

STUDIES OF ACTIVE DIACYLAMIDES OF BENZOTRIAZOLE

I. SYNTHESIS OF POLYAMIDES AND POLYESTERS*

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ABSTRACT

Two new routes to polyamides and polyesters were established, based on the polycondensation of new typical active diacylamide of benzotriazole, such as 1,1'-(isophthaloyl)bisbenzotriazole (IPBBT) and 1,1'-(terephthaloyl)bisbenzotriazole (PBBT) with diamines, diols and diphenol under different mild conditions. The N-acylation of polycondensation occurred at room temperature without added catalyst, the O-acylation of polycondensation had to complete in the presence of triethylamine as a catalyst at 60°C.

INTRODUCTION

The utilization of a number of active dicarboxylic acid derivatives such as esters^[1] and acylamides^[2] which are useful intermediates for the preparation of polyamides has received considerable attention. In this field we have reported the synthesis of polyamides from active O,O'-diacyl derivatives of N-hydroxy compounds such as N,N'-(isophthaloyldioxy) bis (5-norbornene-2,3-dicarboximide), N,N'-(terephthaloyldioxy)bis(5-norbornene-2,3-dicarboximide) and 3,3'-(isophthaloyldioxy) bis (4-oxo-3,4-dihydro-1,2,3-benzotriazine) with diamines under mild conditions and have demonstrated that the active esters of N-hydroxy-5-norbornene-2,3-dicarboximide (HONB) is selectively aminolyzed to aliphatic amines^[3]. More recently, we found the active esters of HONB and N-hydroxysuccinimide (HOSu) are preferable as selective N-acylation of aminoalcohols to give the corresponding N-acylaminoalcohols^[4]. Furthermore, they did not react satisfactorily with aromatic amines and alcohols via aminolysis and alcoholysis to form acylamides and esters.

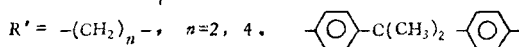
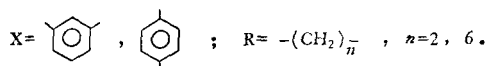
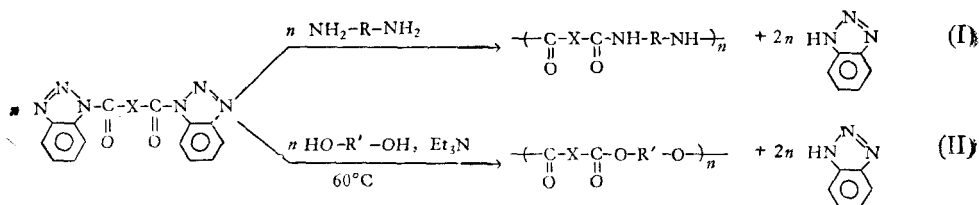
As an extension of our synthetic program, we needed an easily obtainable active diester or diacylamide for the synthesis of bioactive polymers, the active group not only has the ability of aminolysis and alcoholysis with amines and alcohols but also has selective N-acylation with aminoalcohols.

It is known that the benzotriazolides of simple carboxylic acid may react quantitatively with alcohols or amines to give esters and amides under mild conditions^[5]. Ferruti et al. examined the aminolysis and alcoholysis of poly-1-acryloylbenzotriazole with amines and alcohols to give pure polyacrylamides and polyacrylic esters under mild conditions^[6]. Gu, Li and Feng investigated the grafting of aspirin onto polyvinyl-alcohol by the alcoholysis of 1-(acetylsalicylyl) benzotriazole with PVA^[7].

In this communication we briefly reported two successful syntheses of polyamide and

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polyester with a reasonably high molecular weight from diamines, diols or diphenol and the same new active diacylamides; the diacylamide of benzotriazole, such as 1,1'-(isophthaloyl) bisbenzotriazole (IPBBT) and 1,1'-(terephthaloyl)bisbenzotriazole (PBBT) under mild conditions (See eqs. I and II).

