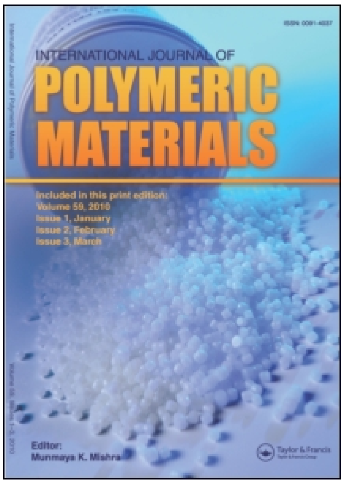

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POLYMERS DERIVED FROM 2-FURALDEHYDE AND AROMATIC DIAMINES CONTAINING KETO-IMINO GROUP

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Poly[imino(cyclopent-2-en-1-one-2,4-diyl)iminoarylenes] were prepared by the condensation of 2-furaldehyde with various aromatic diamines containing keto-imino group in solution at room temperature. All polycondensations were carried out in one step and under identical conditions. It was observed that the most likely condensation reaction is through the furan rearrangement that leads to Poly-[imino(cyclopent-2-en-1-one-2,4-diyl)iminoarylenes]. The structures of all the polymer samples were confirmed by elemental analyses and by comparison of IR spectral characteristics with those of a model compound derived from 2-furaldehyde and aniline. Number average molecular weights of all polymer samples were estimated from nonaqueous conductometric titration. The viscometric measurements of solutions of polymer samples in a formic-acetic acid (85:15) (v/v) mixture exhibited polyelectrolyte behaviour. The thermal properties of polymer samples were revealed by thermogravimetry. The formation of the polymeric product is also explained. The results of preliminary tests for glass reinforcement of commercial epoxy resin and procuced polymer samples suggest that laminate sheets with good mechanical strength can be obtained.

Keywords: 2-furaldehyde, polyimines, poly(ketoimines)

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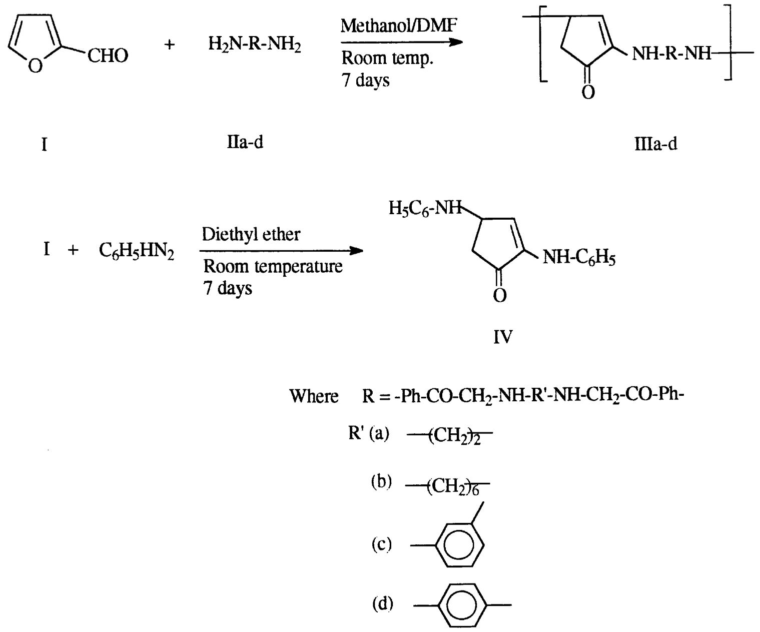
INTRODUCTION

Polymer based on 2-furaldehyde and aromatic diamines such as 1,3- and 1,4-phenylenediamine in the presence of various catalysts have been reported [1–10]. They were studied mainly kinetically [1, 2] as anion-exchangers [3–6] and as epoxy hardners [7–10]. Berlin et al. [11] reported that during the synthesis of bis-Schiff's bases from 2-furaldehyde and diamines, the yield of bis-Schiff's bases was low and it was observed the major product was resinous. Such resins have not yet been studied systematically.

