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UNSATURATED POLYMIDES FROM β(2-ETHOXY-5-METHYLPHENYL) GLUTACONIC ACID AND THEIR CHARACTERIZATION

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ABSTRACT

Some unsaturated polyamide resins were synthesized by condensing β(2-ethoxy-5-methylphenyl) glutaconic acid with six diamines. The polycondensates were characterized by IR, TG, DSC, VPO and elemental analysis. Most of the polymers were found to decompose in the range of ~ 190 to 600°C. They are brownblack in nature. The kinetics of decomposition was studied. The kinetic parameters were evaluated by the method of Broido. It was observed that the energy of activation of polycondensates depends upon the presence of diamine components in the polymer.

INTRODUCTION

In continuation of the work in connection with synthesis and characterization of unsaturated polymers and polyamides [1-3], the present paper describes the synthesis and thermal stability of polyamide resins in which unsaturation linkage is in the acid moiety of the repeat unit. The polyamides listed in Table 1 were prepared by polycondensation of β(2-ethoxy-5-methylphenyl) glutaconic acid (EMPGA) and various diamines.

EXPERIMENTAL

Materials

Chemically pure diamines were used. EMPGA was prepared by the literature method [4].

polymerization

EMPGA (1a), (0.215 mol) and thionyl chloride (44 mL) were refluxed for 4 h. Excess of the thionyl chloride was distilled off and the contents were cooled. A weighed quantity of diamine (2) (0.215 mol) was added slowly. The mixture was heated at 130°C for 2 h and then at 150°C for another 2 h. After completion of the reaction it was poured into ice-water. The solid was crushed, powdered and heated with boiling water. The cruide product was dissolved in acetone, filtered and precipitated with distilled water. These process gives two fraction, acetone soluble and acetone insoluble. Soluble polyamides fused in the range of ~ 85 to 135°C.

Characterization

IR spectra were run with Carl Zeiss Jena, Model UR-10 spectrophotometer in KBr. The number average molecular weights ($\overline{Mn}$) of DMF - soluble polymer samples were measured on a Hewlet - Packard vapour pressure osmometer (VPO) at 70°C, with DMF as solvent and benzil as a calibrant. TGA of polyamide samples was carried out on Du Pont 951 thermogravimetric analyzer in air at a heating rate of 10°C/min. The DSC were obtained on Du Pont Model - 900 Thermal Analyzer.

RESULTS AND DISCUSSION

Synthesis

Six new polyamide resins were synthesized from various diamines (2a - 2f) and diacid chloride.

The condensates obtained from diamines (2a - 2f) gave two fractions (soluble and insoluble). One is soluble in acetone and several other organic solvent such as dioxane and DMF. All the resin samples were

TABLE 1. CHARACTERIZATION OF POLYMER SAMPLES

Resin number	Designation of resin	Name of the Diamine (mole)	Yield %	Softening range (°C)	Physical appearance of the	% C Found (Calcd.)	%H Found (Calcd.)	%N Found (Calcd.)	$\overline{Mn}$	$\overline{DP}$*
3a.	EMPGA-DB	3,3′-dimethyl benzidine	45.5	85-115	Reddish brown powder	75.1 (76.4)	6.0 (6.4)	6.1 (6.4)	3294	8
3a.i		(0.02)	22.0	-	Ash colour	74.9 (76.4)	5.8 (6.4)	5.6 (6.4)		
3b	EMPGA-DMB	3,3′-dimethoxy benzidine	53.3	90-113	black powder	70.0 (71.2)	5.2 (5.9)	5.3 (5.9)	3299	7
3b.i		(0.02)	22.4	-	Reddish brown powder	69.2 (71.2)	5.0 (5.9)	4.2 (5.9)		
3c	EMPGA-BDC	Benzidine -3,3′-dicarboxylic acid	26.3	100-120	Ash colour powder	66.1 (67.2)	4.0 (4.8)	5.2 (5.6)	2353	5
3c.i		(0.02)	15.5	-	Black powder	64.9 (67.2)	3.5 (4.8)	4.9 (5.6)		
3d	EMPGA-DPM	4-4′-diamino diphenyl methane	29.0	110-115	Reddish brown powder	77.2 (76.1)	6.0 (6.1)	6.1 (6.6)	2745	6
3d.i		(0.02)	28.0	-	"	74.1 (76.1)	4.4 (6.1)	5.3 (6.6)		
3e	EMPGA-DPE	4,4′-diamino diphenyl ether	27.0	110-130	"	71.1 (72.9)	5.1 (5.6)	5.9 (6.5)	3294	8
3e.i		(0.02)	36.4	-	Ash colour powder	70.3 (72.9)	4.9 (5.6)	5.0 (6.5)		
3f	EMPGA-DPS	4,4′-diamino diphenyl sulfone	40.8	115-135	Reddish brown powder	64.2 (65.5)	4.9 (5.0)	5.3 (5.9)	2883	
3f.i		(0.02)	20.5	-	Ash colour powder	62.1 (65.5)	4.3 (5.0)	5.0 (5.9)		

