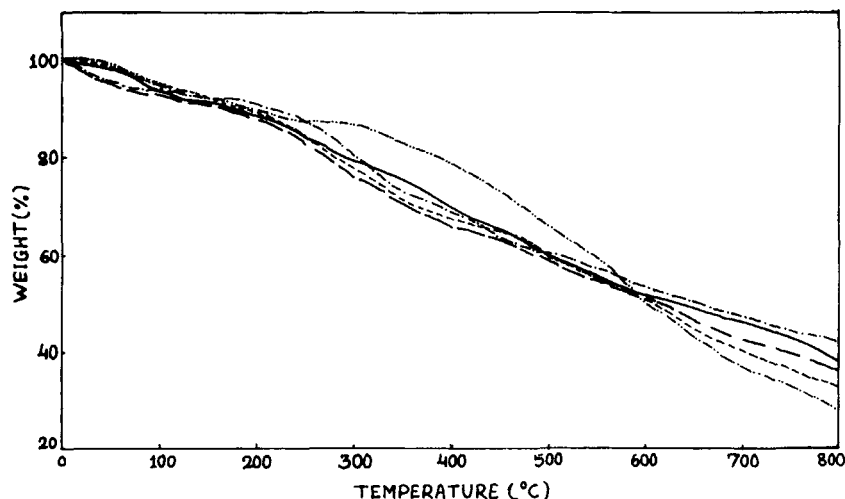
IR spectra were recorded, with a Perkin-Elmer 237 spectrophotometer using a nujol mull or KBr pellets, to ascertain the structures of the copolymers. The IR spectra are shown in Figure 1(a)-(e) and possible assignments of the peaks are described as follows:

#### R-F Copolymer Resin

Bands [Fig. 1(a)] at 3600-3000, 1600, 1460, 1370-1350, 1210, and 880 cm<sup>-1</sup> are due to O-H stretching, aromatic C=C stretching, -CH<sub>2</sub>- bending, phenolic C-O stretching, phenolic O-H stretching, and substituted aromatic C-H bending vibration, respectively. These bands support the resin structure [Fig. 2(a)].



**Figure 2** (Continued)



**Figure 3** Thermogravimetric traces of copolymer resins. (—) R-F, (- · · · · -) R-A-F, (- - - -) R-A-U-F, (- - - - -) R-A-T-F, (- - -) R-A-U-T-F.

#### **R-A-F Copolymer Resin**

Bands [Fig. 1(b)] at 3500–2800, 1600, 1498/1470/1435, 1360/1280, 1210, 1075, and 835  $\text{cm}^{-1}$  are due to O—H/N—H stretching, aromatic C=C stretching, —CH<sub>2</sub>— bending, phenolic C—O stretching, phenolic O—H in-plane bending, O—H bending of the —CH<sub>2</sub>—OH moiety, and C—H bending, respectively. These bands support the resin structure [Fig. 2(b)].

#### **R-A-U-F Copolymer Resin**

Bands [Fig. 1(c)] at 3600–2900, 1610, 1500, 1460, 1360/1200–1300, 1085, and 840  $\text{cm}^{-1}$  are due to O—H/N—H stretching, amide C—O stretching/N—H bending in secondary amine, aromatic C=C stretching, —CH<sub>2</sub>— bending, aromatic C—N vibration, phenolic O—H stretching, and aromatic substituted C—H bending vibration, respectively. These characteristic bands support the resin structure [Fig. 2(c)].

#### **R-A-T-F Copolymer Resin**

Bands [Fig. 1(d)] at 3600–2800, 1585, 1480, 1465, 1360, 1285, 1065, 1020, 915/810, and 750/685  $\text{cm}^{-1}$  are due to O—H/N—H stretching, N—H bending in secondary amine, N—H bending in amine salt, —CH<sub>2</sub>— bending, phenolic C—O stretching, aromatic secondary C—N vibration, C=S stretching, C—N aliphatic stretching, aromatic substituted C—H stretching, and C—H/N—H rocking, respectively. The IR scan supports the resin structure [Fig. 2(d)].

