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Synthesis, Characterization and Polycondensation of Bis-(4-Hydroxybutyl) Terephthalate

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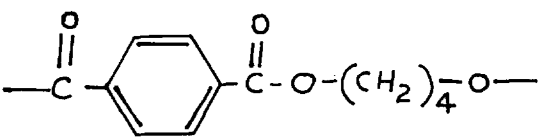
Summary

Monomeric Bis-(4-hydroxybutyl) terephthalate has been synthesized and characterized. Titanium iso-propoxide has been found to be a superior catalyst for transesterification compared to metal acetates. Further polycondensation of Bis(HBT) yields poly(1,4-butylene terephthalate). The effect of various titanium derived catalysts on the polycondensation of Bis(HBT) has been studied. The catalytic efficiency of these derivatives is ascribed to their relative hydrolytic stability and the degree of interaction between the carbonyl oxygen and the metal.

Introduction

Poly(1,4-butyleneterephthalate) (PBT) has gained increasing commercial importance as a valuable engineering thermoplastic material. PBT is prepared by transesterification - polycondensation of dimethyl terephthalate with 1,4-butanediol. The polymer chain consists of a mixed aliphatic - aromatic structure.



Since we wished to undertake a systematic study of the polycondensation reaction, it was felt desirable to prepare bis-(4-hydroxybutyl) terephthalate (Bis-HBT) in its pure monomeric form. It is well known that for polycondensation, the stoichiometries of ester to diol is very critical for achieving the desired degree of polymerization. Apart from reasons such as insufficient weighing or loss due to volatilization during reaction,

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the formation of terahydrofuran as a byproduct during transesterification could lead to an imbalance of molecular proportion of the monomers. Use of Bis (HBT) as a monomer for polycondensation could circumvent this problem. The use of Bis-(2-hydroxyethyl) terephthalate (Bis-HET) as a monomer for PET preparation is well known (LUDEWIG, 1971).

In this paper we report the synthesis and characterization of Bis(HBT) in its pure monomeric form and its polycondensation using variety of titanium derived catalysts.

Experimental

Materials

DMT (m.p. 141°C) was a commercial fiber grade product and was used as received.[1,4] Butanediol (Riedel, W. Germany) was dried to less than 0.1% moisture by passing it over activated molecular sieves 4 A. The acid number of diol was 0.14 mg KOH/g diol. Titanium isopropoxide (b.p. 90-92°C/3 mm Hg) was prepared as per procedures previously reported. (BRADLEY et.al. 1952). Tetraphenoxy titanium, titanium diisopropoxy diacetate and triethanol amine chelate were prepared from titanium isopropoxide as per literature procedures (BRADLEY et.al. 1978).

Analysis

GC analysis was performed on a Perkin-Elmer 900 using a 2 meter porapak Q column, 70-180° at 8° min, N_2 flow of 28 ml/min on TCD detector. Melting point was recorded using a DuPont Model 910 Differential Scanning Calorimeter. IR spectra was recorded on a Beckman Model 4220 spectrometer and NMR on JEOL JNM-FX 100 instrument. Elemental analysis was done on Coleman Model 33 instrument. The intrinsic viscosity was determined using an Ubbelhode Viscometer at 25°C using a 60:40 (W/W) mixture of phenol and tetrachloroethane. Acidity in polyester was determined titrimetrically (POHL 1954).

Preparation of Bis(HBT)

Transesterification of DMT (0.7 mole) with 1,4-butanediol (4.2 mole) in presence of 0.1% by Wt. (on DMT) titanium isopropoxide was performed in a three-necked round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a graduated measuring cylinder used as a receiver and connected through a distillation column. The column was heated to 60-80° to facilitate distillation of methanol. N_2 was continuously bubbled at 40 ml/min through the melt to further aid distillation. The reaction was monitored by quantitatively analyzing the distillates for methanol and terminated when the theoretical amount of methanol was collected. The product was washed with water, filtered, dried (at 50°C at 10 mm Hg for 8 hr). The crude product so obtained was triturated with ether to remove last traces of adhering diol. Additional product could be recovered upon chilling the aqueous filtrate. The product, obtained in quantitative yield had a m.p. 76-76.5°C.