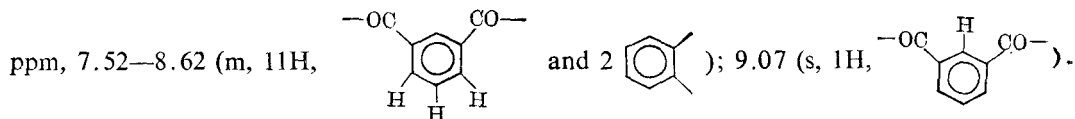


EXPERIMENTAL

Monomers

(1) 1,1'-(Isophthaloyl)bisbenzotriazole (IPBBT)

To a stirred solution of benzotriazole (21.1 g, 177 mmole) and triethylamine (25 ml, 177 mmole) in 100 ml of anhydrous tetrahydrofuran (THF) was dropped a solution of isophthaloyl chloride (18.0 g, 88.7 mmole) in 80 ml of THF at 0–5°C for 1 h. The mixture was stirred at room temperature for 3 h, then the product was isolated by pouring the reaction mixture into 600 ml of water. The yield was 29 g (90%). It was recrystallized from THF to produce white powdery crystals, mp 199–201°C. IR (KBr): 1700 cm⁻¹ (C=O in CONR). NMR (CDCl₃);

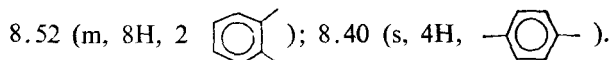


Anal. Calcd for C₂₀H₁₂N₆O₂: C, 65.22%; H, 3.26%; N, 22.83%.

Found: C, 65.21%; H, 3.38%; N, 22.85%.

(2) 1,1'-(Terephthaloyl)bisbenzotriazole (PBBT)

PBBT monomer was prepared from terephthaloyl chloride, benzotriazole, triethylamine and THF, the product was recrystallized from THF with mp 238–242°C (decomp.). The yield was 94%. IR (KBr): 1700cm⁻¹ (C=O in —CONR). NMR (DMSO-d₆), ppm, 7.74–



Anal. Calcd. for C₂₀H₁₂N₆O₂: C, 65.22%; H, 3.26%; N, 22.83%.

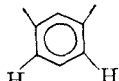
Found: C, 65.28%; H, 3.26%; N, 22.75%.

Polymerization

Two examples of the polycondensation are as follows:

(1) Polyamide from IPBBT and hexamethylenediamine (HMDA)

To a solution of 0.9208 g (2.5 mmole) of IPBBT in 40 ml of NMP was added 0.2901 g (2.5 mmole) of HMDA. The mixture was stirred at room temperature for 48 h, then poured into 600 ml of water. The product was collected, washed thoroughly with hot water and dried. The yield was 0.563 g (92%). Inherent viscosity of the polymer in concentrated sulfuric acid was 0.33, measured at a concentration of 0.5 g/dl at 30°C. IR(KBr); 3300 (γ_{N-H}); 1630 and 1530 cm^{-1} (C=O, secondary —NHCOR—). NMR (DMSO- d_6): ppm, 1.40 (s, 4H, γ —CH₂—); 1.59 (s, 4H, β —CH₂—); 3.25 (s, 4H, α —CH₂—); 7.24 (Bs, 1H, ); 7.95

(Bs, 2H, ); 8.05–8.40 (Bs, 3H, —CONH— and ).

Anal. Calcd. for $(C_{14}H_{18}N_2O_2)_n$: C, 68.27%; H, 7.36%; N, 11.38%.

Found: C, 66.48%; H, 7.28%; N, 11.42%.

(2) Polyester from PBBT and ethylene glycol

To a solution of 1.473 g (4 mmole) of PBBT, 0.2483 g (4 mmole) of ethylene glycol in 40 ml of DMF was added 1.62 ml of triethylamine. The mixture was stirred at 60°C for 48 h and the polymer was precipitated out, then poured into 120 ml of methanol. The polymer was separated by filtration, washed with methanol on the filter, and dried under vacuum. The yield was 0.587 g (76.4%). Inherent viscosity of the polymer was 0.13, measured at concentration of 0.5 g/dl in phenol/tetrachloroethane (40/60 weight) at 30°C. The NMR spectrum was exactly superimposable on that of an authentic sample prepared by polycondensation of dimethyl terephthalate with ethylene glycol^[8].

RESULTS AND DISCUSSION

Before polymer synthesis a model compound was preferred to obtain information regarding the reactivity of 1-benzoylbenzotriazole (BBT) toward amines, alcohols or phenol. It was found that active monoacylamide with —COBT group of aminolysis is more reactive than the alcoholysis and phenolysis. For example, aminolysis of BBT with benzylamine was completed to give benzylbenzamide within 4 h at room temperature. In the case of alcoholysis and phenolysis of BBT with benzylalcohol and phenol, no reaction took place under the same condition, but both reactions could be completed in the presence of triethylamine at 60°C to give benzyl benzoate and phenyl benzoate within 4–5 h. Similarly, two model compounds 1,4-butanediol dibenzoate and p,p'-diphenylolpropane dibenzoate were obtained from the reactions of BBT with 1,4-butanediol and bisphenol A in good yield. Therefore they may be considered valuable tools in the synthesis of polyamides or polyesters.