#### **R-A-U-T-F Copolymer Resin**

Bands [Fig. 1(e)] at 3680–2750, 1600–1500, 1465, 1350, 1220, 1085, 1000, 838, and 750/685  $\text{cm}^{-1}$  are due to O—H/N—H stretching, C=C aromatic stretching, —CH<sub>2</sub>— bending, phenolic C—O stretching/C—N vibration, phenolic O—H bending, C=S stretching/aliphatic C—N stretching, C—O/C—N/C—C stretching, aromatic C—H bending, and C—H/N—H rocking, respectively. These bands support the resin structure [Fig. 2(e)].

#### **Solubility**

Solubility of the copolymer resins in a number of solvents at room temperature was determined by putting different known amounts of the resins in a fixed volume of the solvents in a test tube. The dissolution of the resins was judged carefully after 15 days. It was observed that with solvents like acetone, methanol, benzene, toluene, hexane, *n*-propanol, DMSO, DMF, DMSO-*d*<sub>6</sub>, etc., all the resins are insoluble.

## **RESULTS AND DISCUSSION**

Thermogravimetric analysis (TGA) is an important analytical tool for elucidating the structure of the polymeric resins through evaluation of their thermal stability and estimating the kinetic parameters involved in such pyrolysis.<sup>21-26</sup>

Figure 3 shows the primary thermograms of the copolymer resins. The temperature of decomposition

**Table I Percentage Weight Loss of the Resins in Nitrogen Atmosphere at the Rate of 10°C/Min**

Name of the Copolymer Resins	Temperature in °C ( $T_D$ )							
	100	200	300	400	500	600	700	800
R-F	5.3	12.3	20.3	29.7	41.5	50.0	55.1	64.0
R-A-F	6.6	7.7	12.6	20.4	33.0	50.0	62.6	72.0
R-A-U-F	8.3	10.3	24.3	35.6	45.0	53.4	60.6	67.3
R-A-T-F	6.8	9.5	20.3	31.6	40.0	47.1	53.3	58.2
R-A-U-T-F	6.5	11.5	24.0	35.0	44.2	52.2	59.2	65.0

$T_D$  and the respective weight loss are computed in Table I.

From the primary thermograms, it is seen that the copolymer resins have excellent thermal stability except the R-F resin whose thermal stability is a little less. All the resins are much more stable than simple phenol-CH<sub>2</sub>O and aniline-CH<sub>2</sub>O resins having a thermal stability of nearly 550°C and urea-CH<sub>2</sub>O and thiourea-CH<sub>2</sub>O having a thermal stability of nearly 350°C.

At  $T_D = 600^\circ\text{C}$ , only 50% and even less weight loss is noticed with the present resins (Table I). Further, beyond a  $T_D$  value of 800°C, 58–72% weight loss is observed for all the copolymer resins, whereas for the phenol-formaldehyde resin at and beyond  $T_D = 600^\circ\text{C}$ , a 62–68% weight loss is observed.<sup>27</sup> Thus, the copolymer resins presently synthesized are superior in thermal stability over conventional phenolic resins.

From the residual weight of the resins in Table I, the values of  $\Delta \log dw/dt$  and  $\Delta \log w$  are evaluated, from which the Freeman-Carroll equation<sup>28,29</sup> at constant  $\Delta(1/T)$  is plotted, which yields linear curves. From the slope and intercept of the linear plots, the value of the order of the reaction ( $n$ ) and the activation energy ( $E$ ) involved in the pyrolytic kinetics are evaluated and presented in Table II.

**Table II Order ( $n$ ) and Activation Energy ( $E$ ) in kJ/mol of the Resins According to Freeman-Carroll Equation**

Resin	$n$	$E$
R-F	1.20	3.8
R-A-F	1.04	3.5
R-A-U-F	1.00	8.1
R-A-T-F	1.00	8.1
R-A-U-T-F	1.20	3.5

## CONCLUSION

The results of the IR scan, thermal analysis, and solubility behavior reveal that with the use of a suitable experimental technique involving an easy route it is possible to synthesize mixed condensation copolymer resins of significant thermal stability and which are inert to solvent action. Thus, they are likely to find high-temperature applications and as matrix materials in Fibre Reinforced Plastics.

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