Results and discussion

The product showed IR absorption at 1715 cm^{-1} (C=O), 1050 cm^{-1}(C-OH) and 1280 cm^{-1} (C-O ester). Its NMR spectrum taken in $CDCl_3$ solution (0.5 M) showed (δ) a multiplet at 1.8 ($-(CH_2)_2$-4H), singlet at 2.96 (OH,1H), triplet at 3.70 ($-C\underline{H}_2$-OH,2H), triplet at 4.36 ($C\underline{H}_2$-O-C(=O)-,2H), and singlet at 8.06 (aromatic, 4H). The elemental analysis was in conformity with the empirical formula $C_{16}H_{22}O_6$ (% found C 61.9, H 7.0; % calcd, C 61.9, H 7.1). The Bis (HBT) was found to be soluble in chloroform, methanol and excess hot water and sparingly soluble in methylene chloride (60% by wt.), benzene (30%), carbon tetrachloride (20%) and ether (5%).

The performance of various catalysts were tested both for transesterification of DMT and 1,4-butanediol and for the polycondensation of Bis(HBT). Although a number of claims regarding the utility of a variety of catalysts for the manufacture of PBT exists in the patent literature, no systematic study of their relative performance under controlled conditions has been reported so far.

Transesterification was conducted at 220°C for 1 hr in presence of 0.1 wt.% catalyst based on DMT with a steady stream of nitrogen to aid distillation of methanol. The distillates were analyzed by GC. The results are summarized in Table 1. Results indicate that a conventional transesterification catalyst such as calcium acetate performs poorly in the present case leading to poorest rates of reactions and larger amount of THF formation. As a class, the titanium derivatives appear to be superior transesterification catalysts, the best results being obtained with titanium isopropoxide. In general, it was observed that increased reaction time, higher temperatures and larger stoichiometric excess of 1,4-butanediol led to an increase in THF by product formation.

T A B L E - 1

EFFECT OF CATALYSTS ON TRANSESTERIFICATION OF DMT WITH 1,4-BUTANEDIOL[a]

CATALYST	Products, g[b]			MeOH % theory	THF mole%[c]
	Bis(HBT)+1,4-BD	MeOH	THF		
TITANIUM ISOPROPOXIDE	16.20	3.27	0.33	99	4.1
TITANIUM PHENOXIDE	16.20	2.95	0.31	89	3.8
TITANIUM DIISOPROPOXY DIACETATE	15.97	2.81	0.35	85	4.2
TRIETHANOL AMINE CHELATE	16.20	2.68	0.34	81	4.3
CALCIUM ACETATE	16.00	2.37	0.59	72	7.2

[a] DMT 10.0 g(0.0515 moles), 1,4-butanediol 10.2g (0.113 moles), catalyst 0.1% by wt. of DMT, temperature 220^{o}C, Time: 1 hr; [b] In all cases material balance was greater than 95%; [c] Based on 1,4-butanediol.

TABLE 2

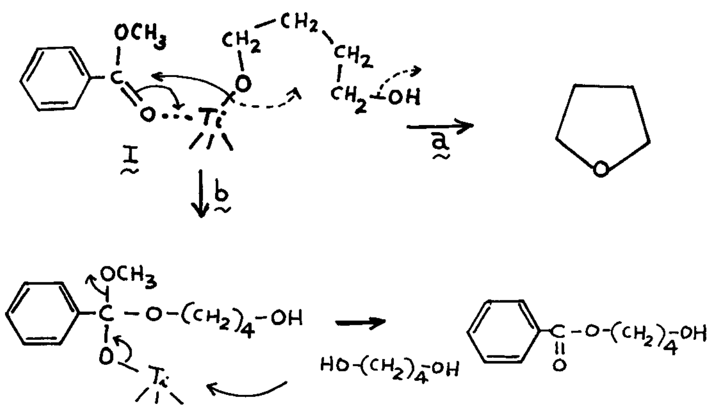
EFFECT OF CATALYSTS ON POLYCONDENSATION OF BIS(HBT)[a]