The reaction of aromatic monoamines with 2-furaldehyde is well documented in the literature. [12] Lewis and Mulquiney clarified that in the reaction of 2 mol of simple aniline derivative and 1 mol of 2-furaldehyde no Schiff's base is formed, but the 2,4-bisarylimino-cyclopent-2-en-1-one is obtained by rearrangement. There is no report on the above mentioned reaction [12] between aromatic diamines and 2-furaldehyde, which may lead to polymerization. Hence, an Indian scientist [13] studied the interesting polymerization reaction of 2-furaldehyde with several aromatic diamines. With kind permission of the author [13], such work is extended. Thus, the present paper



SCHEME 1

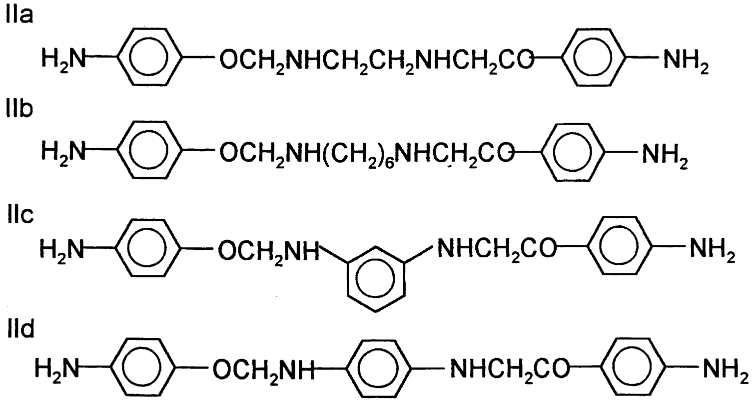
describes the synthesis and characterization of the reaction products obtained from 2-furaldehyde and aromatic diamines containing keto-imino group (Shown in Scheme 1).

EXPERIMENTAL

Materials

2-furaldehyde (I) obtained from SD Fine Chemicals Ltd., Boisar, India was purified by the method reported in the literature [14]. All the diamines (listed below) containing keto-imino groups have been prepared by using reported procedure [15]. Other chemicals used were of analar or chemically pure grade.

Diamines IIa-d used



Preparation of Poly[imino(cyclopent-2-en-1-one-2,4-diyl)-iminoarylenes] IIIa-d

The polycondensation reaction of 2-furaldehyde(I) with various diamines (listed in Scheme 1) was carried out in identical manner. Typical synthesis of a polymer sample based on the reaction of I with IIa is given here. Details about all the polymer samples are furnished in Tables 1 and 2.

Condensation of Diamine IIa with 2-Furaldehyde

To a solution of **IIa** (0.05 mol) in THF-methanol (50:50 v/v) (100 mL), freshly distilled **I** (0.05 mol) was added with continuous stirring

TABLE 1 Synthesis and Characterization of PAIs

			Elemental analysis										
			%C		%H		%N		Important IR Spectral Bands cm $^{-1}$				
Polymer	Yield in %	Softening range (°C)	Calc.	Found	Calc.	Found	Calc.	Found	ν_{N-H}	ν_{CH_2}	ν_{CH_2}	$\nu_{C=C}$	$\nu_{C=N}$
IIIa	95	>230	65.87	65.80	5.48	5.50	13.36	13.60	3380	2930	2870	1610	1190
IIIb	95	>230	66.51	66.50	5.77	5.60	12.93	12.90	3390	2940	2880	1610	1180
IIIc	98	>230	69.37	69.40	4.92	4.80	11.99	11.80	3390	2940	2870	1620	1180
IIId	98	>230	69.37	69.20	4.92	4.70	11.99	11.90	3380	2940	2880	1620	1170

TABLE 2 Results of Molecular Weight Determination, Viscometric Study, and Thermogravimetric Analysis of Polymer Samples IIIa-d

	Molecular weight determination				Viscometric data		% Weight loss (°C)				
Polymer	Mmol of $HClO_4$ at first break X	Mmol of $HClO_4$ at final break* Y	Dp = Y/X	Mn#	A.10^1 ($dL \cdot g^{-1}$)	B.10^1 ($dL^{1/2} \cdot g^{-1/2}$)	200	300	400	500	600
IIIa	24	240	10	4190	1.73	1.55	3	10	20	32	76
IIIb	26	232	8.9	3853	1.63	1.45	4	12	22	35	78
IIIc	24	220	9.1	4248	1.25	0.28	4.5	15	24	32	80
IIId	27	200	7.4	3456	0.56	2.41	5	12	22	36	85

*Considering no-NH group in the repeating unit.