Two novel active acylamides, the diacylamide of benzotriazole (HBT) such as IPBBT and PBBT were synthesized successfully by the reaction of the corresponding diacyl chlorides with HBT in THF at 0–5°C in the presence of triethylamine as an acid acceptor. The new

crystalline monomers had definite melting points and were easily purified from THF by recrystallization. They were freely soluble in many solvents, such as DMF, NMP and DMSO, but solubility of *m*-isomer is higher than *p*-isomer. On the other hand, the *m*-isomer is soluble and *p*-isomer is insoluble in chloroform. The structure of IPBBT and PBBT was determined by elemental analysis, IR and NMR spectroscopy as shown in experimental section.

Following the model reactions, at first, we examined the synthesis of polyamides using the active diacylamide-HBT method. The polycondensation of IPBBT or PBBT was carried out by the solution polymerization technique with diamines that included ethylenediamine (EDA) and HMDA. Dipolar aprotic solvents like DMSO, DMF and NMP were tested as polymerization media. The results of the polymerization are summarized in Table 1.

Table 1 Polycondensation of active diacylamides with diamines^{a)}

Diacylamides	Diamine	Solvent (ml)	Conditions		Polymer	
			Temperature (°C)	Time (day)	Yield (%)	$[\eta]$ inh ^{b)}
IPBBT	EDA	DMSO (30)	25	2	85	0.65
IPBBT	EDA	DMF (40)	25	2	90	0.33
IPBBT	HMDA	DMF (40)	25	2	85	0.17
IPBBT	HMDA	NMP (30)	25	2	92	0.33
PBBT	EDA	DMF (40)	25	2	93	0.20
PBBT	EDA	NMP (30)	25	2	94	0.20
PBBT	HMDA	DMF (40)	25	2	94	0.34
PBBT	HMDA	NMP (30)	25	2	98	0.30

a) Polymerization was carried out with 2.5 m mole of the reactants.

b) Measured at a concentration of 0.5 g/dl in concentrated sulfuric acid at 30°C.

It was found that the inherent viscosities of polyamides greatly influenced by the solvents. DMSO is a good one among these solvents the inherent viscosity of poly(ethyleneisophthalamide) can be reached up to 0.65 dl/g.

All polymers formed were identified as polyamides by elemental analysis, IR and NMR spectra. IR spectra of polyamides, synthesized by KBr method, no longer indicated carbonyl group in —COBT at 1700 cm^{-1} seen in IPBBT and PBBT monomer. All peaks due to heteroaromatic *o*-disubstituted phenyl group were not found, and a peak due to the —CONH— structure appeared in the NMR spectrum.

Next, we tried the active diacylamide-HBT method for the synthesis of polyesters. The polycondensation of IPBBT or PBBT was carried out in DMF and in the presence of triethylamine at 60°C with bisphenol or diols that included ethylene glycol (EGO), 1,4-butanediol (BDO) and bisphenol A. The results of polycondensation are given in Table 2.

From the results, it is clear that the yields of polymerization are satisfactory, above 80% except one case. The inherent viscosities of poly(4,4'-diphenylolpropane isophthalate) and poly(4,4'-diphenylolpropane terephthalate) are 0.20 and 0.24 dl/g, the others are in the 0.11 to 0.16 dl/g region.

Table 2 Polycondensation of active diacylamides with diols and bis-phenol A^a).

Diacylamides	Diols or bisphenols	Solvent (ml)	Conditions		Polymer	
			Temperature (°C)	Time (day)	Yield (%)	$[\eta]$ inh ^b
IPBBT	EGO	DMF (30)	60	2	50	0.15
IPBBT	BDO	DMF (30)	60	2	76	0.16
IPBBT	Bisphenol A	DMF (40)	60	2	83	0.20
PBBT	EGO	DMF (30)	60	2	77	0.13
PBBT	BDO	DMF (30)	60	2	78	0.11
PBBT	Bisphenol A	DMF (40)	60	2	85	0.24

a) Polymerization was carried out with 3 or 4 mmole of the reactants.

b) Measured at a concentration of 0.5 g/dl in phenol/tetrachloroethane (40/60 weight) at 30°C.

The polymers obtained were confirmed as polyesters by comparing their NMR spectra with those of the authentic polyesters. Elemental analysis of the polymers also supported the formation of polyesters.

All the results indicate that HBT-active diacylamides is needed in the synthesis of polyesters and polyamides under different mild condition, and studies in this direction are now under progress in our laboratories.

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