Catalyst	Tm, °C	$[\eta]$, $dl.g^{-1}$ [b]	Acidity, CO_2H equiv. per 10^6 gms.
TITANIUM ISOPROPOXIDE	225.1	0.53	38
TITANIUM PHENOXIDE	223.6	0.55	38
TITANIUM DIISOPROPOXY DIACETATE	224.6	0.52	47.5
TRIETHANOLAMINE CHELATE	222.6	0.56	57
ANTIMONY TRIOXIDE	223.6	0.54	57

[a] Bis(HBT), 10g (0.032 moles), catalyst 0.1 % by wt. of DMT, temperature 250°C/0.5 mm of Hg, Time : ½ hr; [b] in 60:40 phenol-tetrachloroethane at 25°C.

The polycondensation of Bis(HBT) was conducted at 250°C for 0.5 hr and at 0.5 mm of Hg vacuum with 0.1% of above catalysts. In addition, antimony trioxide was also studied for comparison. The results are summarized in Table 2. The catalysts studied showed no difference with respect to the molecular weight attained or the degree of crystallinity as evidenced by the almost similar values of intrinsic viscosity and Tm. However, polyester acidity, which is indicative of undesirable degradation reactions showed a dependence on the nature of catalyst.

The discussion of above results is limited by the fact that little is known at the fundamental level regarding the mode of action of catalysts in transesterification and polycondensation reactions. It has been recognized that factors such as electronegativity and acidity of the metal can play an important role in determining catalytic activity (GOODMAN, 1969). Additional factors such as metal-oxygen bond energy, melting point, decomposition temperature and electronic structure of the metal can also be important. In line with the mechanistic proposals made for transesterification of DMT and ethylene glycol using Zn(II),Mn(II), Co(II) and Sb(III) catalysts (YODA et.al.1964), it is reasonable to assume as a first step in transesterification of DMT and 1,4-butane diol, the formation of an intermediate complex I which can then undergo two competing reactions, one leading to THF formation (path a) and the other leading to transesterification (path b). Path b is likely to be favoured when the



degree of interaction between the carbonyl oxygen and the vacant d orbital of the titanium is larger. The amount of THF formed increases and the extent of transesterification decreases regularly when the catalyst is changed from titanium isopropoxide to phenoxide to diisopropoxy diacetoxy titanium and finally to triethanolamine chelate. Interestingly, this is also the order of increasing hydrolytic stability of the titanium compounds studied (STANLEY 1969). Persumably ease of hydrolysis is also related to the ability of oxygen in water to coordinate with the titanium. By analogy, the degree of interaction of carbonyl oxygen with titanium can be expected to parallel the hydrolytic stability of titanium compounds studied. Relative to titanium, Ca(II) would be expected to enter less readily into coordination with oxygen, in view of its electronic structure, resulting in favouring of path a.

The reasons for the dependence of polyester acidity on catalyst type is not readily apparent. The degradation of polyester is believed to occur via an ester pyrolysis step (GRASSIE 1956; TOMITA 1973; LUM 1979). PBT is also known to be especially sensitive to moisture induced thermal degradation which requires careful drying of PBT prior to molding to minimize melt instability (AVERY 1978; KADYKOWSKI 1977). The superiority of titanium isopropoxide and titanium phenoxide in minimizing acid producing degradation reactions could be therefore ascribed to their ability to react with water with greater ease compared to the other derivatives thereby reducing moisture levels in the reaction medium.

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