* Average degree of polymerization.

highly coloured ranging from ash colour to dark brown black. The polycondensates soften in the range of 80 to 135°C (Table 1).

Characterization of Polyamides

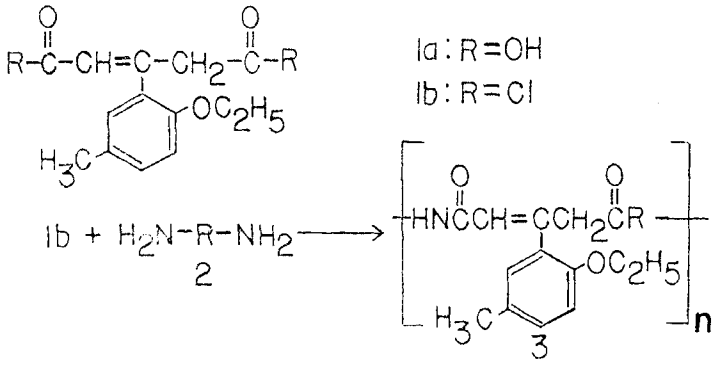
The C and H contents of all the polycondensates agreed well with values calculated on the basis of the structure of repeat unit of the concerned polyamide samples. From the Table 1, it is observed that Mn value of various polycondensates varied from 2700 to 3300. This indicated that there is no speific effect of diol backbone on Mn of polycondensates.

The IR spectra shows characteristic absorption band of :

$-CH_2-$stretching of $-CH_2-\overset{O}{\overset{\|}{C}}-$ at 1430 to 1500 cm^{-1} and 1400 cm^{-1}.

A prominent -N-H band is observed at 3300 cm^{-1} and of the amide band at 1540 cm^{-1}. The aromatic ether band appears at 1220 to 1100 cm^{-1}.

The aromatic -C=C- occur at 1600 to 1630 cm^{-1}. Thus the IR spectra data confirms the various linkages present in the polycondensate chain.



