

Polymers Derived from 2-Furaldehyde and Aromatic Diamines. I

HASMUKH S. PATEL* and GOPAL H. MAJMUDAR

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, India

SYNOPSIS

Poly [imino(cyclopent-2-en-1-one-2,4-diyl) iminoarylenes] were prepared by the condensation of 2-furaldehyde with various aromatic diamines 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 acid-acetic acid (85 : 15) (v/v) mixture exhibited polyelectrolyte behavior. The thermal properties of polymer samples were revealed by thermogravimetry. The formation of the polymeric product is also explained. The result of preliminary tests for glass reinforcement of commercial epoxy resin and produced polymer samples suggest that laminate sheets with good mechanical strength can be obtained.

INTRODUCTION

Polymers 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 hardeners.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 that the major product was resinous. Such resins have not yet been studied systematically.

The reaction of aromatic amines with 2-furaldehyde is well documented in the literature.¹² Lewis and Mulquiney clarified that in the reaction of 2 mol of a simple aniline derivative and 1 mol of 2-furaldehyde no Schiff's base is formed, but the 2,4-bisarylamino-cyclopent-2-en-1-one is obtained by rearrangement. There is no report on the above-mentioned reaction¹² between aromatic diamines and 2-furaldehyde, which may lead to polymeriza-

tion. Hence, it may be interesting to study the reaction of 2-furaldehyde with several aromatic diamines. The present paper describes the synthesis and characterization of the reaction products obtained from 2-furaldehyde and aromatic diamines such as 1,3-phenylenediamine, 1,4-phenylenediamine, benzidine, 4,4'-methylenedianiline, 4,4'-oxydianiline, 4,4'-diamino diphenyl sulfone, *o*-tolidine, and *o*-dianisidine.

EXPERIMENTAL

Materials

2-Furaldehyde (I) obtained from SD Fine Chemicals Ltd., Boisar, India, was purified by the method reported in the literature.¹³ All the diamines and other chemicals used were of analar or chemically pure grade.

Preparation of Poly[imino(cyclopent-2-en-1-one-2,4-diyl)iminoarylenes] III A-H

The polycondensation reaction of (I) with various diamines was carried out in similar manner. Details

* To whom correspondence should be addressed.

Table I Synthesis and Characterization of III A–H

Polymer ^a	Yield in %	Softening Range (°C)	Elemental Analysis (%)						Important IR Spectral Bands in cm ⁻¹						
			C		H		N		ν_{N-H}	ν_{CH_2} Sym	ν_{CH_2} Asym	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{C=N}$	$\nu_{C=N}$
			Calcd	Found	Calcd	Found	Calcd	Found							
III A	98	> 230	70.97	69.03	5.38	5.25	15.05	14.85	3390	2920	2862	1715	1615	1285	1195
III B	98	> 230	70.97	69.01	5.38	5.13	15.05	15.01	3360	2928	2870	1715	1613	1280	1180
III C	82	185–200	77.86	77.43	5.34	4.84	10.69	10.36	3380	2920	2858	1717	1612	1280	1180
III D	98	> 230	78.26	77.62	5.80	5.54	10.14	9.98	3440	2922	2860	1711	1620	1300	1200
III E	85	> 230	73.38	72.92	5.04	4.96	10.07	9.69	3440	2925	2880	1710	1635	1285	1170
III F	70	205–225	62.58	63.71	4.29	4.56	8.59	8.30	3375	2923	2860	1718	1628	1285	1190
III G	30	175–185	78.62	78.26	6.21	5.91	9.66	9.43	3435	2928	2860	1700	1635	1280	1210
III H	55	175–185	70.81	69.76	5.59	5.47	8.70	8.62	3442	2924	2865	1712	1630	1290	1205

^a Polymer samples III A–D and F were prepared in methanol solvent. Polymer samples III E, G, and H were prepared in DMF.

of a typical synthesis of a polymer sample based on the reaction of I with 1,3-phenylenediamine are given here. Details about all the polymer samples are furnished in Tables I and II.

