Polyester Chain Scission by Selective Chemical Site Attack*

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Synopsis

Tribenzylamine moieties copolymerized into poly(ethylene terephthalate) (PET) are selectively cleaved by mild hypochlorous acid oxidation to give dibenzylamines plus aldehyde and/or carboxyl groups. When either 3,3'-dicarboxytribenzylamine (DCTBA) or 4,4'-DCTBA were used, molecular weight was reduced, consistent with a mechanism where only two of the three carbon–nitrogen bonds which cleave can give polyester backbone scission. When copolymerized 3,5-DCTBA was cleaved, no chain scission resulted, but about one-third of the nitrogen content was lost, again consistent with the random statistical oxidative attack at each of the three carbon—nitrogen bonds. Borane ester, $B[(CH_2)_{10}CO_2Me]_3$, copolymerized into PET, lost molecular weight progressively after melt spinning, drawing, and boil off of the resulting fibers. Chain scission resulted from rapid oxidation of borane bonds to borate esters followed by hydrolytic cleavage to boric acid and/or intermediate boronic acids.

INTRODUCTION

Scission of polymers is usually an undesirable effect resulting from chain degradation chemistry during processing and during end use performance. Under some circumstances, controlled scission may be desirable to unmask chemical groups, such as dye sites, to generate functional or reactive end groups, and to facilitate environmental degradation. In the case of polyester, controlled chain scission has been used to deliberately weaken fibers and promote wearoff of "pills" which otherwise detract from the appearance of garments. Copolymerized silicate[1] and borate[2,3] esters in polyester cleave by hydrolysis to control pilling propensity. This article reports on two other sites which cleave chemically in a clean and selective manner to give controlled and predictable molecular weight products.

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The Tribenzylamine System

Tribenzylamines with carboxyl or ester handles were prepared using scheme 1:
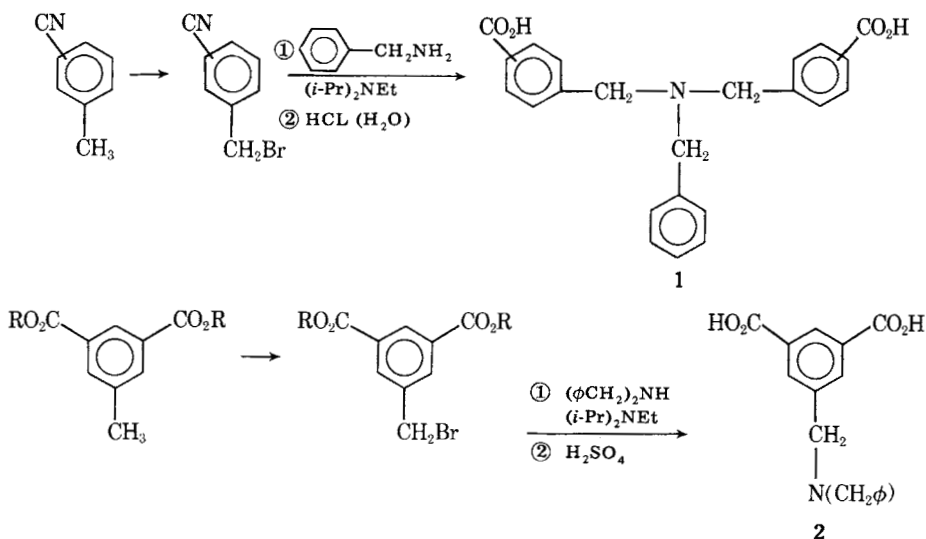
Scheme 1
Preparative Routes to Dicarboxytribenzylamins (DCTBA)

Copolymerization into poly(ethylene terephthalate) (PET) was effected by addition of 1 or 2 to either dihydroxyethyl terephthalate or to PET prepolymer prior to vacuum polymerization. Terpolymer compositions were also made by adding adipic acid along with 1 or 2. Polymer was spun to fiber, drawn, crystallized, and aftertreated to effect chain scission. Although a number of oxidizing agents are known to cleave tribenzylamine,[4-8] the mild conditions found with hypochlorous acid (NaOCl/pH 5.0; 80°C/1 hr) minimized hydrolytic and oxidative side reactions.[9]

Borane Esters

Hydroboration of methyl-11-undecylenate gave $tris$(10-carbomethoxydecyl)borane, 3, which was added to dimethyl terephthalate and ethylene glycol through ester exchange and polymerization. The concentration of 3 was kept low (≤0.5 mole %) to avoid excessive crosslinking because of its trifunctional character.

