

# Degradation of Polyester Waste by Aliphatic and Aromatic Alcohols

K. A. JOSHI, G. A. NAIK, and N. B. NEVREKAR, *Fibre Research Laboratory, Sasmira, Sasmira Marg, Worli, Bombay 400 025 India*

## Synopsis

Polyester waste was degraded with ethanol, *n*-propanol, and benzyl alcohol in an autoclave at 280°C under pressure to give seven unknown compounds. The products of each reaction were isolated by using column chromatography and were identified on the basis of elemental analysis and spectral data.

## INTRODUCTION

Polyester waste is generated (4–6% of total production) during the manufacturing process of polyester yarn and fibers. Survey of the literature showed<sup>1–6</sup> that considerable work has been carried out on degradation of waste. Depolymerization has been studied in the presence of catalysts such as metal acetates, sodium hydroxide, phosphorus compounds, etc., with glycol<sup>1,2</sup> and lower aliphatic alcohol<sup>3–5</sup> to obtain oligomeric polyesters<sup>1,2</sup> and alkyl terephthalate,<sup>3–5</sup> respectively.

The present report deals with the degradation of polyester waste by aliphatic and aromatic alcohols in the absence of catalysts. The aim of this work was to isolate low molecular weight compounds and identify their structures.

## EXPERIMENTAL

Polyester waste (m.p. 259–262°C, intrinsic viscosity 0.59 cP) obtained from demonstration plant for synthetic fibers of Sasmira, was utilized for the degradation reactions. Solvents used for the degradation reaction were of analytical grade. Melting points of the compounds were recorded on a hot plate microscope (Reichert Thermovar). Infrared spectra were recorded on an infrared (IR) spectrophotometer-297 (Perkin-Elmer). <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded (Varian, 100 Hz) in CDCl<sub>3</sub> and acetone. The molecular weights of compounds were determined by mass spectra recorded on GCMS (Finnigan Mat 112 S). Degradation reactions were carried out in an autoclave, fitted inside with a heating mantle, a temperature controller, and a stirrer (Fa. Roth, FRG). Ratio of reaction mixture to volume of autoclave was 1 : 10.

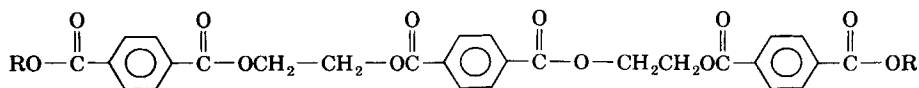
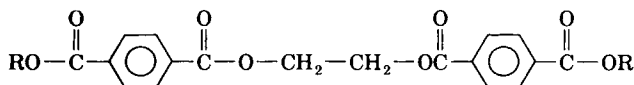
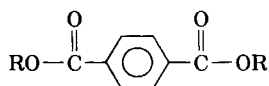
Polyester waste (10 g) was reacted with ethanol, *n*-propanol, and benzyl alcohol in 1 : 1 proportion (w/v). The temperature was raised slowly to 280°C

over 2 hours and was kept constant at this temperature for another 2 hours. The pressure developed during this period was maintained throughout the reaction, namely, for ethanol (25 bar), *n*-propanol (15 bar), and benzyl alcohol (8 bar). The total reaction period for each reaction was 4 hours. The pressure was released and the reaction mixture was extracted with ethyl acetate. The thin layer chromatography (TLC) of the extracted product for each reaction was found to be a mixture of compounds; they were separated by column chromatography using silica gel (BDH-60-120 mesh).

## RESULT AND DISCUSSION

### Degradation of Polyester Waste with Ethanol and Propanol

The reaction product from the degradation of polyester waste with ethanol on separation by column (Table I) gave diethyl terephthalate (I) and 1,2 *bis* (benzyloxy-4'-carbethoxy)ethylene (II) and with *n*-propanol on elutions on column (Table I) gave dipropyl terephthalate (III), 1,2-*bis*-(benzyloxy-4'-carbpropoxy)ethylene (IV), and *bis*-[2-(4'-carbpropoxy-1'-benzyloxyethyl)] terephthalate (V). The structures of the compounds were established on the basis of elemental analysis, IR, <sup>1</sup>H NMR and mass spectra (Table I).



Reaction of polyester waste with ethanol and *n*-propanol at high temperature (280°C) under pressure leads to the formation of compounds with identical end groups, specifically (I), (II), (III), (IV), and (V), respectively, which may be attributed to the degradation of polyester waste to oligomeric stage followed by total transesterification with the respective aliphatic alcohols.