Condensation of 1,3-phenylenediamine II A (1 mol) with 2-furaldehyde I (1 mol) in methanol/DMF

To the solution of II A (5.4 g, 0.05 mol) in methanol (100 mL), freshly distilled I (4.1 mL, 0.05 mol) was added with continuous stirring 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 methanol by decantation until decanted methanol was colorless. Finally, it was air-dried and again washed with hot methanol. Poly [imino (cyclopent-2-en-1-one-2,4-diyl)imino-1,3-phenylene] III A was obtained as a black solid that did not melt up to 230°C; yield 98%.

Synthesis of Model Compound (IV)

2,4-bisphenylamino cyclopent-2-en-1-one IV was prepared by the method reported in the literature; mp 141°C (dec)¹². The IR 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, and S elemental analyzer (Carlo Erba, Italy). The IR spectra of polymer samples were scanned in KBr pellets on a Perkin-Elmer 983 spectrophotometer.

Number average molecular weight (\bar{M}_n) of all polymer samples (III A–H) 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 (\bar{M}_n) of all polymer samples were calculated following the methods reported earlier.^{14,15}

Viscometric measurements of the solutions of polymer samples were carried out in 85 : 15 (v/v) formic acid–acetic acid mixture[†] at 30 ± 0.1°C using an Ubbelohde viscometer. Thermogravimetric analysis of all the polymers was carried out on a DuPont thermobalance in air at a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

The reaction of 2-furaldehyde (I) with various aromatic diamines (II A–H) affording polymeric products (III A–H) was performed in methanol or DMF 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 cases of polycondensation of 2-furaldehyde (I) and diamines such as 1,3-phenylenediamine, 1,4-phenylenediamine, and 4,4'-methylenedianiline the reaction was very fast and yields of

[†] A laboratory grade of formic acid to which an appropriate amount of acetic anhydride was added yielded the mixture that was used as solvent.

Table II Results of Molecular Weight Determination, Viscometric Study, and Thermogravimetric Analysis of Polymer Samples III A–H

Polymer	Molecular Weight Determination by Nonaqueous Conductometric Titration				Viscometric Data ^c		Thermogravimetric Analysis; % Wt Loss at Temperature				
	mmol of HClO ₄ at First Break X	mmol of HClO ₄ at Final Break ^a Y	$\overline{DP}_n = \frac{Y}{X}$	\overline{M}_n^b	$A \cdot 10^1$ (dL g ⁻¹)	$B \cdot 10^1$ (dL ^{1/2} g ^{-1/2})	200°C	300°C	400°C	500°C	600°C
	III A	62	620	10	1860	1.71	7.53	4.5	8	16	25
III B	70	620	8.9	1660	—	—	3	8	20	37	73
III C	70	505	7.2	1890	2.36	6.72	2	5.5	12.5	22.7	93
III D	44	438	10	2760	1.82	1.04	4.2	8	15	25.5	71.3
III E	70	428	6.1	1700	1.29	0.30	1.5	5.5	17	60	96
III F	106	330	3.1	1010	0.58	2.43	1	2.2	26	38	66
III G	70	330	4.7	1360	1.01	1.33	2.5	11.5	23	35	98
III H	185	620	3.4	1090	1.43	2.04	1.5	8.5	24.5	33	76

^a Considering on —NH group in the repeating unit.

^b $\overline{M}_n = \overline{DP}_n \times (\text{mol wt of the repeating unit})$

^c Solvent: formic acid/acetic acid (85 : 15) (v/v); application of empirical relation eq. (1).

the polymers were almost quantitative. All polymer samples based on the condensation reaction of 2-furaldehyde (**I**) with various diamines (**II A–H**) presented here are obtained as dark brown-to-black powders. The polymer samples **III C** and **F–H** melt in the range of 175 to 205°C. The other polymers do not melt up to 250°C. All the polymer samples are insoluble in common organic solvents. They are soluble in formic acid and form dark violet-colored solutions, indicating the Stenhouse salt¹⁶ formation during dissolution of polymer. Carbon, hydrogen, and nitrogen contents of all polymer samples, shown in Table I, agree well with those predicted 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-bis-phenyl(amino cyclopent-2-en-1-one (as indicated earlier¹²), the polycondensation reaction of 1 mol of 2-furaldehyde with 1 mol of aromatic diamines (i.e., 2 mol NH₂ groups) may be postulated to occur by furan rearrangement (mechanism discussed below).

