Preparation of Polymeric Initiators of the Anionic Polymerization of Lactams from Polyetherdiols

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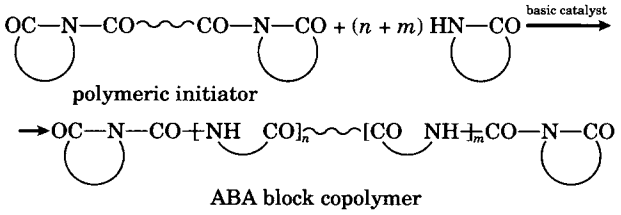
SYNOPSIS

The kinetics of alcoholysis of bis(*N*-acyl-6-hexanelactams) and bis(*N*-carbamoyl-6-hexanelactams) was studied for the purpose of the preparation of bifunctional polymeric initiators of the anionic polymerization of 6-hexanelactam used in the production of polyamide block copolymers by reactive processing. The reaction was carried out with 1-octanol as a model alcohol and with poly(propylene oxide)diol, without catalysis or using anionic and polyesterification catalysts, and in 6-hexanelactam as a solvent. Applicability of this functionalization method is discussed with respect to a broad spectrum of formed products, competition of lactam oligomerization in the presence of basic catalysts, preparation of the initiator component for two-component polymerization systems, and *in situ* functionalization during polymerization. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Modified polyamide plastics with an enhanced impact resistance at low temperatures and in the dry state are produced, among other methods, by incorporating a modifying rubber component as blocks into the polyamide block copolymer. This can be done by the anionic block copolymerization of 6-hexanelactam using telechelic polymeric initiators with *N*-acyl-6-hexanelactam endgroups on which the polyamide chains propagate. If one does not consider side reactions occurring in the anionic polymerization of lactams, an ABA block copolymer should result:



The real products have a multiblock $[AB]_n$ structure[1] and are branched or cross-linked. This block copolymerization forms a base for the reaction injection molding (RIM) of polyamides.[2]

The polymeric initiators are advantageously prepared by the functionalization of commercial telechelic low molecular weight polymers with reactive endgroups, as are polyethers and liquid rubbers with amino, hydroxy, or carboxy endgroups. The transformation of primary or secondary amino endgroups by the partial aminolysis of bis-(*N*-acyllactams) is simple, sufficiently fast, and univocal.[3] The analogous partial alcoholysis is slower and can be accelerated by basic catalysis, as has been reported for the polymerization systems employed in the RIM.[4,5]

In the present paper, we discuss the results of kinetic investigations of both noncatalyzed and catalyzed alcoholysis of various bis(*N*-acyl-6-hexanelactams).

EXPERIMENTAL

Materials

1-Octanol (Fluka, redistilled) and poly(propylene oxide)diol (PPO) ($\bar{M}_n$ = 1050; Koch-Light) were dried over molecular sieves 4 Å. The endgroups of PPO were characterized by ^{13}C-NMR spectra at 75 MHz with Bruker 300 AC spectrometer. 6-Hexane-

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lactam (HL) (technical grade, Spolana Neratovice, Czechoslovakia) was twice recrystallized from benzene and dried in vacuum at 60°C. *N*-Acyl-6-hexanelactams, *N*-phenylcarbamoyl-6-hexanelactam, *N,N'*-isophthaloyl-bis-6-hexanelactam, and bis(*N*-carbamoyl-6-hexanelactams) were synthesized by the methods described earlier.[3,5]

Kinetic Measurements

The reaction mixture was prepared at ≤ 90°C by dissolution of the acyllactam and 1-octanol or PPO in the amount of HL corresponding to the 50 wt % concentration of the reaction products in HL. In catalyzed alcoholyses, only about one-half of this HL amount was used and the remaining HL served for dissolution of the catalyst or for the preparation of the catalysts *in situ*. Sodium 6-hexanelactamate (NaL), potassium 6-hexanelactamate (KL), and magnesium 6-hexanelactamate bromide (MgLBr) were prepared *in situ* by adding an appropriate amount of THF solution of sodium or potassium *tert*-butoxide or diethyl ether solution of ethylmagnesium bromide to the excess of solid HL, evaporation of the solvent in vacuum, and repeated melting, cooling, and evacuation. Magnesium 6-hexanelactamate (MgL_2)[6] was added to HL as a solution in THF. Calcium 6-hexanelactamate (CaL_2) was prepared by dissolving solid CaH_2 in HL. Zinc and antimony acetates and benzimidazole were purified by sublimation and added to HL as solids.