TABLE I  
Data for the Products Isolated after Degradation of Polyester Waste with Aliphatic Alcohols

Degradation of Polymer Waste with	Elemental Analysis				Spectral Data					
	Elution of Column with Solvent System	m.p. of the Products	Found Calcd. for	C% H%	IR Peaks	<sup>1</sup> H NMR			Mass Peaks (M <sup>+</sup> ) Split-up m/e	
						Functional Group and Position	Number of Protons	δ		
Ethanol	Petroleum ether (b.p. range 60-80°C) 100%	(I) 44°C lit. <sup>6</sup> m.p. 44°C)	Found C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	64.90	6.30					
				63.81	5.36					
				63.17	5.32					
n-Propanol	Petroleum ether: benzene (80:20)	(II) 108°C	Found C <sub>22</sub> H <sub>28</sub> O <sub>8</sub> requires	67.24	7.21	—CH stretching at 2920-2980 cm <sup>-1</sup> ester carbonyl at 1725 cm <sup>-1</sup>	p-C <sub>6</sub> H <sub>4</sub> at —OCH <sub>2</sub> CH <sub>3</sub> at	8.12	8	s
				67.20	7.20			1.41	6	t
								4.54	4	q
						4.71	4	s		
Benzene (100%)	Benzene (100%)	(IV) 98°C	Found C <sub>24</sub> H <sub>28</sub> O <sub>8</sub> requires	65.21	5.90	—CH stretching at 2920-2960 cm <sup>-1</sup> ester carbonyl at 1725 cm <sup>-1</sup>	p-C <sub>6</sub> H <sub>4</sub> — at	8.15	8	s
				65.16	5.88			1.10	6	t
								1.90	4	m
						4.38	4	t		
						4.80	4	s		
Benzene: ethyl acetate (95:5)	Benzene: ethyl acetate (95:5)	(V) 168°C	Found C <sub>34</sub> H <sub>34</sub> O <sub>12</sub> requires	64.40	5.38	—CH stretching at 2920-2960 cm <sup>-1</sup> ester carbonyl at 1725 cm <sup>-1</sup>	p-C <sub>6</sub> H <sub>4</sub> — at	8.15	12	s
				64.35	5.36			1.10	6	t
								1.90	4	m
						4.35	4	t		
						4.80	8	s		

TABLE II  
Data for the Products Isolated after Degradation of Polyester Waste with Aromatic Alcohol (i.e., Benzyl Alcohol)

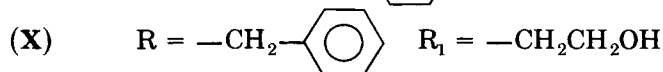
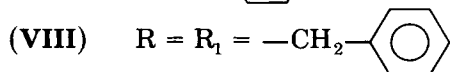
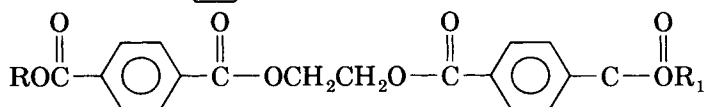
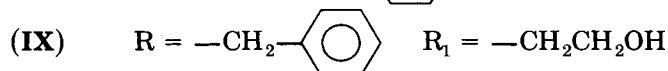
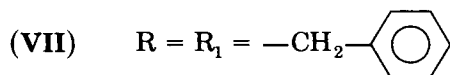
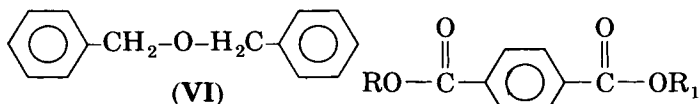
Elution of Column with Solvent System	m.p./b.p. of Products	Elemental Analysis			Spectral Data				Mass ( $M^+$ ) m/e
		Found	Calcd. for	C%	H%	IR Peaks	<sup>1</sup> H NMR		
							Functional Group and Peak Position $\delta$	Number of Protons	
Petroleum ether (b.p. range 60–80°C) 100%	(VI) b.p. 298°C (lit. b.p. 298°C)	Found : 84.91 Calcd. for $C_{14}H_{14}O$ : 84.84	7.10 7.07						
Pet. ether: benzene (90 : 10)	(VII) m.p. 91°C	Found : 76.37 $C_{22}H_{18}O_4$ requires : 76.30	5.23 5.20		—CH stretching at 2920–3060 $cm^{-1}$ ester carbonyl at 1720 $cm^{-1}$	$p-C_6H_4$ at 8.20 $C_6H_5$ at 7.47 $C_6H_5-CH_2O$ at 5.40	4 10 4	s m s	346
Benzene (100%)	(VIII) m.p. 150°C	Found : 71.41 $C_{32}H_{26}O_6$ requires : 71.37	4.85 4.83		—CH stretching at 2920–2960 $cm^{-1}$ ester carbonyl at 1720 $cm^{-1}$	$p-C_6H_4$ at 8.20 $C_4H_4$ at 7.49 $C_6H_5-CH_2-O-$ at 5.40 $-OCH_2CH_2O$ at 4.70	8 10 4 4	s m s s	538
Benzene : ethyl acetate (95 : 5)	(IX) m.p. 65°C	Found : 68.08 $C_{17}H_{16}O_5$ requires : 68.00	5.37 5.33		—OH stretching at 3400 $cm^{-1}$ —CH stretching at 2980 $cm^{-1}$ ester carbonyl at 1720 $cm^{-1}$	$p-C_6H_4-$ at 8.20 $C_6H_5-$ at 7.36 $C_6H_5-CH_2O$ at 5.44 $HOH_2CCH_2O-$ at 4.42 $HOCH_2CH_2O$ at 3.88	4 5 2 2 2	s m s t q	300
Benzene : ethyl acetate (90 : 10)	(X) m.p. 140°C	Found : 65.93 $C_{27}H_{24}O_9$ requires : 65.89	4.89 4.88		—OH stretching at 3400 $cm^{-1}$ —CH stretching at 2910–2960 $cm^{-1}$ ester carbonyl at 1720 $cm^{-1}$	$p-C_6H_4-$ at 8.2 $C_6H_5-$ at 7.46 $C_6H_5-CH_2-O-$ at 5.42 $-OCH_2CH_2O-$ at 4.88 $HOCH_2CH_2O-$ at 4.42 $HOCH_2CH_2O-$ at 3.88	8 5 2 4 2 2	s m s s t q	492

