

A NEW ACTIVE DIESTER FOR SELECTIVE POLYMERIZATION TO FORM FUNCTIONAL POLYAMIDES.

Ji Aixue (季爱雪), LI Shigui (李世桂) and LU Chengxun (陆承勋)

(Department of Chemistry, Peking University)

ABSTRACT

A new synthetic route to polyamides and hydroxyl polyamides was established, based on the selecting N-acylation of three novel typical active diesters: the active diester of N-hydroxy-1,4-epoxy-5-cyclohexene-2,3-dicarboximide (HOEC), such as N,N'-(terephthaloyldioxy) bis(1,4-epoxy-5-cyclohexene-2,3-dicarboximide) (PBOEC), N,N'-(isophthaloyldioxy) bis(1,4-epoxy-5-cyclohexene-2,3-dicarboximide) (IPBOEC) and N,N'-(adipoyldioxy) bis(1,4-epoxy-5-cyclohexene-2,3-dicarboximide) (ADOEC) with aliphatic diamines and 1,3-diamino-2-hydroxypropane. The polycondensation occurs at room temperature in solution without added catalyst. Dipolar aprotic solvents which include dimethyl sulfoxide, N-methyl-2-pyrrolidone and dimethylformamide were used as solvents for polymerization. The selective N-acylation of two active diesters was performed as a model reaction study.

INTRODUCTION

A great deal of interest has been aroused recently by the ability to obtain a series of special polymers including hydroxyl polyamides^[1], poly(amide-ester)s with ordered structure^[2,3], polyamides and polyesters containing nucleic acid base derivatives as a pending side chains^[4-6], nucleic acid bases grafted amino and imino polyurethane^[7,8], copoly(vinylamine-vinylalcohol) containing two different kinds of nucleic acid base derivatives as grafted pendants^[9], and a pair of complementary adeninyl and thyminyl groups grafted copoly(vinylamine-vinylalcohol)^[10] using the selective N-acylation of active esters and O-acylation of active amides. Interestingly, by the use of active esters and amides of different kind, we found two active esters derived from N-hydroxy-5-norbornene-2,3-dicarboximide (HONB) and N-hydroxysuccimide (HOSu) and an active amide derived from benzotriazole (HBT) have the same ability of selective N-acylation to aliphatic amine and aminoalcohol and HBT-active amide has ability of selective O-acylation only in the presence of triethylamine at 60 °C^[11-14].

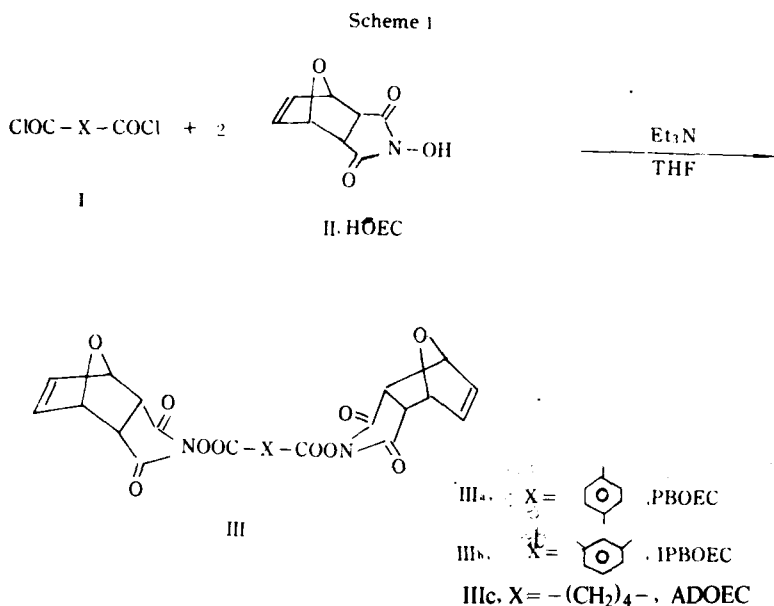
It was reported earlier by Narita et al.^[15] That N-hydroxy-1,4-epoxy-5-cyclohexene-2,3-dicarboximide (HOEC) was prepared by treatment of maleic anhydride adduct of furan with hydroxylamine in good yield in methanol. From the view of molecular structure, HOEC has the same structure as HONB in the key part except the top of bridge is an oxygen atom. It is easy to understand that HOEC will

possess the same reactivity as well as HONB as described before. On the other hand, maleic anhydride is quite easier in obtaining than cyclopentadiene, therefore HOEC is a more available reagent in the preparation, especially in laboratory.