Both parts of the reaction mixture were mixed at 80–90°C, then rapidly transferred under vacuum into ~ 0.1 mL glass ampules with capillary ends, which were then cooled and sealed. The ampules were heated to a chosen temperature in the range 100–145°C in a silicon oil bath HAAKE F3. In a few cases of a relatively fast reaction, the reaction components were mixed at the temperature of measurement and the samples were withdrawn with a syringe in the chosen intervals.

Chromatographic Analyses

Kinetic data were obtained by combined GLC, HPLC, and SEC analyses of the reaction mixtures:

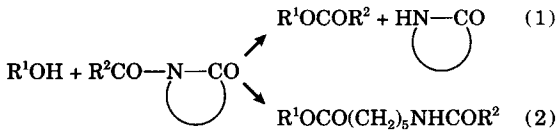
GLC: Chromatograph PE-F11, FID, stainless-steel columns with i.d. 2 mm, carrier gas N_2 50 mL/min. *N*-Propionyl-6-hexanelactam (**Ia**) was determined on a 1 m column packed with 10% Carbowax 20M on Chromosorb W-HMDS at column temperature T_c = 185°C using benzophenone as an internal standard; octyl propionate was determined on a 1 m column packed with 10% Apiezon on Chromosorb W, T_c = 135°C, internal standard octanol; and octyl benzoate was determined on a 1 m column packed with 10% Tridox on Chromaton N-Super (Lachema Brno), T_c = 155°C, internal standard 2-pyrrolidone.

HPLC: Linear pump HPP 4001 (Laboratory Instruments, Prague), UV detector 2112 (Cecil Instruments, Cambridge) at λ = 210 nm, glass column 15 cm, i.d. 3.2 mm packed with the reverse-phase Separon SGX C18 (particle size 7 μm; Tessek, Prague), and mobile-phase methanol–water (75 : 25 v/v) 0.2 mL/min. Using this system, **Ib**, *N*-Phenylcarbamoyl-6-hexanelactam (**Ic**), and octyl *N*-phenylcarbamate were determined; the internal standard was *o*-dichlorobenzene.

SEC: Chromatograph HP1090 with a differential refractometer HP1037A. Samples from the alcoholyses of bis(*N*-acyl-6-hexanelactams) **IIa–d** with PPO were dissolved in THF containing 12-dodecanelactam as an internal standard, and 15 μL was injected into a 60 × 0.75 cm stainless-steel column with PL-gel 100 Å (particle size 10 μm; Polymer Laboratories) and eluted with 1.0 mL/min THF at laboratory temperature.

RESULTS AND DISCUSSION

The transformation of hydroxyl groups to ester–*N*-acyl-6-hexanelactam groups by the partial alcoholysis of bis(*N*-acyl-6-hexanelactams) and bis(*N*-carbamoyl-6-hexanelactams) with poly(propylene oxide)diol ($\bar{M}_n$ = 1025) (PPO) was studied in 6-hexanelactam (HL) as a solvent. Similarly to the hydrolysis and aminolysis, alcoholysis can also proceed by a nucleophilic attack of the cyclic amide group or the amide group outside the lactam cycle and thus leads to the endocyclic or exocyclic cleavage:



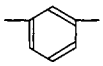
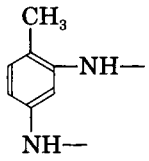
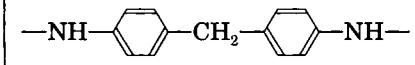
(1)

(2)

