

# SYNTHESIS, CHARACTERIZATION OF *m*-AMINOPHENOL-FURFURAL AND *m*-DIETHYLAMINOPHENOL-FURFURAL RESINS

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**Abstract**—The polycondensations of *m*-aminophenol and *m*-diethyl-aminophenol with furfural has been studied under various reaction conditions. The resin samples have been characterized by i.r. spectral studies, measurement of solution viscosity, estimation of  $\bar{M}_n$  and by thermogravimetric analysis. The curing of selected samples by hexamine has been studied by measuring the proportion of cured material as a function of time at various temperatures.

## INTRODUCTION

*m*-Aminophenol-formaldehyde resins (Aph-F) have been employed for a variety of applications [1-3]. Synthesis of an azo pigment using Aph-F resin as a coupling component has been reported [4]. Furfural (Fu) has been reported to be less reactive than formaldehyde in condensation with phenol [5]; this is expected both on the basis of steric and electronic effects. It has been observed that condensation of *m*-diethylaminophenol (DEAP) with formaldehyde is much slower than that of *m*-aminophenol with formaldehyde [6]. There are no reports about the condensations of *m*-aminophenol (Aph) and *m*-diethylaminophenol (DEAP) with furfural. The condensations of furfural with Aph, *m*-*N*-acetaminophenol (*N*-AcAph) and DEAP have been studied under various experimental conditions. The resins have been characterized. The curing of selected resin samples by hexamine has been studied at selected temperatures using published methods [7-9].

## EXPERIMENTAL

The chemicals and the solvents were chemically pure reagents. Dioxane employed for study of solution viscosity was distilled. Aph and DEAP were purified by crystallization. *m*-*N*-acetaminophenol was prepared by acetylation.

*Condensation of Aph with Fu in aqueous medium in absence of catalyst. Formation of Aph-Fu-1 resin sample*

A mixture of *m*-aminophenol (0.04 mol, 4.3 g), furfural (0.04 mol, 4.0 g) and water (1 ml) was stirred at 50°C for  $\frac{1}{2}$  hr and diluted with water (100 ml). The dark coloured solid was filtered and thoroughly washed with water. The yield was almost quantitative. It fused from 85° to 100°C. Any attempt to remove free *m*-aminophenol by boiling water or free furfural by steam distillation led to an insoluble and infusible product.

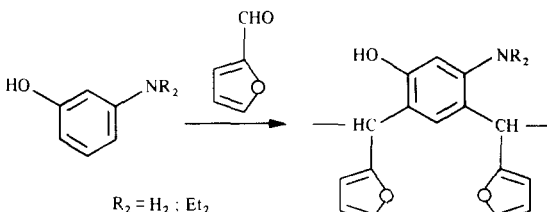
Analysis: Calculated for  $C_{11}H_9O_2N$ : N, 7.3%  
 Found: N, 7.0%

The condensation under similar conditions in the presence of 5% aq. alkali and 2% aq. HCl afforded acetone-insoluble and infusible products designated respectively as Aph-Fu-2 and Aph-Fu-3 resins. It was found that when 2% aq. alkali was employed as a catalyst an acetone-soluble resin, Aph-Fu-4 was formed, fusing from 110° to 130°C. The

condensation of *m*-*N*-acetaminophenol with furfural can only be effected in the presence of 5% alkali at temperatures above 90°C. The sample is designated as AcAph-Fu resin; it is soluble in acetone and fuses between 180° and 190°C.

*Condensation of DEAP with Fu in presence of PTS in amyl alcohol. Formation of DEAP-Fu-5 resin sample*

A suspension of DEAP (0.04 mol, 6.6 g) Fu (0.04 mol, 4 g) and PTS (0.33 g) in amyl alcohol (20 ml) was refluxed at 130°C for 2 hr. Amyl alcohol and free furfural were removed by steam distillation. The reaction mixture was filtered and the solid was repeatedly treated with boiling water. It was dried in air. The yield of the dark coloured solid was 58%. It fused over a range from 130° to 140°C.



Analysis: Calculated for  $C_{15}H_{17}O_2N$ : N, 5.9%  
 Found: N, 5.6%

DEAP was condensed with Fu under conditions mentioned in Table 1. However, it was observed that DEAP does not condense with Fu in the absence of any catalyst in aq. solution and in the presence of aq. base or aq. acid at 50°C. The resin samples prepared from DEAP are listed in Table 1.

