Asian Journal of Chemistry Vol. 7, No. 3 (1995), 584–586

Synthesis and Thermal Stability of Some Unsaturated Polyamides

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Unsaturated resins were prepared by condensing β-(2-methoxy-5-methylphenyl) glutaconic acid (2MMPGA) with various diacetates. Theses resins were characterized by IR spectroscopy, vapour pressure osmometry, thermogravimetric analysis, differential scanning calorimetry and elemental analysis. The kinetics of decomposition of these resins were studied. The kinetic parameters were determined by the Broido method. The results indicated that the resins possess good thermal stability.

INTRODUCTION

The literature[1–4] indicates that unsaturated polyester and polyamide resins possess wide applicability. The previous work[5] indicated that the polyester and polyamide resins prepared from glutaconic acid derivative possess good thermal stability. In the present work an attempt has been made to prepare resins derived from β-(2-methoxy-5-methylphenyl) glutaconic acid and various diacetates and to study its thermal and spectral behaviour.

EXPERIMENTAL

The diacetates used in the synthesis were of pure grade. β-(2-Methoxy-5-methylphenyl) glutaconic acid (2MMPGA) was prepared according to the method described by Limaye and Bhave[6] as follows. A mixture of 1 mole of diacetate and 1 mole of diacid and 0.8 gm of zinc acetate was refluxed at 140°C for 8 h, cooled and mixed with excess of water. The dark brown powder obtained was filtered and dried and washed by refluxing with ethanol to remove unreacted diacetate. The resin thus obtained was in the form of brown amorphous powder and was washed by refluxing with acetone for $\frac{1}{2}$ h. The combined acetone-soluble extracts were diluted with water (200 mL) to get acetone-soluble fraction and this fraction was employed for further study. The insoluble fraction may be a crosslinked product.

RESULTS AND DISCUSSION

Eight new polycondensates were prepared from various diacetates and diacids. All the resins are highly coloured ranging from light brown to black. The polycondensates soften in the range of 106 to 142°C (Table-1). The results of elemental analysis revealed that percentage of carbon of each sample is lower than the calculated value. This may be due to the incomplete decomposition of the resins. The Hewlett-Packard Model 302B vapour pressure osmometer (VPO) was used to determine the number average molecular weight ($\overline{Mn}$) at 70°C using dimethyl formamide (DMF) as solvent and benzil as calibrant. The $\overline{Mn}$ values of the soluble resins varied from 2000 to 2400.

TABLE-1
CHARACTERIZATION OF UNSATURATED RESINS

Resin No.	Designation of resin	Name of the diacetate used	Yield %	Softening point °C	$\overline{Mn}$ ±100
1.	2MMPGA-CTDA	Catechol diacetate	40.05	106	2000
2.	2MMPGA-HQDA	Hydroquinone diacetate	50.18	142	2100
3.	2MMPGA-RSDA	Resorcinol diacetate	48.00	134	2050
4.	2MMPGA-1,5-DNDA	1,5-dihydroxynaphthalene diacetate	56.30	126	2200
5.	2MMPGA-2,7-DNDA	2,7-dihydroxynaphthalene diacetate	58.40	140	2250
6.	2MMPGA-AQDA	Anthraquinone diacetate	68.60	132	2300
7.	2MMPGA-PPDA	Phenolphthalein diacetate	40.10	117	2310
8.	2MMPGA-BPADA	Bisphenol-A diacetate	59.30	108	2400

The IR spectra were run with a Perkin-Elmer 983 model spectrophotometer. The IR spectra showed expected characteristic bands; particularly the ester carbonyl band appears at around 1700 cm^{-1}. A prominent carboxylic hydroxyl stretching is observed from 3600–3000 cm^{-1} with a maximum around 3430 cm^{-1}. The aromatic ethers Ar—O—R band occurs at 1260–1040 cm^{-1}. The bands at 1700–1500 cm^{-1} are attributed to aromatic double bonds (—C═C—). Thus the IR spectral data confirms the various linkages present in the polycondensate chain.

Linseis Thermal Analyzer (West Germany) was used for the TG-measurements. The TG scan was carried out employing 25 mg of the sample and with the heating rate 10°C/min. under static air. The DSC instrument used was Du Pont Model-900 Thermal Analyzer (USA). DSC scan was carried out employing 3–4 mg of the sample with the heating rate 10°C/min under static air. The thermogravimetric data presented in Table-2 reveals that weight loss up to various temperature limits is different for different polycondensates. The activation energies (E_a) of the decomposition of polycondensates calculated using Broido method[7] varied from *ca.* 70 *ca.* 100 kJ mol^{-1}. The order of reaction 'n' for decomposition is 2 for all the polycondensates. The heat of fusion (ΔH_f) obtained from DSC thermogram varied from 3.0 to 9.5 cal g^{-1} indicating no appreciable effect of the nature of diacetate on ΔH_f of resins.

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

Resin No.	Percentage weight loss upto °C				Activation energy $E_a \pm 10$ (kJ mol^{-1})	Heat of fusion ΔH_f (cal g^{-1})
	200	300	400	500		
1.	40	59	64	71	70	9.5
2.	06	83	90	92	80	6.9
3.	00	17	60	82	80	4.9
4.	10	32	67	94	100	4.5
5.	07	28	78	—	100	3.1
6.	17	63	71	88	110	6.0
7.	14	41	52	86	80	5.9
8.	05	21	56	71	100	5.6

From the above results it is clear that the thermal stability, rate of degradation and mode of degradation of resins depend on the diacetate backbone present in polymer chain.

REFERENCES

1. B. Harry, U.S. 2,275,495 (Mar. 10, 1942); *Chem. Abstr.*, **36,** 4234 (1942).
2. J.B. Howard, U.S. 2,410,073 (Oct. 29, 1946); *Chem. Abstr.*, **41,** 1239 (1947).
3. N.W. Lywood and F.A. Franch., Brit. 595,758 (Dec. 16, 1947); *Chem. Abstr.*, **42,** 36164 (1948).
4. A.G. Huela, Brit. 914,457 (Jan. 2, 1963); *Chem. Abstr.*, **59,** 1539f (1963).
5. A.M. Mehta, H.R. Dave and R.M. Patel, *Die. Angew Makro. Chem.*, **154,** 43 (1987).
6. D. Limaye and V. Bhave, *J. Indian Chem. Soc.*, **8,** 137 (1931).
7. A. Broido., *Polym. Sci.*, **2A,** 1761 (1969).

(*Received*: 26 August 1994; *Accepted*: 2 January 1995) AJC-914