Here we wish to report a novel approach to the polyamides and hydroxyl polyamides via the selective N-acylating polycondensation of active diesters—HOEC with diamines and aminoalcohol under mild conditions.

RESULTS AND DISCUSSION

Three novel polymer-forming monomers, such as IIIa, IIIb and IIIc, were prepared successfully from the reaction of the corresponding diacid chloride, such as Ia, Ib and Ic with II in THF at room temperature in the presence of triethylamine as an acid acceptor in good yield (See Scheme 1).



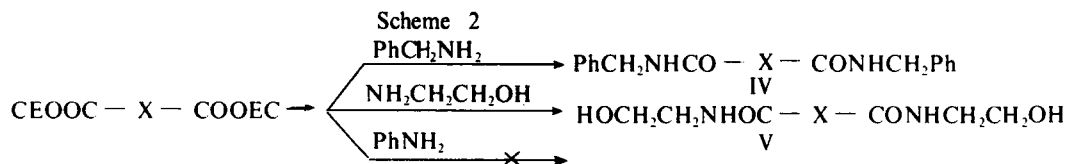
These new crystalline monomers have definite melting points and were easily purified by recrystallization. They are freely soluble in many solvents such as DMF, THF, DMSO and NMP but insoluble in hexane and petroleum ether and not sensitive to atmospheric moisture.

The structure of these monomers were determined by IR and proton NMR spectroscopy. The characteristic absorption of IR spectrum of III monomer was a band at 1780 cm^{-1} due to the carbonyl of imide group. The diactive ester—HOEC monomers have resonated peaks characteristic of disubstituted phenyl or alkyl group in their NMR spectra. The NMR spectrum of IIIa in which the four equivalent aromatic protons of para-disubstituted phenyl resonate at 8.34 ppm as a sharp singlet. In the

NMR spectrum of IIIb, a triplet at 8.06 ppm represents the resonance of , a doublet at 8.55 ppm represents the resonance of and a singlet at 8.68 ppm

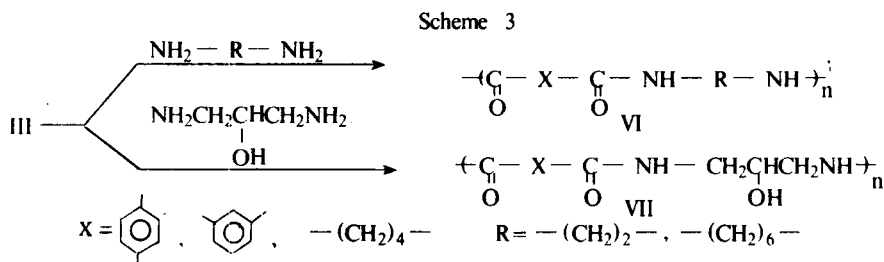
represents the resonance of . In the NMR spectrum of IIIc, a broad singlet for the protons of methylene bonded to ester carbonyl at 2.72 ppm, and a broad singlet at 1.74 ppm due to the protons of $-(CH_2)_2-$ groups. In addition, these have the same peaks characteristic of $-COOEC$ in their spectra; one singlet at 3.2 ppm due to $-CH-O-CH-$; one singlet at 6.6 ppm due to $-CH=CH-$ group, and one singlet at 5.3 ppm due to the protons of $-COCH-$ group. All integration indicated that these monomers were composed of two $-COOEC$ groups in each molecular structure. Elemental analysis of the monomers also supported the formation of diactive ester-HOEC.

Prior to polymer synthesis two monomers, IIIa and IIIb, were formed to obtain information regarding the reactivity of $-COOEC$ toward amines and aminoalcohol. As shown in Scheme 2, the active ester with $-COOEC$ group has the ability of selective N-acylation to aliphatic amine and aminoalcohol. For examples, aminolysis of IIIa and IIIb with benzylamine gave the corresponding IVa and IVb in high yield at room temperature without addition of catalyst, respectively. In the case of aniline with III no reaction took place under the same condition, on the other hand, treatment of IIIa and IIIb with aminoethanol in THF at room temperature produced the corresponding Va and Vb in good yield, respectively. It is clearly that active ester of HOEC has the ability of selective N-acylation to aminoalcohol and aliphatic amine as well as active ester of N-hydroxy-5-norbornene-2,3-dicarboximide (HONB) and N-hydroxysuccinimide (HOSu)^[11-13]. Therefore, the active ester of HOEC can be used as a new, hopeful active ester for the synthesis of polyamides and functionalized polymers including hydroxy polyamides, amino and imino polyurethanes.