$$BH_3 + CH_2{=}CH - (CH_2)_8 - CO_2Me \longrightarrow B[(CH_2)_{10}CO_2Me]_3$$
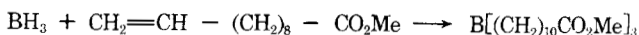
3

Tris(10-Carbomethoxydecyl)Borane

EXPERIMENTAL

Materials

3,3'-Dicarboxytribenzylamine (3,3'-DCTBA)

m-Bromomethylbenzonitrile, 78.4 g (0.40 mole), 21.44 g of benzylamine (0.20 mole), and 51.72 g of diisopropylethylamine in methylene chloride were stirred and refluxed overnight. After washing three times with 100-ml portions of water, methylene chloride was removed under vacuum and the product stirred and refluxed overnight with 400 ml of concentrated hydrochloric acid. The hydrolysis was exothermic at first and had to be cooled several times. Product was filtered, dissolved in $2\overline{M}$ sodium hydroxide, and the solution saturated with salt. The insoluble sodium salt was dissolved in 200 ml of water and 200 ml of methanol, and acidified hot with 50 ml of acetic acid to yield 20.3 g of solid, mp 178–180°C. It was recrystallized from xylene–acetic acid to give a mp of 180–182°.

4,4'-Dicarboxytribenzylamine (4,4'-DCTBA)

The 4,4'-isomer was prepared by a cognate procedure from 4-carbomethoxybenzylbromide and benzylamine using diisopropylethylamine as acid acceptor. Saponification in KOH and acidification to pH 6.5 gave the diacid, mp 210°C.

3,5-Dicarboxytribenzylamine (3,5-DCTBA)

This isomer was prepared by reaction of dimethyl-5-bromomethylisophthalate with dibenzylamine. The diacid melted at 277–279°C after dissolution in dimethylformamide and precipitation into methanol.

Polymerization Method

From Dihydroxyethylterephthalate (DHET)

A 500-ml, three-necked round-bottom flask was fitted with a capillary inlet tube (nitrogen bleed), a glass Trubore stirring rod and 304 stainless-steel stirring blade, and a distilling head attached to a vacuum system. This flask was charged with 123.0 g of DHET (recrystallized from water; 0.485 mole); 5.6-g 4,4'-dicarboxytribenzylamine; 0.015 mole) and 20 ml ethylene glycol containing 0.040-g antimony oxide. The mixture was immersed in Wood's metal bath at 245°C while nitrogen gas was passed through the flask. The bath temperature was gradually raised to 275°C over a 30-min period with stirring, while the vacuum was incrementally increased in 5-lb intervals from a 5- to 30-lb gauge with nitrogen bleed. Ethylene glycol and some unreacted DHET were collected through the distilling head. Polymerization was continued at 275°C and at full vacuum (0.1–0.2 mm) for an additional 60 min, and was discontinued when the stirrer twisted from the shaft. The molten polymer acquired a pale yellow color at this stage. Vacuum was discontinued with nitrogen bleed over the polymer melt pool, and the stirrer was raised to drain the molten polymer. The heating bath was

lowered, and the glass pot was quenched in powdered dry ice. The polymer plug surface was ground to remove residual glass and ground up in a Wiley mill.

From Prepolymer

Polyethylene terephthalate prepolymer [intrinsic viscosity 0.25 (Table I); 300-ppm Sb; carboxyl titer 1.2 equiv/10^6 g; DTA mp 248°C] was cast, ground to pellet form, and vacuum dried. Into an apparatus as described previously was charged 100.4 g of PET prepolymer (0.49 mole assuming an average oligomer weight of 205) and 3.75 g of 3,3'-DCTBA (0.01 mole). The ingredients were melted with stirring under nitrogen atmosphere at a Wood's metal bath temperature of 275°C. After 10 min heating, the vacuum was incrementally increased from a 5- to 30-lb gauge over 10 min. The mixture was polymerized under full vacuum (0.12–0.16-torr) and at 275°C with stirring for an additional 90 min. Polymer melt subjective visual color was good. The vacuum cycle was discontinued and the polymer was recovered as described.