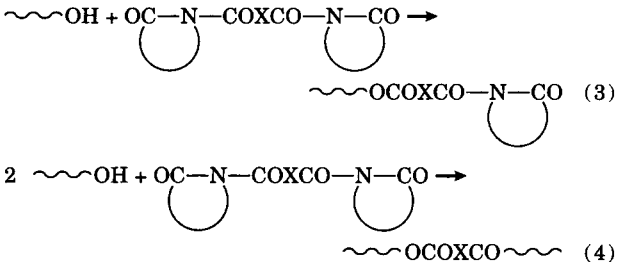
The proportion of reaction pathways (1) and (2) and additional kinetic data were obtained with the monofunctional model systems 1-octanol–*N*-acyl-6-hexanelactam or *N*-(phenylcarbamoyl)-6-hexanelactam. A survey of the used *N*-acyl-6-hexanelactams (**Ia–c**) and bis(*N*-acyl-6-hexanelactams) (**IIa–d**) is given in Table I.

The quantitative conversion of the OH endgroups to *N*-acyllactam groups (3) can be always achieved

Table I *N*-Acyl-6-hexanelactams (HL) Used in the Alcoholyses

R—CO—N—CO (I)			OC—N—CO—X—CO—N—CO (II)		
R	Name		X	Name	
C_2H_5	*N*-Propionyl-HL	(**Ia**)		*N,N'*-isophthaloyl-bis-HL	(**IIa**)
C_6H_5	*N*-Benzoyl-HL	(**Ib**)	—$NH(CH_2)_6NH$—	*N,N'*-(hexamethylene-biscarbamoyl)bis-HL	(**IIb**)
				*N,N'*-(2,4-tolylene-biscarbamoyl)bis-HL	(**IIc**)
C_6H_5NH	*N*-Phenylcarbamoyl-HL	(**Ic**)		*N,N'*-[methylenedi(1,4-phenylene)biscarbamoyl]bis-HL	(**IId**)

with a large excess of bis(*N*-acyllactam) when the competing coupling reaction (4) of the diol is suppressed:



Suppression of reaction (4) can be also expected with bis(*N*-acyllactams) having both reacting groups on one aromatic system, where the reactivity of the first group is higher due to electronic and steric effects, e.g., with **IIa** (Ref. 3) and **IIc** (similarly to TDI).

Because the reaction mixture containing the polymeric initiator should be directly used as a polymerization component for mixing with the solution of the anionic catalyst in HL, e.g., in the RIM systems, it is suitable to study the alcoholysis without the excess of bis(*N*-acyllactam) and in HL as a solvent. The similar reaction conditions are also in the *in situ* preparation of the polymeric initiator where the solution of diol and bis(*N*-acyllactam) in HL is mixed with the catalyst solution in HL and directly polymerized without completed alcoholysis. Possible consequences of these reaction conditions [incomplete conversion of hydroxyl endgroups and the presence of unreacted initial bis(*N*-acyllactam)] for the synthesis of block copolymers have been discussed earlier.[5] We measured the kinetics of alcoholysis under the conditions leading to a 50 wt % solution of the polymeric initiator in HL, i.e., at the 1 : 1 molar ratio of OH groups and bis(*N*-acyllactam) and the initial concentrations $[OH]_0 = [\mathbf{II}]_0 = 0.50$–$0.53$ mol/kg or, with models, $[\text{octanol}]_0 = [\mathbf{I}]_0 = 1.4$–$1.7$ mol/kg.

Model Alcoholysis with 1-Octanol

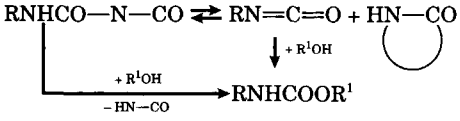
Table II shows the rates of *N*-acyllactam alcoholysis with 1-octanol as second-order rate constants calculated from the consumption of *N*-acyllactam **Ia, b,** and **c.** The proportions of exocyclic cleavage were determined from the amounts of formed esters. The degree of acyllactam consumption, up to which the second-order kinetic plot was linear, ranged from 30 to 95% depending on the type of *N*-acyllactam and catalyst. Basic catalysts used were usual catalyst of the anionic HL polymerization and were used mostly in the concentration of 1 mol % related to OH groups.

