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Block copolymers of 6-hexanelactam and 12-dodecanelactam

Jaroslav Stehlíček*, Jan Hauer and Rudolf Puffr
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
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Poly(6-hexanelactam)-*block*-poly(12-dodecanelactam) (polyamide-6-*block*-polyamide-12) diblock copolymers containing a small portion of the corresponding homopolymers were prepared by the anionic polymerization of 6-hexanelactam using poly(12-dodecanelactam)s with diacylamine branching sites as precursors of polymeric initiators (PPI). The PPI were prepared by the acidolytic copolymerization of 12-dodecanelactam with *N*-benzoyl-12-dodecanelactam. The effect of PPI molecular structure on the composition and properties of the block copolymers was followed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: aliphatic block copolyamides; anionic polymerization; polymeric initiator)

INTRODUCTION

The anionic polymerization of lactams (APL) using polymeric initiators is a suitable method for the preparation of block copolymers with polyamide blocks. The best-known application of this method is the NyRIM technology producing tough block copolymers of propylene oxide with 6-hexanelactam (HL)[1]. Numerous diblock and triblock copolymers of polyamides with a variety of non-polyamide blocks have been prepared in this way in laboratories[2].

However, the preparation of copolymers consisting of blocks of different aliphatic polyamides is still a problem. The formation of block copolymers may be expected in the copolymerization of different lactams of diverse polymerizability under conditions when transamidation reactions can be neglected[2,3]. On the other hand, these transamidation reactions proceed during melt blending of two different homopolyamides relatively easily *via* the reactive end-groups and lead first to block and then to random copolyamides[4]. By the ways mentioned above, only poorly defined mixtures of homopolyamides with block to random copolymers of uncertain composition can be formed.

This study describes a polymerization method for the preparation of diblock copolyamides, viz. poly(6-hexanelactam)-*block*-poly(12-dodecanelactam) (polyamide-6-*block*-polyamide-12, PA6-*block*-PA12), by the anionic polymerization of 6-hexanelactam (HL) on poly(12-dodecanelactam) (PA12) initiators.

Initiators in APL are substances bearing an *N*-acyllactam grouping or its precursor, which is generally an acylating agent. Analogously, the polymeric initiator for the synthesis of diblock and triblock copolymers is a polymer with one and, respectively, two *N*-acyllactam end-groups. A polymeric acylating agent, e.g. acyl chloride, acyl anhydride, diacylamine, etc., giving the initiator by reaction with lactam monomer or its anion can be used as the precursor of polymeric initiator (PPI). The polyamide block propagates on this initiator by addition of lactam anions (activated monomer), which are continuously formed from the lactam (*Scheme 1*).

We have prepared PA12 PPI by the acidolytic copolymerization of 12-dodecanelactam (DL) and *N*-benzoyl-12-dodecanelactam (BDL). Such copolymerization of lactams having more than eight ring atoms with their *N*-acyl derivatives, which is initiated with carboxylic acids (or cationically in general), proceeds faster than the homopolymerization of unsubstituted lactams[5] and has been employed in the activated (accelerated) polymerization of higher lactams[6,7].

It was proved by ^{13}C n.m.r. spectroscopy[8] that the resulting polymer is not a simple copolymer consisting of monomeric units of DL and BDL but has a branched structure with diacylamine branching sites, where only a part of branches are the original benzoyls (*Scheme 2*). Its final structure corresponds to the transacylation equilibria between carboxylic, amide, imide and anhydride groups containing acyls of the initiating acid, starting acyllactam and also acyls of polyamide segments[6] (*Scheme 3*).

EXPERIMENTAL

Chemicals

6-Hexanelactam (HL) (technical grade, Spolana, Czech Republic) was twice crystallized for benzene; 12-dodecanelactam (DL) (technical grade, Hüls, Germany) was crystallized from benzene and methanol; benzoic acid (analytical grade) was sublimed. The method for preparation of *N*-benzoyl-6-hexanelactam (BHL) and *N*-benzoyl-12-dodecanelactam (BDL) was described elsewhere[9]. Before polymerization, all polymerization components were dried at ambient temperature and 13 Pa.

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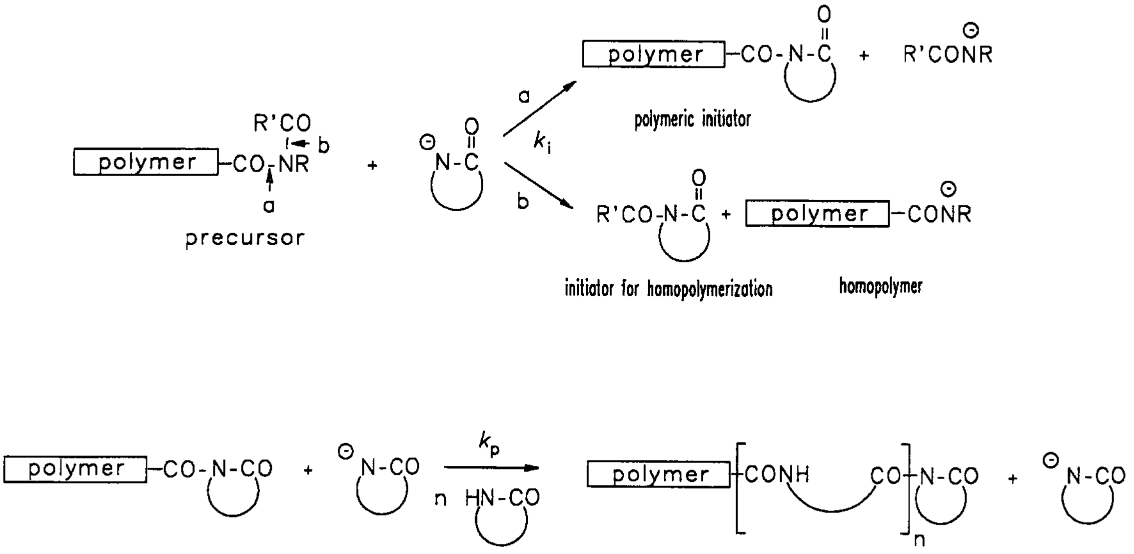
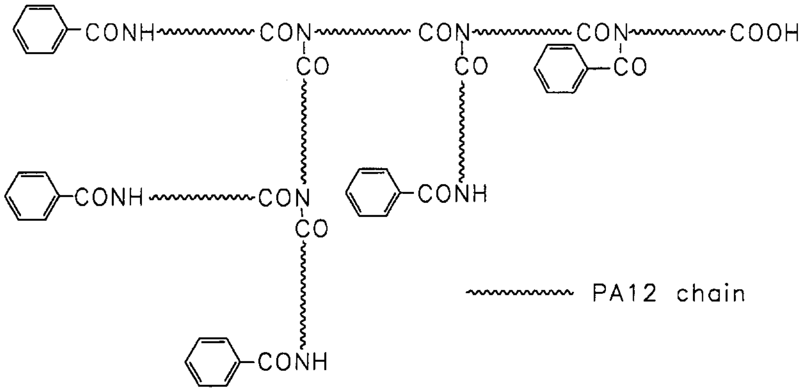
* To whom correspondence should be addressed