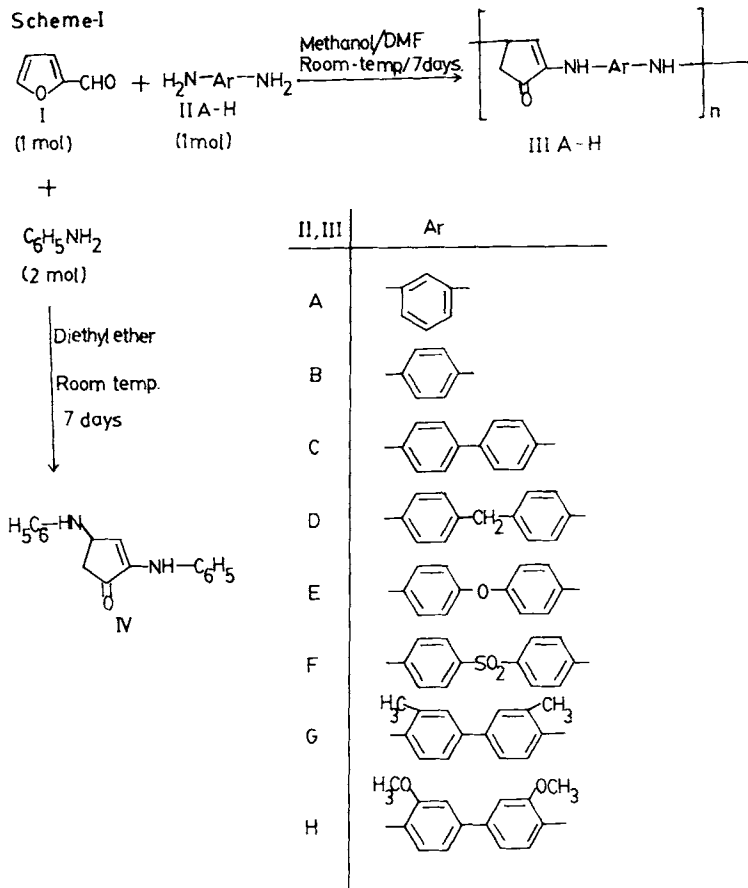
Typical IR spectra of the polymers and also of model compound (**IV**) are shown in Figure 1. Important IR spectral bands of the IR spectra of the polymers are furnished in Table I. Examination of the IR spectra of all polymer samples reveals that all the polymer samples show identical IR spectral bands of important characteristic groups. Each IR spectrum comprises a broad band at 3600–3200 cm⁻¹ with a maxima around 3400 cm⁻¹ assigned to secondary amino groups bonded to carbonyl oxygen by a hydrogen bridge.¹⁷ 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 furfuryliene (—CH=N—) and —NH₂ 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**) (Fig. 1) shows that almost all essential features are in common. Hence, the structure of produced polymer samples is consistent with that proposed in Scheme 1.

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

The number average molecular weights (\overline{M}_n) (Table II) of the **III A–H** determined by nonaqueous conductometric titration were found to be in the range of 1000–2800 depending upon the nature of the polymer. The variations are expected to be due to the difference in reactivities of diamines under study.

The typical viscometric solution behavior in the formic acid–acetic acid mixture[†] (85 : 15) (v/v) of polymer samples **III A** is shown in Figure 2. The viscosities of all the polymer samples do not obey the relations found by Huggins, but show the be-