Via Ester Exchange and Polymerization

The procedure used was described in detail by S. B. Maerov.[10]

HOCl Treatment

The fiber treatment procedure is described by E. F. Evans.[9]

RESULTS AND DISCUSSION

The Tribenzylamine System

Table I summarizes analytical results on fibers following a standard HOCl oxidation and acid bisulfite antichlor treatment.[9] Chain scission, measured by the drop in intrinsic viscosity, [n], resulted in the 3,3'- and 4,4'-dicarboxytribenzylamine (DCTBA) isomers. No drop in molecular weight resulted with 3,5-DCTBA compositions until very high molar ratios of HOCl/amine (>9) were reached. Virtually no loss of nitrogen content occurred with the 3,3'- and 4,4'-isomers, although losses approaching 30% resulted from treatment of 3,5-DCTBA. Classical oxidation studies of tribenzylamine[4] reported products that are mixtures of benzaldehyde, benzoic acid, and dibenzylamine. Indeed, benzaldehyde was easily detected by odor from the HOCl oxidation step and was proved by derivative formation. Further oxidation of aldehyde end groups to carboxyls resulted, especially when HOCl:amine ratios >2 were used. Oxidized and antichlored fibers contained significant amounts of chlorine and small amounts of sulfur. Presence of these elements in the fibers resulted from formation of the hydrochloride and sulfuric acid salts of the generated secondary amine during the course of oxidation and antichlor treatments, respectively.

For the 3,3'- and 4,4'-isomers, backbone chain scission will result when two out of the three carbon—nitrogen bonds, which are part of the chain, cleave. If every oxidation results in backbone cleavage, the number of new chains/10^6 g:

$$C_{ox} = C_I \cdot (f + 1)$$

TABLE I
Analysis of HOCl-Treated Fibers

Code	Isomer	Polymer composition	Mole HOCl:amine	$[\eta]^a$ Initial	$[\eta]^a$ Final	Δ^b COOH	% N	% Cl	% S
47 Control	4,4'-	2GT/DCTBA(98/2)	—	0.68		(37)	0.145	<.001	<0.001
47-1			0.9		0.57	4	0.13	—	—
53-4			1.9		0.47	3	0.14	0.15	0.01
47-2			2.8		0.48	17	0.16	0.14	—
53-6			3.7		0.415	5	0.14	0.242	0.01
45-9	4,4'-	2GT/DCTBA(96/4)	—	0.64		(74)	0.30	<0.001	<0.001
45-4			0.95		0.39	19	0.31	0.148	0.04
47-6			1.4		0.37	0	0.28	0.22	—
50-1			1.4		0.35	0	0.26	0.167	0.04
50-3			1.9		0.35	9	0.27	0.168	0.07
45-6			2.4		0.333	35	0.29	0.317	0.001
30-6				0.48		(62)	0.28	—	—
30-2			2.4		0.32	43	0.27	0.147	—
30-3			4.8		0.27	59	0.27	0.26	—
264 C	3,3'-	2GT/DCTBA/6(93/2/5)	—	0.58		(9)	0.15	—	—
246			3.72		0.39	86	0.15	0.18	—
266 C		(91/2/7)	—	0.64		(10)	0.16	—	—
248			3.7		0.38	87	0.14	0.16	—
262		(97/3)	3.7	0.71		(25)	0.22	—	—
250			3.8		0.41	98	0.21	0.206	—
267		92/3/5	—	0.59		(10)	0.20	—	—
251			3.7		0.33	109	0.20	0.231	—
328	3,5-	2GT/DCTBA/6(92/2/6)		0.58		(13)	0.14	—	—
328-2			3.7		0.59	67	0.12	0.219	0.06
328-5			9.2		0.59	87	0.11	0.178	0.14
328-10			18.5		0.55	106	0.10	0.131	0.21
382-15			27.8		0.54	103	0.10	0.156	0.20

a Intrinsic viscosity, $[\eta]$ in trifluoro acetic acid/methylene chloride 25/75, v/v.
b Numbers in brackets are the initial carboxyl titer in equiv/10^6 g.