REACTION SCHEME

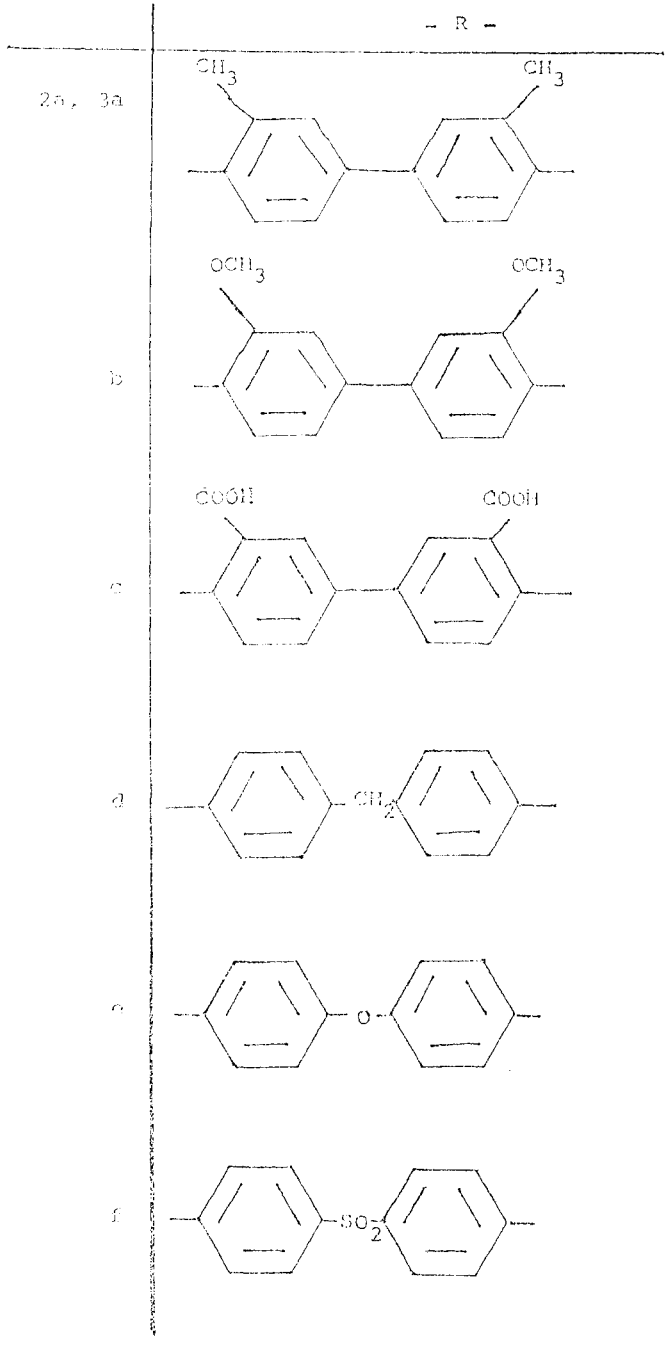


TABLE 2. KINETIC PARAMETERS FROM THERMOGRAVIMETRY (TG) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Resin number	Percentage weight loss upto					Decomposition temperature range	Energy of activation * 'E_A' Kcal.mol^{-1}	Order of reaction	Heat of fusion 'ΔH_f'
	200°	300°	400°	500°	600°C	(°C)	(Kj mol^{-1})		(Cal.g^{-1})
3a	01	36	52	68	92	195-630	16.0 (67.0)	2	4.9
3a.i	0	1	53	84	-	290-535	20.5 (85.9)	2	-
3b	6	29	48	62	88	185-610	19.1 (80.0)	2	5.6
3b.i	0	31	46	84	88	220-560	25.5 (106.8)	2	-
3c	10	50	80	92	-	150-535	18.6 (77.9)	2	5.4
3c.i	0	30	60	80	90	250-625	25.8 (99.7)	2	-
3d	6	40	60	68	82	185-650	19.9 (83.4)	2	5.3
3d.i	0	3	45	68	82	245-650	26.1 (109.3)	2	-
3e	5	40	53	67	90	185-650	14.2 (59.5)	2	5.3
3e.i	0	12	60	75	80	245-610	20.9 (87.9)	2	-
3f	5	30	60	78	99	190-585	18.9 (79.2)	2	6.0
3f.i	0	8	50	90	-	250-500	22.4 (93.8)	2	-

Thermal properties

From TG data presented in Table 2, it is seen that the weight loss upto various temperature limit is different for different polycondensates. Thermal stability of insoluble fraction (3 a.i-3 f.i) is higher compared to their soluble fraction. The weight loss for soluble polycondensates is $\sim$ 5% of their weight at 200°C. Most of the resins undergoes about 50% weight loss below 400°C. While about 70 to 90% weight loss was observed near 500°C for most of the resins.

Activation energy (E_A) calculated using Broido [5] method from TG thermogram, varied from $\sim$ 14 to 26 Kcal mol^{-1}. And order of reaction for decompositon is 2 for all polycondensates. Heat of fusion (ΔH_f) obtained from DSC thermogram of polyamides varied from $\sim$ 5 to $\sim$ 6 cal gm^{-1}. There is no appreciable effect of diamines on ΔH_f of polycondensates.

From the above results it is clear that the thermal stability, rate of degradation and mode of degradation depends upon the diamine back bone present in polymer.

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