Scheme 1

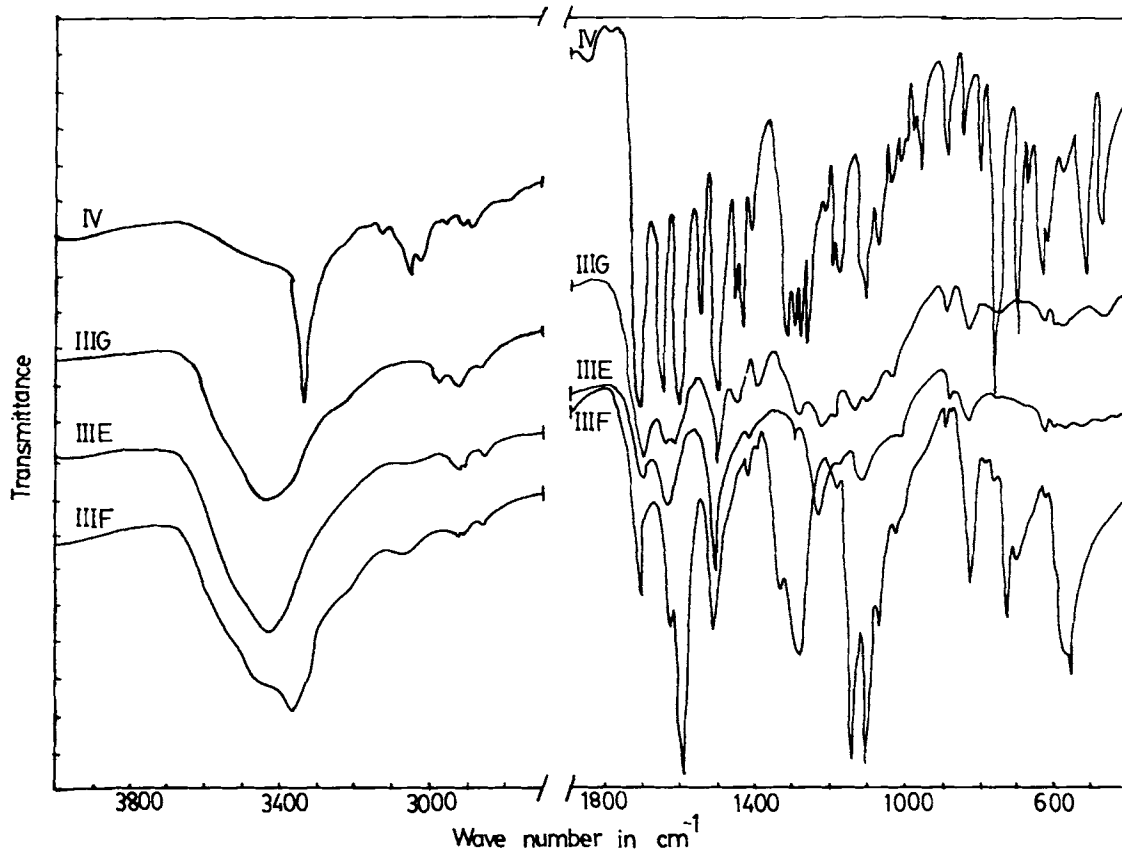


Figure 1 IR spectra of model compound (IV) and polymer samples III G, E, and F.

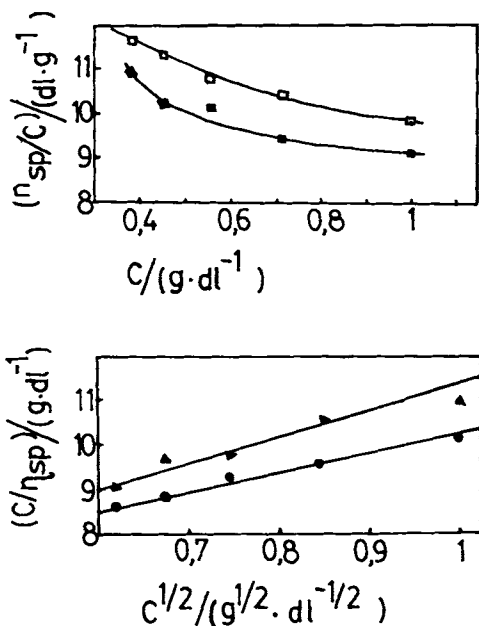


Figure 2 (i) Plots of reduced viscosity η_{sp}/C vs concentration of polymer samples (\square) III A; (\blacksquare) III D. (ii) Fuoss-Strauss plots of polymer samples [application of eq. (1)]: (\bullet) III A; (\blacktriangle) III D.