where C_I is the initial chains/10^6 g from the relation[11] developed for poly(ethylene terephthalate): $[n] = 0.032\,N^{0.682}$, where N is the number average degree of polymerization, and f is the initial frequency factor of amine sites per chain. If random, statistical scission results, the number of new chains

$$C_{ox} = C_I + C_I \cdot f \cdot P$$

where P is the probability factor $\frac{2}{3}$ for the dicarboxytribenzylamines and

$$P = (C_{ox} - C_I)/C_I \cdot f$$

Calculation of P values from the data in Table I are shown in Table II. Probability factors approached the expected two-thirds value especially at higher molar ratios of HOCl/amine. Two factors may be responsible for P values failing to reach 0.67: (1) the relationship between intrinsic viscosity and $\overline{DP}$ derived for PET will certainly be different for the copolymers and especially for the terpolymer compositions where up to 9 mole % modification was used; (2) the extent of molecular weight degradation will depend on the location of the amine site in the chain. Sites at or near chain ends cleave without significantly lowering the number average molecular weight. The probability for amine sites to reside at chain ends: (0.04 at 2 mole %; 0.08 at 4 mole %, . . .) must be subtracted from 0.67 to correct for the chain position effect. When this adjustment is made to the P factor of Table II, results become more consistent with expected probability factors.

Borane Copolymer

Melt polymerization of $B[(CH_2)_{10}CO_2Me]_3$ copolymerized into PET (scheme 2) was carried to a melt viscosity as close as possible to that of unmodified control.
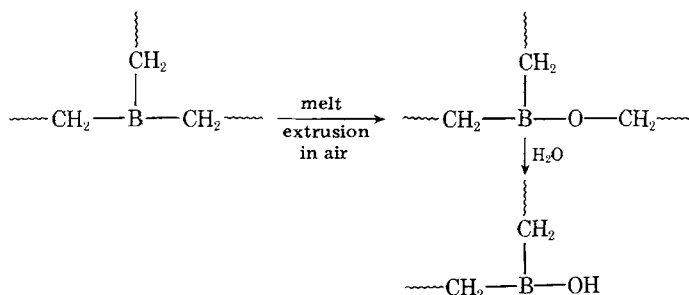
Scheme 2
Chain Scission with Boranes

Copolyesters were stable in the melt in the absence of oxygen. However, after extrusion and flaking, the molecular weights of the polymers were lower than expected even though chain branching would be expected to affect the measured intrinsic viscosity (Table III). This indicated that some oxidation and hydrolysis had occurred in the bulk polymer resulting in chain scission. A further drop in molecular weight occurred sequentially after melt spinning and after drawing plus boil off of the resulting fibers. These results confirm that oxidation of boranes to borate esters is a rapid process whose rate is probably governed by the diffusion rate of oxygen into the polymer. This reaction will be very fast with

TABLE II
Probability Factor for HOCl Chain Scission

DCTBA isomer	Code	Polymer composition	Amine frequency, f, chain	Mole HOCl:amine	Initial chains, C_I	Oxidized chains, C_{ox}	Probability factor, P
4,4'-	47C	2GT/DCTBA(98/2)	1.74		59		
	47–1			0.9		76	0.17
	53–4			1.9		100	0.40
	53–6			2.8		120	0.59
4,4'-	45–9	2GT/DCTBA(96/4)	3.11		64		
	45–4			0.95		132	0.34
	45–6			2.4		166	0.51
4,4'-	30–6	2GT/DCTBA(96/4)	2.01		99		
	30–2			2.4		172	0.37
	30–3			4.8		214	0.58
3,3'-	264C	2GT/DCTBA/6(93/2/5)	1.38		74		
	246			3.7		133	0.58
	266	(91/2/7)	1.59		65		
	248			3.7		139	0.71
	262	(97/3)	2.77		55		
	250			3.7		122	0.44
	267	(92/3/5)	2.12		71		
	251			3.7		170	0.65
3,5-	328	2GT/DCTBA/6(92/2/6)	1.44		71		0
	328–10			18.5		80	0.09
	382–15			27.8		83	0.12

TABLE III
Copolymerized B[(CH$_2$)$_{10}$CO$_2$Me]$_3$ in PET

Code	Description	Flake	$[\eta]$ free fall yarn	$[\eta]$ drawn boil off yarn	Physical properties		
					drawn ten	yarn % elong.	modulus
PA–84	PET control	0.66	0.61	0.61	4.9	27	116
53A	0.25 mole % borane	0.59	0.43	—	—	—	—
53B	0.50 mole % borane	0.575	0.49	0.37	3.4	21	119

melt-spun yarn at spinning temperatures and also because of the high ratio of surface area to polymer weight. Hydrolysis of the resulting borate esters offers an easily controlled route to chain scission of the polyester backbone chains.

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