Table II Rate Constants k (kg/mol s) and Proportions of Exocyclic Cleavage *exo* (%) in the Alcoholysis of *N*-Acyl-6-hexanelactams I with 1-Octanol in HL

Catalyst[a]	Amount[b] (mol %)	T (°C)	Ia		Ib		Ic	
			$k \times 10^5$	*exo*	$k \times 10^5$	*exo*	$k \times 10^5$	*exo*
None	—	100	1.4	66	1.6	100	0.62	100
	—	130	4.4	54	8.3	100	5.1	—
NaL	0.5	70	—	—	1560	47	5790	100
	1.0	100	0.55	78	—	—	—	—
	1.0	130	3.0	61	—	—	—	—
MgL_2	0.5	70	—	—	46	58	44	80
	1.0	100	2.3	52	—	—	—	—
	1.0	130	12	25	—	—	—	—
MgLBr	1.0	100	6.6	23	22	—	18	—
	1.0	130	31	—	140	57	310	27
	1.5	100	7.9	27	—	—	—	—
	1.5	130	55	25	—	—	—	—
	4.0	100	29	16	—	—	—	—
	4.0	130	100	15	—	—	—	—

[a] For the abbreviations of catalysts, see Experimental section.
[b] Related to OH groups.

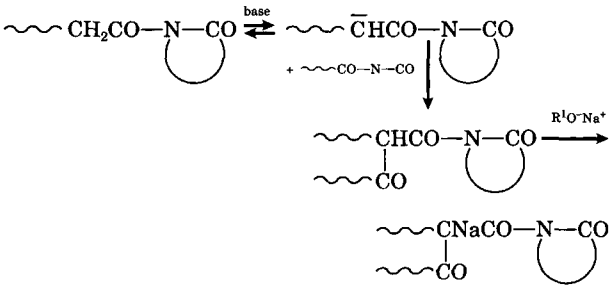
The differences between individual *N*-acyllactams may be explained in several ways. The *N*-carbamoyllactams should be also considered the lactam-blocked isocyanates that are liable to thermal dissociation giving free isocyanate and lactam.[5] The addition reaction of isocyanate and alcohol competes with the alcoholysis and gives the same urethane as the exocyclic cleavage[1]:



(5)

(6)

As the reaction mixture contains all components for the anionic polymerization of HL, i.e., lactam *N*-anions, *N*-acyllactam initiator, and monomer, the formation of lactam oligomers is probable. This will not affect the alcoholysis too much because the concentration of lactam anions is very low. On the other hand, the formation of C-anions on the α-carbon atoms of aliphatic acyl will be favored in the presence of a strongly basic catalyst, viz., alkaline metal lactamate. Their acylation of the Claisen-condensation type gives rise to β-ketoimide, which is a relatively strong C-acid and consumes the basicity of the catalyst[7] (7):



(7)

This is probably the reason why the alcoholysis of **Ia** is not accelerated by NaL in contrast to **Ib** and **Ic** and in contrast to MgL_2 and MgLBr. The proportion of exocyclic alcoholysis depends really on all variables: type of *N*-acyllactam, catalyst, and temperature. The basic catalysis increases the contribution of endocyclic cleavage.

Preparation of the Polymeric Initiator

The alcoholyses of bis(*N*-acyllactams) with PPO–diol are surveyed in Table III. The polymeric diol reacts with bis(*N*-acyllactams) much slower than does octanol with *N*-acyllactams. One of the reasons may consist in the fact that the used PPO contained

Table III Rate Constants $k \times 10^5$ (kg/mol s) of the Alcoholysis of Bis(*N*-acyl-6-hexanelactams) II with Poly(propylene oxide) diol in HL at 100 and 130°C