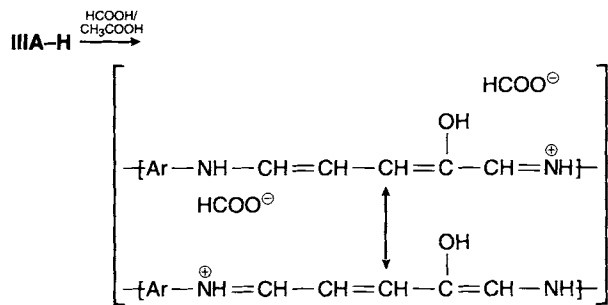
behavior of polyelectrolytes according to eq. (1) proposed by Fuoss and Strauss¹⁸ for the reduced viscosity of solutions containing linear polyelectrolyte:

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

where A and B are constant characteristics of each sample.

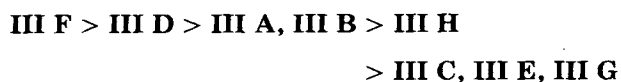
The plots according to eq. (1) are linear (typical examples are shown in Fig. 2). Values of A and B are listed in Table II. The plots indicate that the polymer samples are polyelectrolytes that transform in formic acid-acetic acid to the corresponding polyiminium compound. It has been reported that the 2,4-bisphenylaminocyclopent-2-en-1-one (IV) with acid forms a dark purple Stenhouse salt. Hence, the produced polymer samples may form poly(Stenhouse salt)s during dissolution in formic acid-acetic acid mixture, which is observed visually by its dark purple color.¹⁶ The structure of a polyiminium Stenhouse ion is proposed to be as shown in Scheme 2.

Typical TG curves of polymer samples III A and C are shown in Figure 3 and the results are in Table II. Examination of the TG traces of all polymer samples reveals that they all degrade in a single step. The degradation commences in the range of 200–



Scheme 2

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. Comparison of the thermal stability of all the polymers reveals that the thermal stability decreases as follows:



The unexpected high thermal stability of III F may be due to the presence of sulfonyl groups.