#Mn = Dp × (mol. Wt of the repeating unit).

at room temperature. The reaction mixture was left for 7-days at room temperature (27–30°C) with occasional agitation. From the resulting reaction mixture, the supernatant liquid was decanted and the solid mass was washed with THF-methanol mixture by decantation until the decanted liquid was colorless. Finally, it was air-dried and again washed with hot methanol. Poly[imino(cyclopent-2-en-1-one-2,4-diaryl)iminoarylenes] **IIIa** was obtained as a black solid that did not melt up to 230° C; yield 98%.

Synthesis of Model Compound (IV)

2,4-bisphenylimino cyclopent-2-en-1-one IV was prepared by the method reported in the literature; m.p. 141° C (dec) [12]. The spectrum of the compound is shown in Figure 1.

Measurements

The C, H and N contents of all the polymer samples were estimated on a C, H, N, O elemental analyser (Carlo Erba, Italy). The IR spectra of

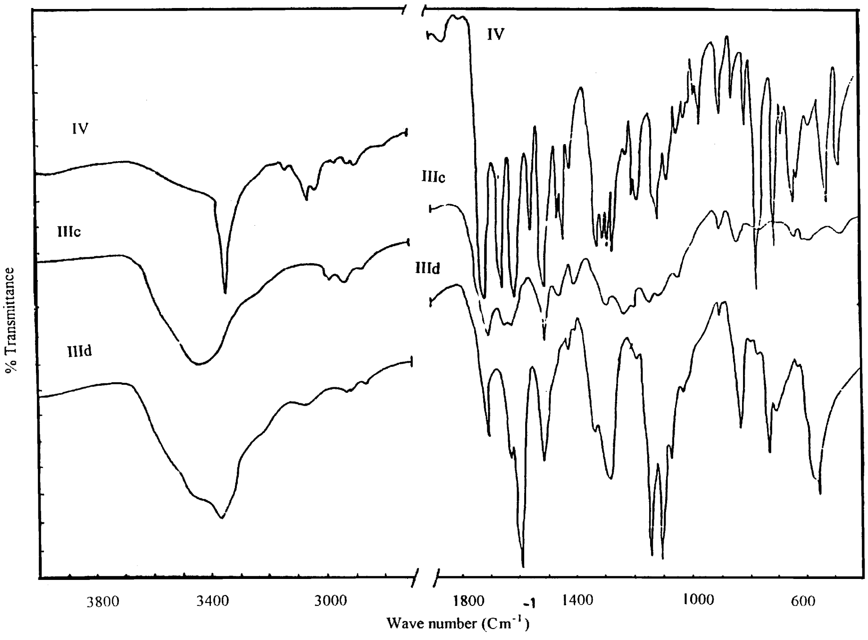


FIGURE 1 IR spectra of model compound (IV) and Polymer sample IIIc and IIId.

polymer samples were scanned in KBr pellets on a Perkin-Elmer 983 spectrophotometer.

Number average molecular weight ($\overline{\mathrm{Mn}}$) of all polymer samples **(IIa-d)** was estimated by non-aqueous conductometric titrations. The titration of polymer samples was carried out in 85:15 (v/v) formic acid–acetic acid mixture against standard perchloric acid in glacial acetic acid. A digital conductivity meter (Toshniwal, India) was used for this purpose. Molecular weight values ($\overline{Mn}$) of all polymer samples were calculated following the methods reported earlier. [16, 17].

Viscometric measurements of the solutions of polymer samples were carried out in 85:15 (v/v) formic acid-acetic acid at $30 \pm 0.1^{\circ}$C using a Ubbelohde viscometer. Thermogravimetric analysis of all the polymers was carried out on a DuPont thermobalance in air at a heating rate of $10\,\mathrm{K\,min^{-1}}$.

