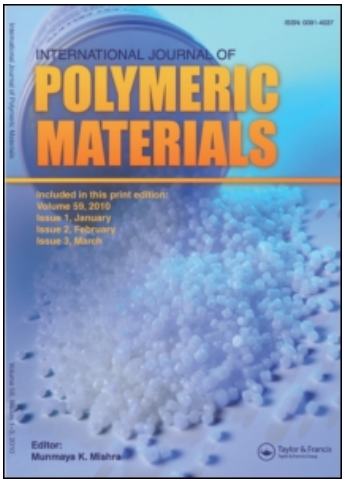

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Synthesis and Characterization of Polyimides Based on Furan Resins

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Preparation of polyimides was carried out by the Diels-Alder (DA) reaction of furan resin namely; Poly [4-(2-furanyl)-3-methylbutan-2-one] with different types of bismaleimides. The reaction was carried out in solution as well as in bulk and this was followed by aromatization of tetrahydrophthalimide intermediate. The molecular structure of resultant polyimides was established by elemental analysis and IR spectral studies. Thermogravimetric technique was used to evaluate thermal behaviour. The glass and carbon fiber reinforcement using lab synthesized polyimides was attempted for the preparation of composites.

KEY WORDS Polyimides, furan resin, Diels-Alder reaction, bismaleimides, IR spectroscopy, thermogravimetry.

INTRODUCTION

Polyimides (PIs) are known for their exceptionally high heat and fire resistance but difficulty in molding and high cost prohibit their use for various application.[1–3] Furan based PIs are quite economical due to the low cost of base material i.e. furfural.[4] Furfural-methyl ethyl ketone resin, in particular exhibit remarkable resistance to chemicals and heat.[5] In the uncured state, the structure of furfural-methyl ketone resin has been well established as poly[4-(2-furanyl)-3 methylbutane-2-one] (PFMB).[6] The Diels-Alder (DA) reaction of furan derivatives with active dienophiles e.g. maleimides has been well documented in literature.[7,8] The bismalimides play a major in the formation of high performance polyimides.[9,10] In this study PIs based on PFMB have been synthesized and characterized for their molecular composition. An attempt has also been made to prepare their composites with glass and carbon fiber.

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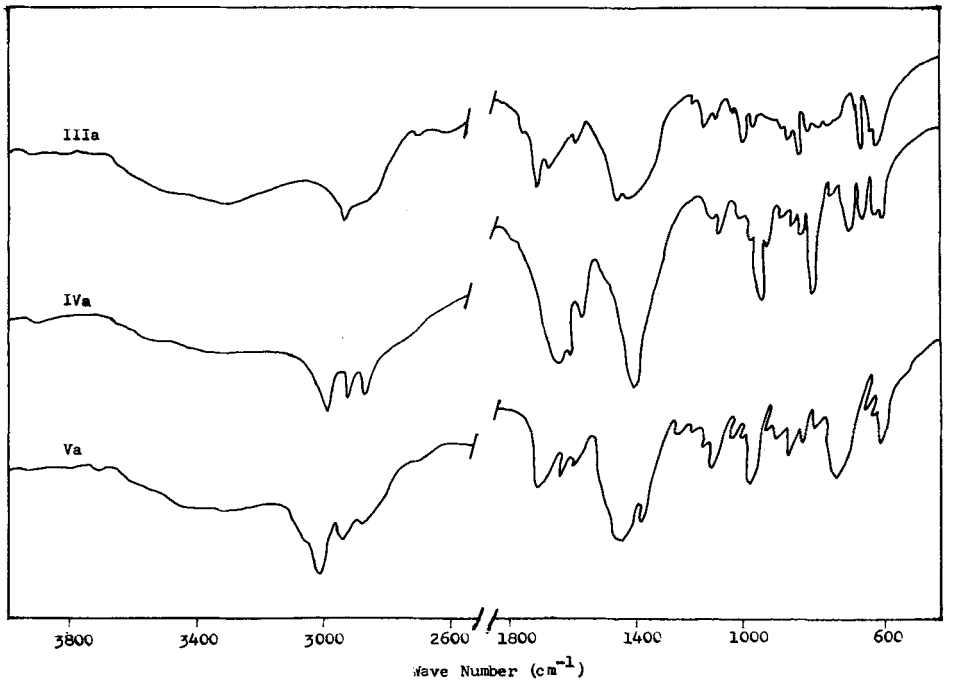


FIGURE 1 I. r. Spectra of polyimides.