The outstanding selectivity of active ester-HOEC for the amino group of the aminoalcohol and aliphatic amine indicate the mild leaving group of $-COOEC$ is less readily attacked by the hydroxy and aromatic amino groups than the aliphatic amino group because the former both are less nucleophilic than the latter.

The polycondensations of PBOEC, IPBOEC and ADOEC, were carried out by the solution polycondensation technique with diamines and diaminoalcohol which included ethylenediamine (EDA), hexamethylenediamine (HMDA) and 1,3-diamino-propanol-2 (AHP). Polar aprotic solvents such as DMF, DMSO and NMP were used as the polymerization media (Scheme 3).



The results of polymerization of III with various diamines are summarized in Table 1.

The polymerization was greatly influenced by the polymerization solvent as shown in Table 1 and DMSO was found to be the best polymerization medium among these polar aprotic solvents for high polymer formation.

Table 1 Results of the polycondensation of active esters III with various diamines at 25 °C^{a)}.

Active ester	Diamine ^{b)}	Solvent (25 — 30 mL)	Time (h)	Polyamide	Yield (%)	$\eta_{inh}^{c)}$ (dL/g)
IIIa	HMDA	DMF	48	VIa	99	0.18
	HMDA	DMSO	48	VIa	98	0.30
	HMDA	NMP	48	VIa	97	0.28
	EDA	DMF	48	VIb	91	0.11
	EDA	DMSO	48	VIb	88	0.14
	EDA	NMP	48	VIb	93	0.15
IIIb	HMDA	DMSO	48	VIc	99	0.46
	EDA	DMSO	48	VIc	91	0.24
IIIc	HMDA	DMSO	48	VIe	76	0.19 ^{d)}
	EDA	DMSO	48	VIe	73	0.54 ^{d)}
IIIa	AHP	DMSO	48	VIIa	84	0.23 ^{e)}
IIIb	AHP	DMSO	48	VIIb	70	0.46 ^{e)}
IIIc	AHP	DMSO	48	VIIc	78	0.22 ^{d)}

a) Polymerization was carried out with 2.5 mmol of reactants.

b) HMDA : hexamethylenediamine ; EDA : ethylenediamine ; AHP : 1,3 - diamino - 2 - hydroxypentane.

c) Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25 °C.

d) Measured in 90% of formic acid.

e) Measured in DMSO.

All polymers formed in the case of III with HMDA and EDA identified as polyamides by comparing their NMR spectrum with those of the authentic polyamides. Elemental analyses of the polymers also supported the formation of polyamides.

Three functional polyamides with hydroxyl group, VIIa, VIIb, and VIIc were also prepared (Scheme 3). The NMR spectra of the hydroxyl polyamides in DMSO- d_6 indicated at 5.1 or 5.3 ppm for polyamide VII containing hydroxyl residue. This shows no participation of reactive sites of hydroxyl group in the polycondensation reaction. In addition, the NMR and IR spectra of VIIa and VIIb were exactly superimposable on that of two authentic samples prepared by the polycondensation of N, N' - (terephthaloyl) - bis (5 - norbornene - 2, 3 - dicarboximide) and N, N' - (isophthaloyl) bis (5 - norbornene - 2, 3 - dicarboximide) with AHP as reported in our previous paper⁽¹¹⁾. In the case of the new aliphatic hydroxyl polyamide VIIc, the absorption bands arising from the adipic acid protons resonate at 1.76 and 3.71 ppm. The methylene groups of the AHP moiety appear as a multiplet band from 3.25 to 3.42 ppm. Two singlet bands at 3.81

and 5.25 ppm arise from the methine group bonded to the hydroxyl residue. At 8.31 ppm is observed a band due to the secondary amide protons in the polymer.

The results presented herein demonstrate the feasibility of preparing polyamides and hydroxyl polyamides through the selective N-acylation of active ester derived from N-hydroxy-1,4-epoxy-2,3-dicarboximide.

EXPERIMENTAL

Materials and Methods

N-Hydroxy-1,4-epoxy-5-cyclohexene-2,3-dicarboximide (HOEC) was prepared according to the method of literature^[15]. Ethylenediamine, (EDA) and hexamethylenediamine (HMDA) were distilled under reduced pressure before use. All solvents were purified as usual. Melting points were uncorrected. The NMR spectra were recorded on a Varian FT-80A and a Varian XL-400 spectrophotometers, respectively. TMS was used as internal standards. The IR spectra were recorded on Shimadzu IR-408 spectrophotometer. Microanalyses were performed by Microanalytical Laboratory, Institute of Chemistry, Academia Sinica, Beijing.