Catalyst[a]	Amount[b] (mol %)	IIa		IIb		IIc		IId	
		100	130	100	130	100	130	100	130
None	—	0.31	5.6	0.15	1.3	2.7	29	2.3	82
		5.6[c]	30[d]	0.48[c]	5.3[d]	—	—	—	—
NaL	1	0.79	4.0	1.5	4.0	32	370	—	—
	2	1.1	4.4	—	—	—	—	—	—
	4	0.41	2.9	—	—	—	—	—	—
KL	1	2.3	5.0	3.4	6.2	10	21	48	107
CaL_2	1	0.64	3.5	0.22	2.1	0.53	110	5.9	128
MgL_2	1	0.88	4.5	0.41	15	—	—	19	60
MgLBr	1	1.6	29	4.5	24	8.3	143	18	80
	2	1.3	20	—	—	—	—	73[e]	134[e]
	4	3.1	89	—	—	—	—	—	—
$Zn(OAc)_2$	1	0.86	5.3	0.36	1.6	5.8	142	9.0	107
$Sb(OAc)_3$	1	1.0	4.8	0.23	11	6.0	110	5.3	111
Benzimidazole	10	0.64	4.3	0.07	4.3	3.3	63	3.2	22

[a] For the abbreviations of catalysts, see Experimental section.
[b] Related to OH gropus.
[c] 115°C.
[d] 145°C.
[e] 2.5 mol %.

exclusively secondary OH groups. This was proved by ^{13}C-NMR spectra where the H<u>C</u>—OH signals were identified by APT and occurred at 63.6–65.2 ppm, whereas H_2<u>C</u>—OH peaks usually occurring at 68.6 ppm were absent.[8]

The reaction rates are derived from the consumption of bis(*N*-acyllactam) determined by SEC and, thus, they correspond to the alcoholysis of the first acyllactam group in the molecule. As the OH groups may be consumed also in the coupling reaction (4), the molar ratio of reactants can change in time. This is the reason why the second-order plot used for the calculation of rate constants is linear up to 26–95% of bis(*N*-acyllactam) conversion, depending on the type of bis-acyllactam and catalyst.

Among the tested basic catalysts, only MgLBr and, to some extent, KL were effective in the alcoholysis of **IIa** and **IIb.** Evidence for the deactivation of NaL by its consumption in the Claisen-type condensation of **IIa** is shown in Figure 1. The SEC shows the formation of oligomers as the increasing peak B. These oligomers are likely acidic α-C condensation products of **IIa** (7) with molecular weight 600–700, because the simple oligo(6-hexanelactams) of this molecular weight are insoluble in the mobile phase.

The changing shape of the PPO peak A well reflects a variety of products formed by the alcoholysis. Assuming the possible combinations of exocyclic and endocyclic cleavage [reactions (1) and (2)] caused by both OH endgroups and a simple coupling of two PPO molecules [reaction (4)], 23 different products with $\bar{M}_n$ 1025–3119 may result from PPO–diol ($\bar{M}_n$ 1025) and **IIb** (M = 356.4). Of course, peak A cannot be quantitatively interpreted because the individual products differ in the responses of the differential refractometer due to the different proportions of incorporated aromatic moieties. The shift of the product peak A to a shorter elution time corresponding to a higher molecular weight as well as the development of polymodality were observed in all cases in the advanced stage of functionalization.

The aromatic bis(*N*-carbamoyllactams) **IIc** and **IId** are alcoholyzed faster and the efficiency of the catalysts is proportional to their basicity. The side reaction (8) is obviously suppressed, which can be also seen from a very small peak B found by SEC for the alcoholysis of **IIc** (Fig. 1). A larger participation of the dissociation–addition mechanism (6) is very probable.

