PREPARATION OF POLYMERS AND REACTIVE PREPOLYMERS BY THE AMINOLYSIS OF ACYLBIS(HEXANELACTAMS)

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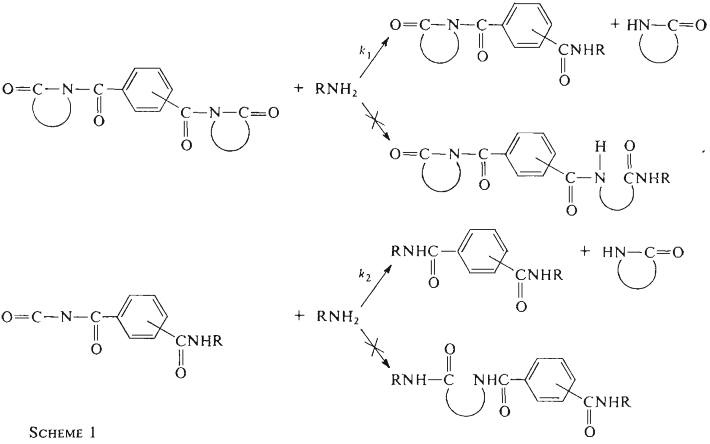
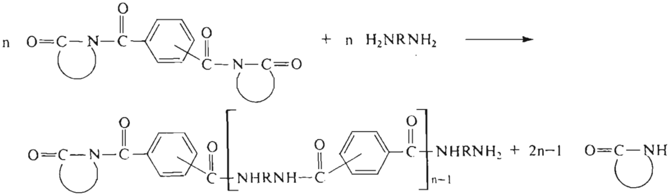
The aminolysis of N,N′-isophthaloyl and N,N′-terephthaloyl-bis(6-hexanelactam) with aliphatic diamines was used in the preparation of semiaromatic polyamides, in the extension of polymer chains and in the preparation of N,N′-[poly(oxyethylene)di(carbamoylbenzoyl)]bis(6-hexanelactams) under mild conditions (50—80°C).

In our earlier paper[1] we examined the kinetics of aminolysis of N,N′-isophthaloylbis(hexanelactam) and N,N′-terephthaloylbis(hexanelactam) to the first and second degrees:



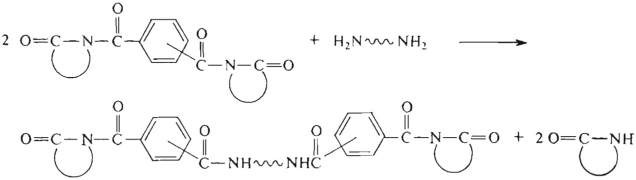
SCHEME 1

It was proved that the aminolysis of these acylbis(lactams) with aliphatic amines proceeds in various solvents at lower temperatures (up to 50°C at least) selectively *via* splitting of the exocyclic amide bonds with the splitting-off of hexanelactam, and that the rate to the first degree is always higher than that to the second; *e.g.* in the aminolysis with butylamine at 50°C in THF in the case of the isophthaloyl derivative, $k_1 = 36{\cdot}5 \,.\, 10^{-3}$ and $k_2 = 4{\cdot}9 \,.\, 10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, and in the case of the terephthaloyl derivative $k_1 = 23{\cdot}9 \,.\, 10^{-3}$ and $k_2 = 5{\cdot}1 \,.\, 10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$. These findings have been employed in the preparation of defined semiaromatic polyamides, in the controlled coupling of polymers with amino endgroups



SCHEME 2

and in the preparation of reactive prepolymers for defined block copolymers

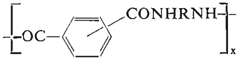


SCHEME 3

Acylbis(lactams) derived from aromatic and aliphatic dicarboxylic acids and lactams with rings of various sizes have already been employed for similar purposes without any deeper knowledge of their reactivities and the proportion of the competitive splitting of the exo- and endocyclic amide bonds. Ogata[2] has described the preparation of polyamides by the aminolysis of acylbis-(lactams) derived from adipic acid and 2-pyrrolidone, hexanelactam and dodecanelactam and of N,N′-isophthaloyl-bis(4-butanelactam) with various aliphatic diamines at 30 and 60°C. In agreement with our findings, he obtained polyamides with a higher degree of polymerization only from the hexanelactam derivative. Korshak and coworkers[3] investigated the preparation of polyamides by the aminolysis of N,N′-isophthaloylbis(6-hexanelactam) with 1,6-diaminohexane and aromatic diamines in various solvents at 100—250°C. The ratio of the exocyclic and endocyclic splitting was estimated from the polymer yield obtained, which above the stoichiometric limit for polyamide of the AB type indicated the incorporation of hexaneamide units. (At the temperatures used, however, the transamidation reactions of the forming polymer with hexanelactam also compete with aminolysis, so that the ratio of the exo- and endocyclic splitting cannot be estimated). The polymers thus obtained from 1,6-diaminohexane using 5 mol% excess of acylbis(lactam) in hexanelactam as solvent were used by these authors without isolation in the preparation of block copolyamides by the anionic polymerization of hexanelactam[4]. Lincoln[5] employed a similar route when he reacted terminal amino groups of copolyamide 6—66