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Monomers

NN'-(Terephthaloyldioxy) bis (1,4-epoxy-5-cyclohexene-2,3-dicarboximide) (IIIa, PBOEC): To a stirred solution of HOEC (7.25 g, 40 mmol) and triethylamine (5.6 mL, 40 mmol) in 140 mL of THF was added a solution of terephthaloyl chloride (4.06 g, 20 mmol) in 50 mL of THF. The mixture was stirred at room temperature for 30 min and the product was isolated by pouring the reaction mixture into 400 mL of water. 9.85 g of a colorless crystalline solid was precipitated. mp 192–194 °C. The yield was 90.4 %. Crystallization from DMF-ethanol or DMF-water gave white powder crystals, mp 199–200 °C (decp.). IR(KBr); 1780(imide); 1740 cm⁻¹ (ester). NMR (DMSO-d₆); ppm, 3.20 (s, 4H, 2-CHOCH-); 5.30 (s, 4H, CO-CH-); 6.61 (s, 4H, 2-CH=CH-); 8.34 (s, 4H, 2 paradisubstituted phenyl).

Anal. Calcd for C₂₄H₁₆N₂O₁₀; C, 58.54 %; H, 3.28 %; N, 5.69 %.

Found: C, 58.30 %; H, 3.53 %; N, 6.03 %.

N, N'-(Isophthaloyldioxy) bis (1,4-epoxy-5-cyclohexene-2,3-dicarboximide) (IIIb, IPBOEC): By analogy with the above, IPBOEC monomer was prepared from 4.06 g (20 mmol) of isophthaloyl chloride and the same quantities of HOEC, triethylamine and THF. The product was recrystallized from dichloromethane-ether to give a colorless granular crystals, mp 171–172 °C. The yield was 96.4 %. IR (KBr); 1775 (imide); 1735 cm⁻¹ (ester). NMR 8DMSO-d₆. ppm, 3.20 (s, 4H, 2-CHOCH-); 5.32 (s, 4H, -COCH); 6.62

(s, 4H, 2-CH=CH-); 8.06 (t, 1H, ); 8.55 (d, 2H, );

8.68 (s, 1H, ). Anal. Calcd for C₂₄H₁₆N₂O₁₀; C, 58.5 %; H, 3.28 %; N, 5.69 %.

Found: C, 58.17 %; H, 3.20 %; N, 5.48 %.

N, N' - (Adipoyldioxy) bis (1, 4 - epoxy - 5 - cyclohexene - 2, 3 - dicarboximide) (IIIc, ADOEC): Dissolve 5.85 g (40 mmol) of adipic acid in 15 mL of redistilled thionyl chloride. Allow to reflux for 2 h, then distill off the excess thionyl chloride and dilute with 10 mL of anhydrous THF to gave a light red solution. To a stirred solution of 14.48 g (80 mmol) of HOEC and 11.2 mL of triethylamine in 140 mL of DMF is dropped a solution of adipic chloride which is prepared before at room temperature for 1 h. After stirring at room temperature for 3 h, the product is isolated by pouring the mixture into 700 mL of water. The yield is 13.79 g (73.0%). Recrystallization from dioxane give colorless crystals, mp 178 - 179 °C (dec.). IR (KBr); 1780 (imide); 1740 cm^{-1} . NMR (DMSO- d_6); ppm, 1.74 (bs, 4H, 2 β -CH₂-); 2.72 (bs, 4H, 2 α -CH₂-); 3.07 (s, 2H, -CHOCH-); 5.22 (s, 2H, 2 OCH-); 6.57 (s, 2H, -CH=CH-). Anal. Calcd for C₂₂H₂₀N₂O₁₀; C, 55.93%; H, 4.27%; N, 5.93%. Found; C, 56.20%; H, 4.19%; N, 5.75%.

Model Reactions

N, N' - Dibenzylterephthalamide (IVa): From IIIa and benzylamine. To a stirred solution of 2.46g (5 mmol) of IIIa in 15 mL of THF was added 0.535g (5 mmol) of benzylamine at ambient temperature. The mixture was stirred for 3 h, then poured into 300 mL of 1% aqueous sodium carbonate. The precipitate that formed was collected, washed with water, and dried. The yield was 16.5 g (96%), mp 103 - 105 °C (lit⁽¹¹⁾ 105 - 106 °C).