EXPERIMENTAL

Materials

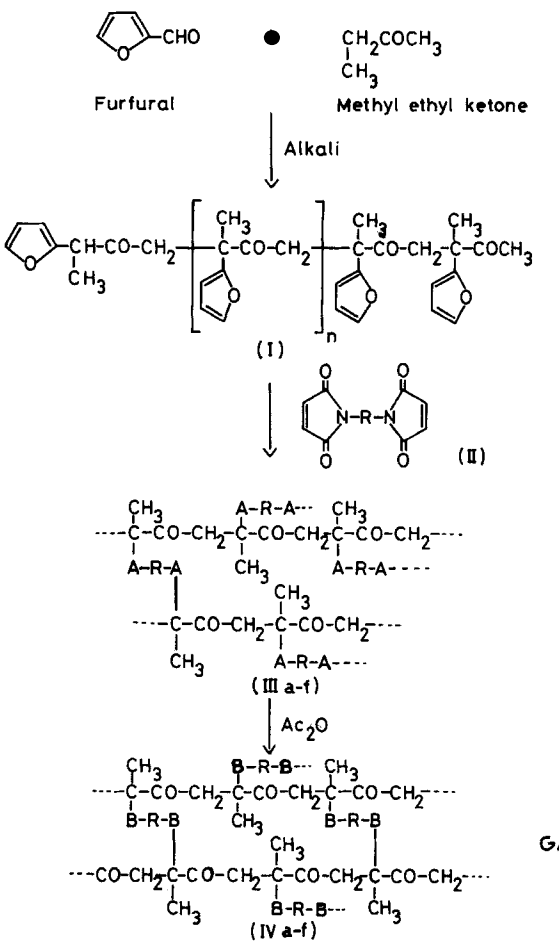
All the chemicals were obtained from SDS chemicals, Boisar (India). Furfural was distilled before use.

Synthesis of Furan Resin PFMB (I)

Furfural (20 ml, 0.2 mol), and methyl ethyl ketone (24 ml, 0.4 mol) in presence of alkali (20% w/v, 100 ml) were allowed to react at room temperature for 2 hrs and then heated at 75°C for 3 hrs (Scheme I). The resultant reaction mixture was then cooled and poured into cold water (200 ml) with gentle stirring. The solid was filtered, treated with dil. acetic acid, washed with water and then dried. The resin so prepared has been found to have the following characteristics.

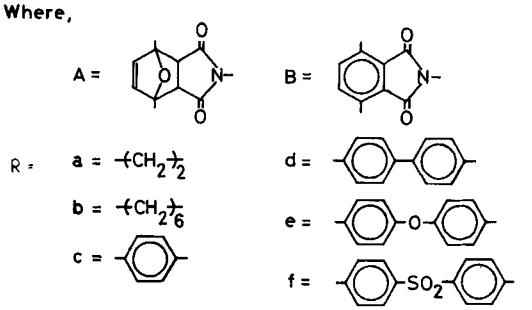
Fusion range: 75–80°C
Solubility: soluble in almost all organic polar solvents
Molecular mass: 1600 ±15 estimated by VPO, (dioxane solvent at 343°K)
ηred (1% soln. in dioxane at 35 ± 0.2°C): 3.52×10^{-2} dl g^{-1}
$-(C_9H_{10}O_2)-_n$, $-(150)_n-$

C, H Contents:	%	calcd.	found
	C	77.08	76.50
	H	7.13	6.90



$$\text{I} + \text{II} \xrightarrow[\text{Polymerization}]{\text{Bulk}} \text{IV}'\text{a-f}$$

Where,



SCHEME I

TABLE I

Bismaleimides used

	Bis(maleimide) (II)	m.p. (°C)
a.	N,N'-ethylene bismaleimide	189-190
b.	N,N'-hexamethylene bismaleimide	138-139
c.	N,N'-1,3-phenylene bismaleimide	202-203
d.	N,N'-(1,1'-biphenyl)-4,4'-diyl bismaleimide	>300
e.	1,1'-(Oxy-di-4,4'-phenylene)-bismaleimide	179-182
f.	1,1'-(Sulfonyl-di-4,4'-phenylene)-bismaleimide	253-255

Synthesis of Bismaleimides

The bismaleimides (II a–f) listed in Table I were prepared by the methods reported earlier.[11,12]

Preparation of PIs

The unaromatised (III) and aromatised PIs (IV) were prepared through the DA reaction of PFMD (I) with bismaleimides (II) in solution as well as bulk phase system (Scheme I) as reported earlier.[4]

RESULTS AND DISCUSSION

Scheme I shows the steps involved in the preparation of PIs (III and IV) from reactants I and II. The unaromatised products (III) were aromatised in the presence of acetic anhydride to yield polymers IV. On heating PFMB in THF at 75°C, no change in properties has been observed. Bismaleimides alone are also found to be stable under similar conditions, whereas at elevated temperatures or in the presence of an initiator they get polymerized by addition reaction.[9,10]