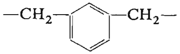
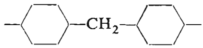
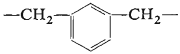
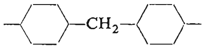
TABLE I

Preparation of Polyamides



by the Aminolysis of Acylbis(6-hexanelactams) with Diamines H_2NRNH_2 in Hexamethylphosphortriamide at 50°C

c mol of monomers/dm^3 of solvent, *t* reaction time, *u* content of hexanelactam or hexaneamide units estimated from ^1H-NMR spectra.

Diamine R	*c* mol/dm^3	*t* h	η_{rel} $cm^3 g^{-1}$	*u* mol%
Aminolysis of N,N′-isophthaloylbis(6-hexanelactam)				
$-(-CH_2-)-_4$	0·28	380	47	13
$-(-CH_2-)-_6$	0·45	170	420	—
	0·51[a]	400[a]	140[a]	1·4[a]
	0·57[b]	188[b]	175[b]	8[b]
$-(-CH_2-)-_{12}$	0·31	330	324	0
	0·41	265	121	10—14 3—8[c]
	0·36	200	169	—
Aminolysis of N,N′-terephthaloylbis(6-hexanelactam)				
$-(-CH_2-)-_4$	0·28	380	61	12
$-(-CH_2-)-_6$	0·40[b]	170[b]	420[b]	—
$-(-CH_2-)-_{12}$	0·26	330	152	0
	0·46	265	80	6—11 4—8[c]
	0·48	200	142	—

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[a] Solvent N,N-dimethylacetamide with 5% LiCl. [b] Reaction temperature 80°C. [c] Reprecipitated samples.

with N,N'-terephthaloylbis(6-hexanelactam) in hexanelactam and obtained a block copolyamide after the addition of sodium.

Miwa and Kuze[6] described the preparation of polyamide by the aminolysis of N,N'-isophthaloylbis(6-hexanelactam) with 3,3'-diaminodiphenylsulphone at 260°C. Coupling of identical or different polyamide oligomers containing amino endgroups by reacting them with acylbis(lactam) in the melt or in solution has also been described in several patents[7-10].

Preparation of Polyamides

Polyamides derived from isophthalic and terephthalic acids were prepared with a sufficiently high degree of polymerization by the aminolysis of N,N'-isophthaloylbis(6-hexanelactam) and N,N'-terephthaloylbis(6-hexanelactam) with aliphatic diamines. The basic prerequisite is a sufficient purity of diamine which would guarantee the equimolarity of the two monomers. Polyisophthalamides are soluble in hexamethylphosphortriamide, and the process of aminolysis may be followed by means of the increasing viscosity of the reaction mixture. On the contrary, polyterephthalamides are insoluble in the reaction mixture, and the latter solidifies after a rather short time of aminolysis. Aminolysis proceeds also in the solidified system, but the molecular masses attained are generally lower than those of polyisophthalamides.

Table I is a review of the prepared semiaromatic polyamides, preparation conditions and reduced viscosities obtained in concentrated sulphuric acid. A comparison with the results of Ogata[2] shows that polymers of sulfficiently high degrees of polymerization can be obtained using the derivatives of hexanelactam which undergo aminolysis more readily than acyllactams derived from 4-butanelactam or 12-dodecanelactam and at reaction times corresponding to the slower aminolysis to the second degree.