N, N' - Dibenzyisophthalamide (IVb): From IIIb and benzylamine. By analogy with above, IVb was prepared from IIIb with benzylamine in DMF. The yield was 90%, mp 152 - 156 °C (lit⁽¹⁶⁾ 156 - 158 °C).

N, N' - Bis (2 - hydroxyethyl) terephthalamide (Va): From IIIa and aminoethanol. A solution of 0.985 g (2 mmol) of IIIa in 25 mL of DMSO was added 0.244 g (4 mmol) of aminoethanol. After stirring for 2h at room temperature, the solvent was evaporated. The residue was added with 25 mL of methanol and the resulting product filtered. The product was collected and dried. The yield was 0.385 g (76.4%). Recrystallization from methanol gave colorless crystals. mp 229 - 230 °C (lit⁽²⁾ 227 - 229 °C).

N, N' - Bis (2 - hydroxyethyl) isophthalamide (Vb): From IIIb and aminoethanol. To a stirred solution of 0.985 g (2 mmol) of IIIb in 20 mL of chloroform was added 0.244 (4 mmol) of aminoethanol. The reaction mixture was stirred for 2 h at room temperature. The solvent was evaporated, the residue was chromatographed on silica gel using acetone as an eluent to afford the product. Recrystallization from methanol gave colorless crystals, mp 137 - 139 °C. (lit⁽¹²⁾ 138 - 140 °C). The yield was 0.432 g (86%).

Polymerization

Three examples of polycondensation are as follows;

(1) Polyamide from PBOEC and HMDA

To a solution of 1.231g (2.5 mmol) of PBOEC in 30 mL of DMSO was added 0.290 g (2.5 mmol) of HMDA. The mixture was stirred at room temperature for 48

h, then poured into 500 mL of water. The precipitated polymer was collected, washed with hot water repeatedly, and dried under vacuum at 60 °C. The yield was 0.604 g (98%). Inherent viscosity of the polymer in concentrated sulfuric acid was 0.30, measured at a concentration of 0.5 g/dL at 25 °C. IR(KBr): 3350 (γ N—H); 1630 and 1500 cm^{-1} (C=O, secondary —CONH—). NMR (TFA); ppm 1.19 (s, 4H, γ —CH₂—); 1.45 (s, 4H, β —CH₂—); 3.31 (s, 4H, α —CH₂—N—); 7.57 (s, 4H, para substituted phenyl).

Anal. Calcd for (C₁₄H₁₈N₂O₂)_n; C, 68.27%; H, 7.36%; N, 11.38%. Found; C, 66.86%; H, 7.32%; N, 11.56%.

(2) Flexible Polyamide VIe from IIIc and HMDA

A mixture of IIIc (1.181 g, 2.5 mmol), HMDA (0.290, 2.5 mmol) in DMSO (25 ml) was stirred at room temperature for 48 h. The resulting suspension solution was pouring into 400 mL of water. The precipitated polymer was collected, washed with hot water repeatedly, and dried under vacuum at 60 °C. The yield was 0.430 g (76%). The IR spectrum of polymer VIe was exactly superimposable on that of an authentic sample prepared by polycondensation of adipic acid with HMDA.

(3) Hydroxyl Polyamide VIIc from ADOEC with AHP

To a solution of 0.181 g (2.5 mmol) of IIIc in 25 mL of DMSO was added 0.255 g (2.5 mmol) of AHP. After stirring at room temperature for 48 h. The mixture was evaporated to one sixth its original volume, then the mixture was added with 150 mL of ethanol and the resulting polymer filtered, washed with ethanol, and dried under vacuum at 60 °C. The yield was 0.390 g (78%). IR (KBr); 3300—3460 ($\gamma_{\text{N—H}}$ and γ_{OH}). 1500 and 1640 cm^{-1} (C=O in secondary amide). NMR (DMSO-d₆); 1.76 (s, 4H, 2 β —CH₂—); 3.25—3.42 (m, 4H, 2 CH₂N—); 3.71 (s, 4H, 2 —CH₂CO—); 3.81 (m, 1H, —CH—O—); 5.25 (bs, 1H, HO—); 8.13 (s, 1H, 2 —NHCO—).

Anal. Calcd. for (C₉H₁₆N₂O₃)_n; C, 53.98%; H, 8.05%; N, 13.99%. Found; C, 51.63%; H, 7.75%; N, 13.51%.

Keywords:

Active ester selective Polymerization; Hydroxyl Polyamides.

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