RESULTS AND DISCUSSION

The reaction of 2-furaldehyde (**I**) with various aromatic diamines (**IIa-d**) affording polymeric products (**IIIa-d**) was performed in THF-methanol mixture solvent at room temperature according to the method reported for the model reaction of aniline with 2-furaldehyde [12]. It was observed that polycondensation in all cases could be effected at room temperature. In all cases of polycondensation of 2-furaldehyde (I) and diamines(IIa-d) the reaction was fast and yields of polymer were almost quantative. All polymer samples based on the condensation reaction of 2-furaldehyde (**I**) with various diamines (**IIa-d**) presented here were obtained as dark brown to black powders that do not melt up to 250°C. All the polymer samples are insoluble in common organic solvents. They are soluble only in formic acid and form dark violet-coloured solutions, indicating the Stenhous salt [18] formation during the dissolution of polymer. Carbon, hydrogen, and nitrogen contents of all polymer samples shown in Table I, agree well with those predicated on the basis of the structure of the respective units (Scheme 1). Hence, since the reaction of 1 mol of 2-furaldehyde with 2 mol of aniline affords, 2,4-bisphenyl(imino cyclopent-2-en-1-one) (as indicated earlier [12]), the polycondensation reaction of 1 mol of 2-furaldehyde with 1 mol of aromatic diamines (*i.e.*, 2 mol of NH_2 groups) may be postulated to occur by furan rearrangement (mechanism discussed later).

Typical IR spectra of the polymers and also of model compound (**IV**) are shown in ure 1. Important IR spectral bands of the IR spectra of the polymers are furnished in Table 1. Examination of the IR spectra of all polymer samples reveals that all the polymer samples show identical IR spectral bands of the important characteristic groups. Each IR spectrum comprises a broad band at 3600–3200 cm^{-1} with a maximum around 3400 cm^{-1} assigned to secondary imino groups bonded to carbonyl oxygen by a hydrogen bridge [19]. Bands at about 3030 and 3070 cm^{-1} can be assigned to the aromatic C–H stretching vibration. Each spectrum comprises a strong band at about 1709 cm^{-1} attributed to $\nu_{C=O}$ of the cyclopent-2-en-1-one ring 12. The band due to the conjugated C=C of cyclopent-2-en-1-one could not be identified because of overlapping with one of aromatic bands. The strong bands around 1300 and 1200 cm^{-1} due to ν_{C-N} are observed in all spectra. Several bands appear in the double-bond region, and they are due mainly to the aromatic ring present in the polymer chains. Bands due to furfurylidiene (–CH=N–) and $-NH_2$ group (*i.e.*, end groups of polymers) are not observed discernibly. Comparison of IR spectra of all polymer samples with that of model compound (**IV**) (Figure 1) shows that almost all essential features are in common. Hence, the structure of proposed polymer samples is consistent with that proposed in Scheme 1.

As all polymer samples are insoluble in common organic solvents, their NMR study was not attempted.

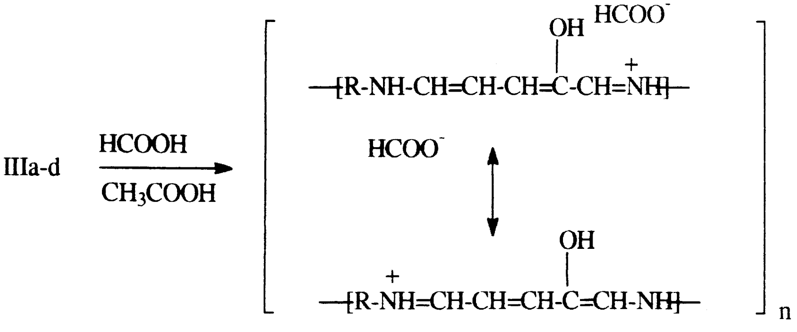
The number average molecular weights (Mn) (Table 2) of **IIIa-d**, determined by non-aqueous conductometric titration, were found to be in the range of 3400–4200 depending upon the nature of the polymer. The variations may be due to the difference in reactivates of diamines under study.