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

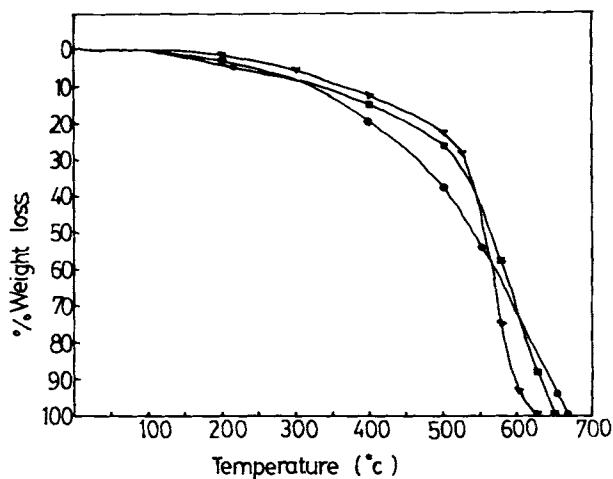
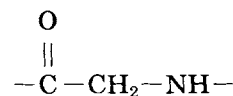
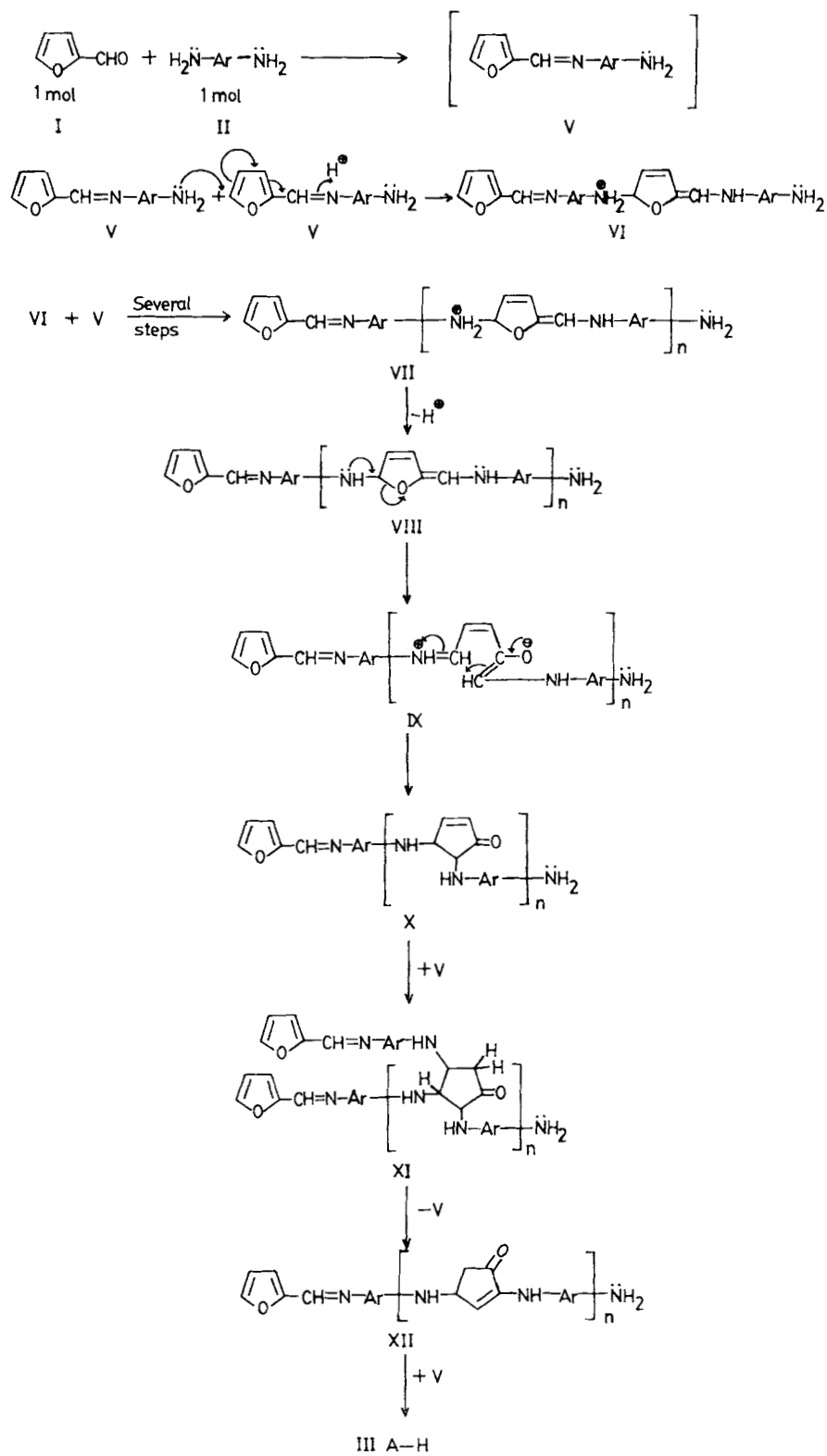


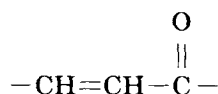
Figure 3 TG thermograms of polymers obtained at 10°C/min heating rate in air: (\bullet) III B; (\blacktriangle) III C; (\blacksquare) III D.

Scheme - III



Scheme 3

bridges between arylene units.^{15,19} However, the produced polymers have a lower thermal stability than do poly(ketoamines).^{15,19} This may be due to the thermooxidation reaction²⁰ during degradation of the



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

The Possible Mechanism of Formation of Polymers III A-H

It is assumed that the mechanism of formation of polymer samples III A-H proceeds through the possible steps as shown in Scheme 3.

It is consistent with the equimolar reaction of 2-furaldehyde (I) and aromatic diamine II (1 : 1) required for the synthesis of poly[imino(cyclopent-2-en-1-one-2,4-diyl) iminoarylenes].¹² The first step involved in the formation of 2-furfuryl Schiff's base-V is well established.²¹ The first nucleophilic attack of the primary amino group of V at position 5 of the furan ring (which is a self-polymerization of V) is postulated in the related cases.^{21,22} This reaction yields a protonated intermediate VII, which upon proton loss yields the neutral species VIII. Compound VIII may then react to form the open-chain intermediate IX that cyclizes,²³ leading to structure X. As suggested by Lewis and Mulquiney,¹² the polymer is formed by initial conjugate addition of the aromatic amine to system X to form the triarylaminocyclopentanone XI that then undergoes elimination of aromatic amine to form the more stable 2,4-diaryl-amino system XII.