The temperature dependence of rate constants for the noncatalyzed alcoholysis of **IIa** and **IIb** at

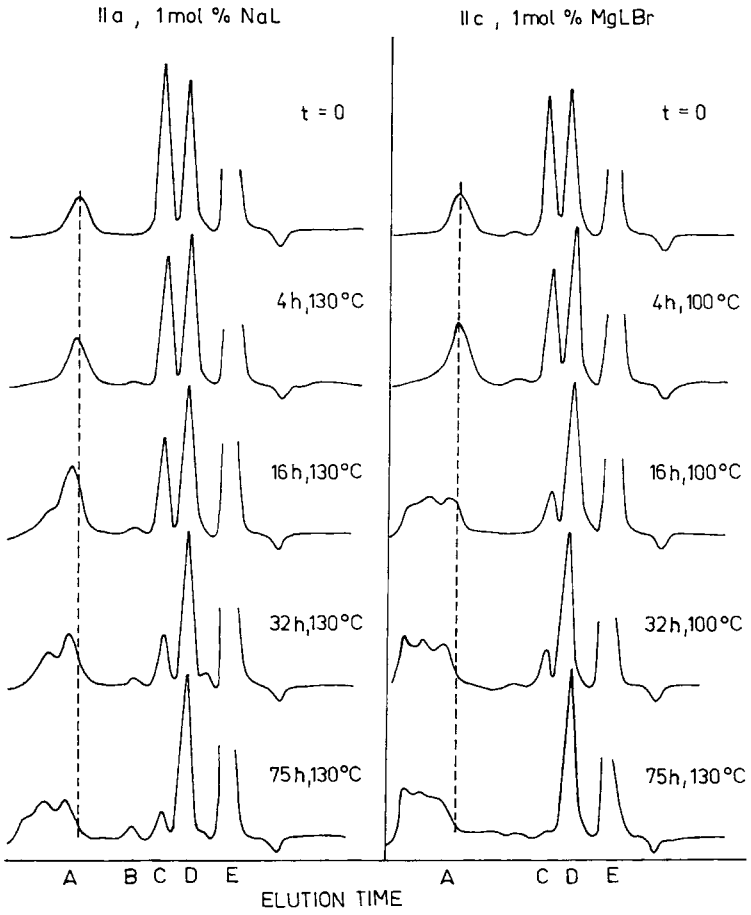


Figure 1 Time course in the catalyzed alcoholysis of **IIa** and **IIc** with PPO–diol shown by the SEC separation of reaction mixtures; (peaks A) PPO; (B) oligomers of HL derivatives; (C) bis(*N*-acyllactam); (D) 12-dodecanelactam (internal standard); (E) HL.

100–145°C gave the activation energies 56 and 44 kJ/mol, respectively. The linear Arrhenius plot for **IIb** did not indicate the change of mechanism [(1), (2)] to [(5), (6)] in this temperature region.

It has been claimed that the reaction is also promoted by the catalysts usually used in the transacylation synthesis of polyesters.[9] We found only a small effect of zinc(II) acetate, antimony(III) acetate, and benzimidazole on the alcoholysis, except for **IIc** where metal acetates increased the rate at 130°C.

CONCLUSIONS

It follows from the kinetics of alcoholysis that the preparation of polymeric initiators for the anionic polymerization of lactams from commercial polymeric diols is feasible but not so advantageous as the aminolytic preparation from polymeric diamines.[3,5,10] The main difference is a lower reaction rate requiring the use of a catalyst, multiplicity of the reaction pathways, and side reactions caused by basic catalysts. Fortunately, the alcoholysis of **IIa,** representing the bis(*N*-acyllactams) derived from dicarboxylic acids, is accelerated by MgLBr, which is also a highly efficient catalyst for the anionic block copolymerization of HL[2,4] generally used in the systems for RIM. The alcoholysis of aromatic bis(*N*-carbamoyllactams) **IIc** and **IId** to polymeric initiators proceeds faster than that of **IIa** also with NaL and KL. This is again a suitable initiator–catalyst combination for the anionic preparation of block copolymers.[11] This fact is very important for the *in situ* preparation of polymeric initiators during mixing the components for the anionic copolymerization. In the copolymerization, the concentration of basic catalyst is similar to the concentration of initiator groups and thus attains about 100 mol % with respect to the OH groups participating in alcohol-

ysis. The acceleration is so high that the period of mixing before polymerization of HL is mostly sufficient for the complete incorporation of polymeric diol into the block copolymer as shown for the OH-capped rubber Hycar HTBN[5] as well as for PPO–diol.[12]

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