The typical viscometric solution behaviour is determined in a formic acid–acetic acid mixture (85:15) (v/v). The viscosities of all the polymer samples do not obey the relations found by Huggins, but show the behaviour of polyelectrolites according to Eq. (1) proposed by Fuoss and Strauss [20] for the viscosity of solutions containing linear polyelectrolite:

$$\frac{\eta_{sp}}{C} = \frac{A}{1 + BC^{1/2}} \tag{1}$$

where A and B are constants characteristic of each sample.

Values of A and B are listed in Table 2. The plots (not shown) indicate that the polymer samples are polyelectrolytes that transform in formic acid–acetic acid to the corresponding polyiminium compound. It has been reported that the 2,4-bisphenyliminocyclopent-2-one (**IV**) forms with acid a dark purple Stanhous salt. Hence, the procuced polymer samples may form poly(Stanhous salt)s during dissolution in formic acid–acetic acid mixture, which is observed visually



SCHEME 2

by dark purple colour [18]. The structure of a polyiminium Stenhouse ion is shown in Scheme 2.

Typical TG curves of polymer samples **IIIa** and **IIIc** are shown in Figure 2 and the results are in Table 2. Examination of TG traces of all polymer samples reveals that they all degrade in a single step. The

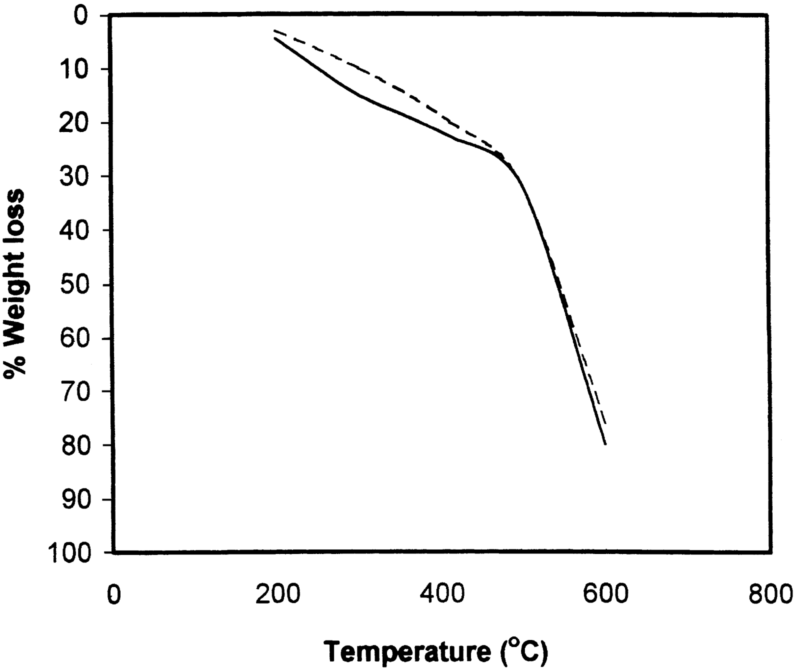
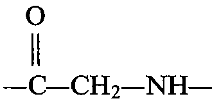


FIGURE 2 TG thermogram of polymers: – – – IIIa——IIIc.

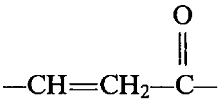
degradation commences in the range of 200−300°C depending upon the nature of the polymer. The rate maximum is observed at 500°C, and at about 600°C, loss is almost complete. Intermolecular hydrogen bonding may play a significant role in the considerable stability of the polymer.

As expected, the insolubility and infusibility of the produced polymers resemble that of polymers containing



$$-\overset{O}{\overset{\|}{C}}-CH_2-NH-$$

bridge between arylene units [17, 21]. However, the produced polymers have a lower thermal stability than do poly(ketoamines) [17, 21]. This may be due to a thermooxidation reaction [22] during degradation of the