All the PIs, obtained with about 85% yield, were dark brown powdery samples. They were found insoluble in common organic solvents and do not get affected by concentrated mineral acids and formic acid. The results of elemental analysis of all PI samples have been consistent with their predicted structure (Table II). Examination of IR spectroscopy of PIs reveal that all the spectra contain prominent characteristic bands of the imide group at 1700, 1600, 1050 and 720 cm^{-1}.[4] The band at 780 cm^{-1} might be due to C—H bending vibrations of three adjacent hydrogen atoms of phthalimide moiety arising from the aromatization of polytetrahydrophthalimide intermediate (III). Bands around 2875 and 2920 cm^{-1} ap-

TABLE II

Characterization of unaromatized polyimides (III_{a-f}) (solution polymerization)

Polyimide	Yield,%	Elemental Analysis,%						TG Analysis %,Wt.loss at various temperatures, °C				
		C		H		N						
		Calcd.	Found	Calcd.	Found	Calcd.	Found	300	400	500	600	700
III_a	60	64.61	62.90	5.38	5.25	5.38	5.29	8	32	45	58	78
III_b	70	64.08	62.47	4.98	4.80	4.92	4.83	6	38	46	63	76
III_c	75	64.08	62.40	4.92	4.80	4.92	4.85	6	38	44	60	73
III_d	78	70.80	68.50	4.96	4.35	4.34	4.26	8	28	30	56	68
III_e	78	69.10	67.40	4.84	4.70	4.24	4.25	8	25	33	58	70
III_f	78	64.40	62.30	4.52	4.41	3.95	3.86	8	37	40	66	78

TABLE III

Characterization of aromatized polyimides (IV_{a-f}) (solution polymerization)

Polyimide	Yield,%	Elemental Analysis,%						TG Analysis %, Wt.loss at various temperatures,°C				
		C		H		N						
		Calcd.	Found	Calcd.	Found	Calcd.	Found	300	400	500	600	700
IVa	65	69.42	68.13	4.95	4.80	5.78	5.62	3	26	40	55	70
IVb	70	72.18	70.90	4.51	4.42	5.26	5.22	3	32	41	55	72
IVc	75	72.18	71.10	4.51	4.40	5.26	5.15	3	34	40	53	70
IVd	75	75.00	74.20	4.60	4.50	4.60	4.48	5	20	23	53	70
IVe	78	73.07	72.60	4.48	4.36	4.48	4.35	5	18	26	52	73
IVf	80	67.85	66.80	4.16	4.08	4.10	4.00	4	18	32	54	78

TABLE IV

Characterization of polyimides (bulk polymerization ($IV_{a'-f'}$)

Polyimide	Yield,%	Elemental Analysis,%						TG Analysis				
		C		H		N		%, Wt. loss at various temperature, °C				
		Calcd.	Found	Calcd.	Found	Calcd.	Found	300	400	500	600	700
IVa'	70	64.92	68.30	4.95	4.75	5.78	5.60	2	24	36	50	70
IVb'	70	72.18	71.10	4.51	4.40	5.28	5.28	3	28	38	50	72
IVc'	80	72.18	71.30	4.51	4.40	5.26	5.18	2	30	38	52	70
IVd'	80	75.00	74.10	4.60	4.53	4.60	4.50	4	20	21	54	72
IVe'	85	73.07	72.80	4.48	4.31	4.48	4.40	3	18	25	55	75
IVf'	80	67.85	66.60	4.16	4.00	4.10	3.80	2	18	32	54	78

pear in the spectra of all polimides are attributed to ν—CH_2— of I.[4] The data of thermogravimetric analysis are given in Table II. The weight loss starts at about 275°C depending upon the nature of PIs. The rate of weight loss has been found higher in the temperature range of 500–600°C. Depending on chemical structure of PIs, weight loss was found to be >68% at about 700°C.

The weight loss of unaromatized PIs (III) starts in lower temperature range (~250°C) as compared to aromatised PIs (IV) (~300°C). This may be due to aromatization of the former by condensation reaction with the rise in temperature and thus liberating water molecules. While comparing the aromatized PIs (IV) with commercial PIs, the lower thermal stability of the former may be due to unsymmetrical moelcular structure; the higher thermal stability of the latter is mainly because of linear and symmetrical structure.[12] The major advantage of the reported PIs is their resistance to solvent, weather, acid and alkali solutions.

Because of the non-processability of the present insoluble PIs, qualitative observations were made on 'in situ' glass and carbon fiber reinforcement using the mixture of PMFB (I) and bismaleimides (II) in an organic solvent. It was noted that laminate sheets or bars could be easily made.

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