### Degradation of Polyester Waste with an Aromatic Alcohol

The study was extended by reacting benzyl alcohol with polyester waste at high temperature (280°C) under pressure. From the degradation reaction five products were isolated on elution with the solvent systems (Table II).

The first product, b.p. 298°C, was identified as dibenzyl ether (VI) (lit.<sup>7</sup> b.p. 298°C). From the elemental analysis, IR, <sup>1</sup>H NMR, and mass spectra, the second and third products of melting points 98°C and 150°C, were found to be dibenzyl terephthalate (VII) and 1,2-bis-(benzyloxy-4'-carbenzoyloxy)ethylene (VIII), respectively. Further elution with benzene:ethyl acetate as solvent gave two more products, m.p. 65°C and 140°C.

Elemental analysis of both compounds did not tally with the expected esterified trimer and tetramer, but matched with the half-esterified product of the monomer and dimer, respectively. Therefore, the structures of these products, m.p. 65°C and 140°C, could be identified as 4-carb-2'-hydroxy ethoxy-1-benzyl benzoate (IX) and 1-[*p*-carb-(2'-hydroxy ethoxy)-benzoyloxy]-2-[(*p*-carbenzoyloxy-benzoyloxy)]ethylene (X), and were further confirmed on the basis of the IR, <sup>1</sup>H NMR,



and mass spectra (Table II). The <sup>1</sup>H NMR of the compounds (IX) and (X) did not show prominent peaks for the terminal —OH. However IR showed a distinct —OH peak at 3400 cm<sup>-1</sup>, and the mass spectrum had recorded first split-up of 18 units which proved the presence of terminal —OH groups in the compounds (IX) and (X). The <sup>1</sup> NMR of the compounds displayed triplets for —OCH<sub>2</sub>CH<sub>2</sub>OH along with a peak at δ 4.41, which may be due to the terminal —OH group. Formation of transesterified and partially transesterified products of both monomer and dimer in the case of the benzyl alcohol reaction may be attributed to the bulky nature of the benzyl group.

### CONCLUSION

The study revealed that the degradation of polyester waste with aliphatic alcohol results in the formation of compounds (I–V, Table I) having identical groups at both the ends, while in the case of benzyl alcohol the reaction

products had both identical (VII and VIII) and different (IX and X) end groups.

### References

1. S. N. Tong, D. S. Chen, C. C. Chen, and L. Z. Chang (Union Industrial Research Laboratories, Industrial Technology Research Institute, Hsinchu, Tiwan ROC), *Polymer*, **24**, 469-472 (1983).
2. Eto, Zusitebe (Toboyo Co. Ltd), Japan Kokai, 7882 028 (cl CO7C BO15), Jul. 3, 1975, Appl. 73, 131, 428, Nov. 21, 1973, 4 pp.
3. Padampat Research Centre, Indian 147,511 (cl CO7C69/820) March 22, 1980, Appl. 78/DE 337, May 8, 1978, 11 pp.
4. K. Yukitaka, Yomadora (Toboyo Co. Ltd.), Japan Kokai, 73,68,537 (cl 16 C61), Sep. 18, 1973, 71, 104, 793, Dec. 22, 1971, 4 pp.
5. K. T. Barkly, E. B. Lefferts, and D. C. May, U.S. Patent 3,488,298. January 6, 1970 assigned to Eastman Kodak Co.
6. *Dictionary of Organic Compounds*, Vol. 1, 5th ed., Chapman and Hall, London, p. 533.
7. Aldrich Chemical Co., *The Aldrich Library of Infrared Spectrum 567E*, 2nd ed., 1975.

Received January 7, 1987

Accepted August 24, 1987