## Measurements

The properties of the resin samples were measured by the usual methods.  $N_2$  contents of all the samples are slightly below the calculated values. The values of  $\bar{M}_n$  of the soluble Aph-Fu-1 and Aph-Fu-4 samples are  $1100 \pm 100$  and  $1200 \pm 100$  respectively. The values of  $\bar{M}_n$  of DEAP-Fu resin samples are presented in Table 1. The intrinsic viscosities of the soluble resin samples in dioxane lie between 0.05 and 0.06 dl g<sup>-1</sup>. The values of intrinsic viscosity estimated by the Huggin's [10] and Kreamer's [11] relations agree closely. The i.r. spectra were measured in KBr.

TGA of selected samples were carried out in air at a heating rate of 10°C min<sup>-1</sup>. The curing of Aph-Fu-1 was studied at 100°, 120° and 140°C and that of DEAP-Fu-2 also at 200°C using 12% hexamine as curing agent and following the method reported earlier [7-9]. Plots of %

Table 1. Reaction conditions and characteristics of DEAP-Fu resin sample. Reaction time: 2 hr. Reaction temperature: 100°C (130°C for sample 5 and 7)

Designation DEAP-Fu-No.	Reaction conditions				Yield (%)	Fusion range (°C)	$[\eta]^* \times 10^2$ (dl g <sup>-1</sup> )	$\bar{M}_n \pm 100$ by VPO
	Molar ratio (DEAP):(Fu)	Catalyst (% by wt of DEAP)	Medium (% by wt of DEAP)					
1	1:0.8	5% NaOH	H <sub>2</sub> O (20)		68	120-130	5.9	1200
2	1:1	5% NaOH	H <sub>2</sub> O (20)		78	125-130	6.0	1300
3	1:1.2	5% NaOH	H <sub>2</sub> O (20)		83	128-135	6.0	1400
4	1:1	10% conc. HCl	H <sub>2</sub> O (20)		60	136-145	6.7	1200
5	1:1	5% PTS	Amyl (300) alcohol		88	130-146	6.8	1450
6	1:1	5% K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O (20)		55	120-130	4.8	1200
7	1:1	5% K <sub>2</sub> CO <sub>3</sub>	Amyl (300) alcohol		70	130-140	5.2	1450
8	1:1	5% PTS	dioxane (300)		62	132-145	6.2	1300

\*In dioxane at 35°C.

cured material vs time at selected temperatures showed that APh-Fu-1 resin sample is cured completely in about 2 min at 140°C and the resin sample DEAP-Fu-2 could be cured completely only at 200°C in 2 to 3 min.

## RESULTS AND DISCUSSION

The resins are formed in nearly quantitative yields from *m*-aminophenol and furfural. Among the AP-Fu resin samples, only the APh-Fu-1 and -4 samples (formed respectively in the absence of any catalyst and in the presence of 2% alkali at 50°C) are soluble in acetone and are fusible. These observations indicate high reactivity of *m*-aminophenol in its condensation with furfural. In this respect *m*-aminophenol closely resembles resorcinol. It has been observed by the present authors that resorcinol reacts with furfural even at room temperature in the absence of any catalyst. These observations indicate that the high reactivities of resorcinol and *m*-aminophenol in the electrophilic substitution reaction more than compensates the lower reactivity of furfural as a weak electrophile. The formation of insoluble products on condensation of *m*-aminophenol with furfural under slightly more vigorous conditions is due to occurrence of a crosslinking reaction during resin synthesis; the latter is a consequence of high reactivity of *m*-aminophenol.

In such electrophilic substitution reactions, steric effect on acetylation of NH<sub>2</sub> or OH reduces the reactivity of the substrate undergoing electrophilic substitution. The results presented here support this view. *m*-*N*-acetaminophenol condenses with furfural in the presence of 5% alkali at 90°C affording a soluble and fusible resin. The reaction failed when carried out at lower temperature. *m*-Diethylaminophenol condenses with furfural under all the reaction conditions described in Table 1 affording soluble and fusible resins in yields ranging from 55 to 80% depending upon the reaction conditions. However, DEAP does not condense with furfural under milder conditions. This reflects lower reactivity of DEAP in the present reaction.