Although model aminolyses[1] have demonstrated that the acylbis(lactams) investigated in this study undergo a selective splitting of the exocyclic bond, the ^{1}H-NMR spectra of solutions of some polyamides in formic or trifluoroacetic acid indicate the presence of hexanelactam or hexaneamide units. The amounts of hexaneamide units in the polymers derived from *m*-xylylenediamine could be estimated from the weak signals of —N—CH$_2$—C, C—CH$_2$—CO and C—(CH$_2$)$_3$—C in the range of ϱ 6·7—9·2 ppm, while these amounts in other polymers (with the exception of derivatives of 4,4'-diaminodicyclohexylmethane) could be guessed from the peak of C—CH$_2$—CO— (ϱ 7·8 ppm). The upper boundaries of these estimates are given in Table I. The polymers prepared from *m*-xylylenediamine exhibited after reprecipitation (from a 3 : 1 mixture of formic and trifluoroacetic acids into ethanol) a certain decrease in these peaks, so that at least a part of them is due to free hexanelactam absorbed in the polymers.

Aminolysis with 1,n-*Diaminopoly(oxyethylene)*

The different reactivities of N-carbonylhexanelactam groups in N,N'-isophthaloylbis(hexanelactam) in the aminolysis to the first and second degrees[1] were utilized in the preparation of poly(oxyethylenes) containing terminal N-acyllactam groupings and in the extension of poly(oxyethylene) chains. Slow addition of the polymeric diamine to the excess of acylbis(lactam) dissolved in THF (procedure *A*) results in a modification of endgroups of the individual poly(oxyethylene) chains by aminolysis to the first degree without any perceptible chain coupling (Scheme 3); the reactive polymer thus formed may serve as an activator in the preparation of block copolymers of oxirane *via* the anionic polymerization of lactams[11]. Long-term aminolysis performed with various stoichiometric ratios of acylbis(lactam) and amine groups (procedure *B*) gave extended poly(oxyethylene) chains composed of basic chains joined with isophthalamide segments; in some cases, this polymer was employed in the preparation of extended-chain poly(oxyethylene) terminated with N-acyllactam groupings.

Table II contains a review of polyoxyethylenes modified by a reaction with N,N'-isophthaloylbis(hexanelactam). They are characterized by intrinsic viscosity measured in benzene at 25°C and the number average molecular mass calculated from the equation $M_n = 137{\cdot}6[\eta]^{1{\cdot}37}$ (*cf.* Experimental). Benzene was used as solvent according to the results of Müh[12]. The number average molecular mass of polymers terminated with acyllactam groups was assessed from the endgroup determination by alkaline hydrolysis. The molecular masses thus obtained are in a relatively good agreement with the values calculated from the molecular mass of the initial 1,n-diaminopoly(oxyethylene) ($M_n = 1950$) determined by the VPO method and from the increments of isophthalamide links and isophthaloyl-6-hexanelactam endgroups.

EXPERIMENTAL

Chemicals

The preparation of N,N'-isophthaloylbis(hexanelactam) and N,N'-terephthaloybis(hexanelactam) and the purification of solvents have been described earlier[1]. 1,6-Diaminohexane, 1,4-diaminobutane and *m*-xylylenediamine (Fluka) have been repeatedly distilled under argon at reduced pressure with the addition of solid KOH. 1,12-Diaminododecane (Aldrich) and 4,4'-diaminodicyclohexylmethane (mixture of isomers, Fluka) were transformed into dihydrochlorides which were purified by crystallization from aqueous ethanol. After their release from the aqueous solution of dihydrochloride by hydroxide, the diamines were extracted into benzene and crystallized from concentrated benzene solutions. 1,n-Diaminopoly(oxyethylene) (prepared at the Petrochemical Research Institute, Nováky) contained 1·083 mol NH_2/kg after reprecipitation into diethyl ether; $M_n = 1950$ was determined by the VPO method in benzene.

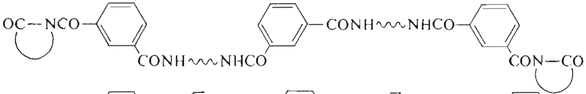
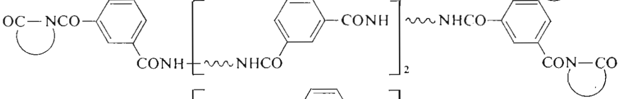
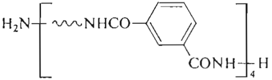
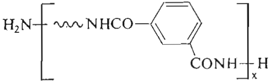
Semiaromatic Polyamides by the Aminolysis of Acylbis(lactams)

In a 15 or 50 cm^3 glass ampoule provided with two ground necks, a solution of N,N'-isophthaloyl or N,N'-terephthaloyl-bis(6-hexanelactam) was prepared under inert atmosphere. The solution was mixed with a corresponding amount of diamine in a flask attached to the ampoule, the latter was sealed and placed in a thermostat at 50°C (80°C). On completed aminolysis, the polymer was precipitated (polyisophthalamides) or additionally precipitated (polyterephthal-

TABLE II

Chain Extension of 1,n-Diaminopoly(oxyethylene) and Synthesis of Polymeric N,N'-Dicarbonylbis(hexanelactams) by Aminolysis of N,N'-Isophthaloylbis(6-hexanelactam) (THF, 50°C)

Wavy line in the structure indicates the poly(oxyethylene) chain.