Because of nonprocessability of the present insoluble polymers, qualitative observations were made on glass reinforcement using a mixture of commercial epoxy resin (diglycidyl ether of bisphenol-A) and polymer sample III A in an organic solvent. It was noted that laminate sheet could be made with good mechanical strength (flexural strength = 199 MPa, compressive strength = 235 MPa). This work is under progress and will be communicated shortly.

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REFERENCES

1. M. A. Askarov, G. T. Ibragimova, and M. S. Mirkamilova, *Uzb. Khim. Zh.*, **17**, 55 (1973); *Chem. Abstr.*, **80**, 27535s (1974).
2. M. A. Asharov, G. T. Ibragimova, and M. S. Mirkamilova, (USSR) Deposited Doc, VINITI 7076-73, 9 pp (1973).
3. N. Hojyo and M. Kotera, *J. Chem. Soc. Jpn. Ind. Chem. Sect.*, **55**, 733 (1952).
4. M. S. Mirkamilov, G. T. Ibragimova, and A. T. Dzhalilov, *Uzb. Khim. Zh.*, **14**, 84 (1970); *Chem. Abstr.*, **74**, 76892r (1971).
5. M. A. Asharov, M. S. Mirkamilova, and G. T. Ibragimov, Tr. Tashk. Politekh. Inst., **90**, 126 (1972); *Chem. Abstr.*, **83**, 132378c (1975).
6. Y. Sumita, S. Seko, M. Watanabe, and T. K. Misumi, *Jpn. Pat.* 7195, (August 23, 1958); *Chem. Abstr.*, **54**, 1770e (1960).
7. G. Lorentz and L. C. Heuck, *Ger. Pat.* 1,110,407 (1961); *Chem. Abstr.*, **55**, 25363c (1961).
8. Ev. Orobchenko, N. Yu. Pryanishnikova, and Tk. Latyshko, *USSR Pat.* 161,923 (1964); *Chem. Abstr.*, **61**, 10841gh (1964).
9. *Jpn. Kokai* 7460393 (1974) (to Frain Plastics Inc.); *Chem. Abstr.*, **84**, 122852j (1976).
10. F. N. Hirose, U. S. Pat. 3,917,702 (1975) (to Furane Plastics Inc.); *Chem. Abstr.*, **84**, 45383c (1976).
11. A. A. Berlin, B. I. Liogonikii, B. I. Zapadinskii, E. A. Kazantzev, and A. O. Stankevich, *J. Macromol. Sci. Chem. A*, **11**, 1 (1977).
12. K. C. Lewis and C. E. Mulquiney, *Aust. J. Chem.*, **23**, 2315 (1970).
13. A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 4th Ed, Longmans, New York, 1979.
14. S. K. Chatterjee and L. D. Puchav, *J. Macromol. Sci. Chem. A*, **8**, 451 (1974).
15. R. N. Patel and S. R. Patel, *Angew. Makromol. Chem.*, **96**, 85 (1981).
16. J. Stenhouse, *Justus Liebigs Ann. Chem.*, **156**, 199 (1870).
17. L. J. Belamy, *Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.
18. (a) R. M. Fuoss and U. P. Strauss, *Ann. N.Y. Acad. Sci.*, **51**, 836 (1949). (b) R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.*, **3**, 246 (1948).
19. H. S. Patel, R. N. Patel, and S. R. Patel, *Angew. Makromol. Chem.*, **99**, 125 (1981).
20. B. Malm, *Angew. Makromol. Chem.*, **107**, 143 (1982).
21. K. G. Lewis, *J. Chem. Soc.*, 531 (1957).
22. H. Yasuda, T. Hayashi, and W. Midorikawa, *J. Org. Chem.*, **35**, 1234 (1970).
23. A. H. Blatt and N. Gross, *J. Org. Chem.*, **29**, 3306 (1964).

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