Examination of the data in Table 2 reveals that increase in the furfural: DEAP ratio increases the yield, the softening range and the molecular weight of the DEAP-Fu resins. It has been observed by Arora and Patel that increasing the proportion of furfural

during formation of the phenol-furfural resin increases the molecular weight of the resin without leading to crosslinking [5]. The change in the nature of the medium and the nature and concentration of the catalyst have no large effect on the molecular weight of the resins from DEAP and furfural. In the latter type of reactions when the conditions were made very vigorous, resins having higher molecular weight up to 2000 and more were formed; they softened at temperatures above 200°C.

The resin sample APh-Fu-1 was acetylated by acetic anhydride in aqueous solution affording an *N*-acetylation polymer product softening from 110° to 127°C. APh-Fu-1 resin sample afforded a polymeric azo pigment. These observations indicate that the NH<sub>2</sub> group in the APh-Fu resin sample is free.

The i.r. spectra of all the resin samples contain asymmetric and symmetric stretching CH bands at ~2980 cm<sup>-1</sup> and ~2850 cm<sup>-1</sup> respectively. Each spectrum has a band at ~880 cm<sup>-1</sup> characteristic of aromatic isolated H atom.

Comparison of the spectra of base and acid catalyzed resin samples (such as APh-Fu-1 and -3) reveals that there is a small but distinct difference between these spectra. This may be due to a partial ring rupture of  $\alpha$ -furyl pendant groups and subsequent crosslinking in the acid catalyzed reaction. This conjecture is partly supported by the observation that the acid catalyzed resin sample is much darker in colour than the base catalyzed resin sample.

The i.r. spectra of the base and acid catalyzed resin samples DEAP-Fu-2 and -4 resemble each other. It

Table 2. TGA in air at heating rate of 10°C min<sup>-1</sup>

Resin sample	% wt loss at °C						IPDT [14] °C
	200	300	400	500	600	700	
APh-Fu-1	8	10	18	40	91	96	520
Cured <sup>a</sup>	2	9	12	28	63	81	560
APh-Fu-1	2	10	15	38	82	92	530
APh-Fu-3	6	13	27	41	96	98	480
ACPh-Fu	5	17	45	68	96	96	440
DEAP-Fu-2	5	14	32	40	62	82	530
Cured <sup>b</sup>	5	14	32	40	62	82	530
DEAP-Fu-2	3	18	36	64	90	96	428
DEAP-Fu-5	—	3.0	10.0	23	78	100	570
Ph-Fu	—	3.0	10.0	23	78	100	570

Cured by hexamine (12% by wt of X-phenol) for 2 min (a) at 140°C and (b) at 200°C.

seems that the acid employed as catalyst is used up in transforming more basic  $-\text{NEt}_2$  into  $-\text{N}^+\text{HEt}_2$ . The latter functions as a Lewis acid catalyst for the resin formation. The absence of free acid in the solution prevents possible degradation of the furan ring during the acid catalyzed reaction.

The PMR spectra of APh-Fu resin samples and most of the DEAP-Fu resin samples were not measured as the resins were insoluble in  $\text{CDCl}_3$ . The base catalysed resin sample DEAP-Fu-2 had slight solubility in  $\text{CDCl}_3$  and its PMR spectrum was recorded. In this spectrum the signals from methyl and methylene protons of N-Et group and a complex signal from aromatic protons are seen at around the expected positions. The most significant feature of this spectrum was a signal at 5.8 ppm due to the bridge  $-\text{CH}(\alpha\text{-Fu})$ -proton. The downfield shift of the signal of this proton is due to the fact that it is like a triaryl CH proton [13].

Comparison of the TG data and more particularly of the values of integral procedural decomposition temperature (IPDT) [14] presented in Table 2, reveals that APh-Fu resin sample is more stable than the DEAP-Fu resin sample prepared similarly. It is also observed that there is not much difference between the thermal stabilities of resins prepared from the same pair of monomers under different conditions. Comparison of the TG data of the base catalyzed phenol-furfural resin [5] and APh-Fu-1 resin reveals that the phenol-furfural resin is more stable. Com-

parison of the TG data reveals that cured products of APh-Fu-1 and DEAP-Fu-2 resins are thermally more stable than the parent resin samples. The difficult curing of DEAP-Fu-2 sample seems to be due to the steric effect exerted by the  $\text{NEt}_2$  group during curing.

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