Structure of product	Procedure	Ratio NH_2/lactam	t h	$\overline{M}_n{}^a$	$\overline{M}_n{}^b$	$\overline{M}_{calc.}{}^c$
	*A*	1 : 2·4	2	2 472	2 682	2 436
	*B* *A*	4 : 1 1 : 2·4	145 2	4 614	4 843	4 486
	*B* *A*	3 : 1 1 : 2·4	168 2	6 216	7 657	6 578
	*B*	8 : 3	150	9 869	—	8 192
	*B*	2 : 1	150	17 520	—	—

Molecular mass determined: [a] from intrinsic viscosity in benzene (25°C); [b] from the concentration of N-carbonyl-6-hexanelactam terminal groups; [c] from the suggested structure.

amides) in ethanol (polyamides prepared from 1,4-diaminobutane and 1,12-diaminododecane were precipitated in water), extracted with boiling water and dried *in vacuo* 0·13 kPa at 50°C. The viscosities in 96% H_2SO_4 were measured at 25°C and concentrations 4 g dm^{-3}. ^{1}H-NMR spectra of 10% solutions in formic or trifluoroacetic acids were recorded with a JEOL 100 spectrometer.

Aminolysis with 1,n-Diamino(polyoxyethylene)

Procedure A — *preparation of modified poly(oxyethylene)*: To a solution of 2·0 g N,N′-isophthaloyl(6-hexanelactam) (5·6 mmol) in 50 cm^3 of absolute THF stirred and heated to 50°C, a solution of 2 g 1,n-diaminopoly(oxyethylene) (2·16 mmol NH_2) and 0·05 cm^3 triethylamine in 30 cm^3 THF was added within 2 h, and the reaction mixture was heated for another 3 h. The THF solution was evaporated *in vacuo*, the residue was dissolved in distilled water and unreacted acylbis(lactam) was removed by filtration; the aqueous filtrate was evaporated *in vacuo*, the residue was dehydrated by repeated evaporation with benzene, extracted with heptane (removal of hexanelactam) and lyophilized from benzene solution. A similar route was employed n the modification of endgroups of extended-chain POE prepared by procedure *B*.

Procedure B - *extension of poly(oxyethylene) chains*: 5 g of 1,n-diaminopoly(oxyethylene) and a corresponding amount of N,N′-isophthaloyl(6-hexanelactam) were dissolved in 5 cm^3 THF in a glass ampoule, a drop of triethylamine was added, the ampoule was rinsed with argon, sealed and placed in a thermostat at 50°C. After aminolysis, the reaction solution was treated as sub procedure *A*.

The relation between the intrinsic viscosity $[\eta]$ and molecular mass of poly(oxyethylene) $M_n = 137{\cdot}6[\eta]^{1{\cdot}37}$ was ascertained from the viscosities of commercial polymers on the basis of the number average molecular mass indicated by the producer, *i.e.* without fractionation and reprecipitation of the samples. The relation was derived by linear regression of data log M_n *vs* log $[\eta]$ with an accuracy expressed through the correlation coefficient 0·9963. The $1/[\eta]$ values were determined by extrapolation of the value of $0{\cdot}5[c/(\eta_{rel} - 1) + c/\ln \tau_{rel}]$ to $c \rightarrow 0$; η_{rel} was measured in benzene at 25°C in the concentration range $c = 4$—67 g dm^{-3}. Poly(oxyethylene) — mol.mass (producer), determined $[\eta]$ (cm^3 g^{-1}): 1000 (Koch-Light), 4·52; 2000 (Fluka), 6·66; 4000 (Fluka), 12·56; 6000 (Merck), 15·28; 10000 (Merck), 21·12; 20000 (BHD), 40·52.

The N-carbonyl-6-hexanelactam endgroupings were determined by hydrolysis of the polymer in 0·05M-NaOH (25°C, 15 min) and back titration of the excessive NaOH with 0·05M-HCl to phenolphthalein.

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