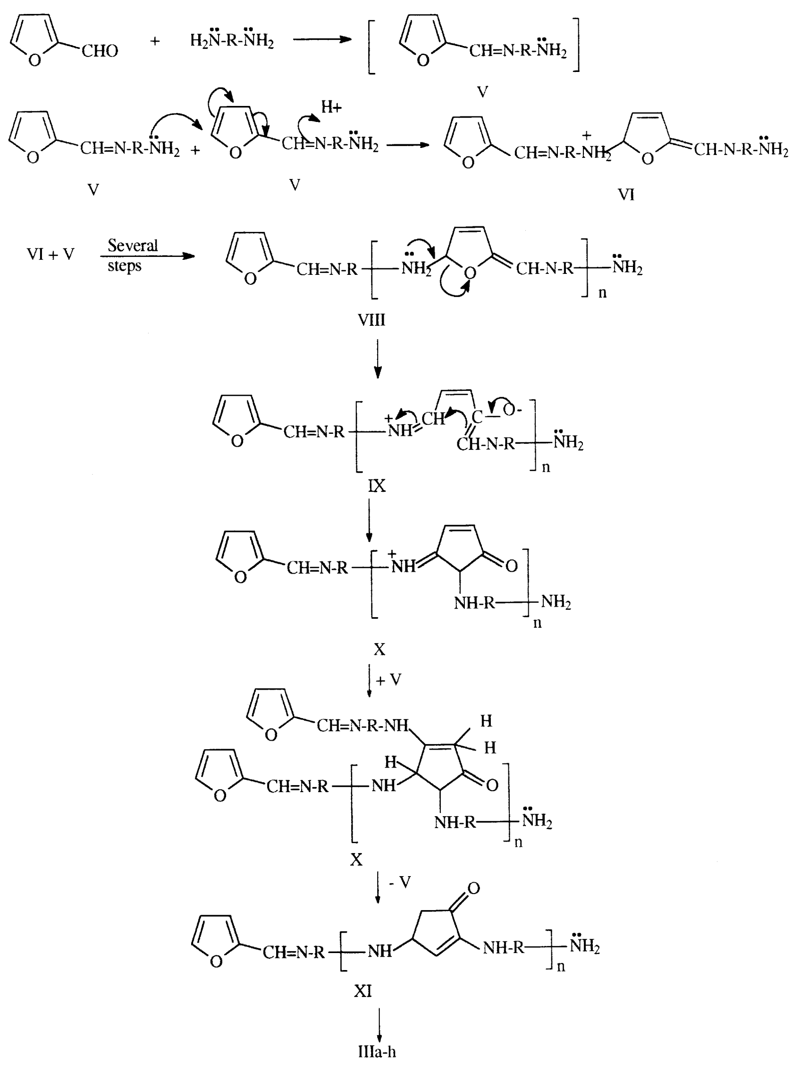
$$-CH{=}CH_2-\overset{O}{\overset{\|}{C}}-$$

group present in the cyclopent-2-en-1-one ring.

The Possible Mechanism of Formation of Polymer IIIa-d

It is assumed that the mechanism of formation of polymer samples IIIa-d proceeds through the possible steps shown in Scheme 3.

It is consistent with the equimolar reaction of 2-furaldehyde (**I**) and diamine **II** (1:1) required for the synthesis of poly[imino(cyclopent-2-en-1-one-2, 4-diyl)iminoarylenes] [12]. The first nucleophilic attack of **V** is well-established [23]. The first nucleophilic attack of the primary imino group of **V** at position 5 of the furan ring (which is a self-polymerization of **V**) is postulated in the related cases [23, 24]. This reaction yields a protonated intermediate **VII**, which upon protonation yields the natural species **VIII**. Compound VIII may then react to form the open-chain intermediate **IX** that cyclizes [25] leading to structure **X**. As suggested by Lewis and Mulquiney [12] the polymer is formed by initial conjugation addition of the aromatic amines to system **X** to form the triaryliminocyclopentanone **XI** that then undergoes elimination of aromatic amines to form the more stable 2,4-diarylimino system **XII**.



SCHEME 3

Because of nonprocessability of the present insoluble polymers, qualitatively observations were made on glass reinforcement using a mixture of commercial epoxy resin (diglycidyl ether of bisphenol-A) and polymer sample IIIa in an organic solvent. It was noted that laminate sheet could be made with good mechanical strength. This work is under progress.

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