Scheme 1



Scheme 2

Model imides were prepared by benzoylation of the corresponding aliphatic amide in benzene (~0.4 mol l^{-1}) with an equivalent amount of benzoyl chloride in the presence of an equivalent amount of triethylamine at ambient temperature. After 3–4 days, triethylamine hydrochloride was filtered off. The concentrated filtrate was separated on a column of silica gel by elution with benzene and the collected imide fractions were fractionally distilled.

N-Acetyl-*N*-benzoylethylamine: b.p. approx. 115°C/ 13 Pa. $C_{11}H_{13}NO_2$ (191.23: calc. C 69.09, H 6.85, N 7.32; found C 69.10, H 6.85, N 7.25.

N-Butyryl-*N*-benzoylethylamine: b.p. 97°C/4.6 Pa. $C_{13}H_{17}NO_2$ (219.29): calc. C 71.21, H 7.81, N 6.39; found C 71.22, H 7.58, N 6.39.

N-Butyryl-*N*-benzoyloctylamine: b.p. 135°C/5.2 Pa. $C_{19}H_{29}NO_2$ (303.45): calc. C 75.21, H 9.63, N 4.62; found C 75.16, H 9.96, N 4.46.

Polymerizations and characterizations of polymers

Precursors of polymeric initiators (PPI) based on poly(12-dodecanelactam) (PA12) (*Table 1*) were prepared in sealed ampoules under vacuum. The product was disintegrated, extracted three times with boiling dry toluene, and dried at 60°C and 26 Pa for 10 h. The unreacted DL in the extract was determined by h.p.l.c. using a 150 × 3.2 mm column with Separon SIX C18 (7 μm, Tessek), methanol/H_2O (75/25 v/v, 0.5 ml min^{-1}) as an eluent and HL as an internal standard with u.v. spectrophotometric detection at 210 nm.

The content of pendent benzoyl groups was determined by heterogeneous aminolytic cleavage of 0.1 g PPI in 2 ml benzene with 7–20 μl butylamine (100–200% excess on imide groups) at 50°C for 200 h (Ar atmosphere, sealed ampoules). *N*-Butylbenzamide was determined by h.p.l.c. (column as above, eluent methanol/H_2O 60/40 v/v, 0.5 ml min^{-1}, *N*-ethylbenzamide as internal standard, detection at 254 nm).

The ratio of aminolytic cleavage of benzoyl to that of aliphatic acyl was determined with the model imides under the same conditions (imide concentration 0.4–0.5 mol l^{-1}) from the ratio of formed *N*-butylbenzamide to *N*-ethylbenzamide or *N*-octylbenzamide.

The sample of linear PA12 for polymerization blending (Lin in *Table 1*) was prepared in the same way as PPI and characterized by the viscometric number-average degree of polymerization (*m*-cresol, $c = 0.4\,g\,dl^{-1}$, 25°C)[10].

Anionic copolymerization of HL was carried out either in glass ampoules (i.d. 6 mm) with 2.5–3.0 g polymerization mixture or in a two-part aluminium mould, with a cavity 70 × 60 × 4 mm^3 and glass filling and venting necks, charged with 30 g polymerization mixture. PPI was dissolved in 60–80% of the total HL at 100–140°C, whereas the other part of HL

Table 1 Preparation of PA12 precursors of polymeric initiators (PPI)

	Components[a] (mol%)			Conditions				
No.	$[DL]_0$	$[BDL]_0$	$[A]_0$	T (°C)	t (h)	DL/DL_0[b]	$[I]$[c] (mmol g^{-1})	$\bar{P}_n$[d]
A1	94.6	3.6	1.8	240	15	0.046	0.188	52.4
A2	94.6	3.6	1.8	180	50	0.182	0.216	45.3
A3	74.5	17.1	8.4	180	5.5	0.139	0.906	9.7
A4	96.6	2.3	1.0	240	30	0.103	0.130	86.4
A5	85.2	11.4	3.4	200	9	0.115	0.609	25.6
A6	89.5	8.3	2.2	200	9	0.170	0.476	37.3
A7	95.0	4.5	0.5	200	123	0.213	0.279	176
Lin	98.6	–	1.4	280	50	0.289	0	50.1[e]

[a] DL, 12-dodecanelactam; A, benzoic acid; BDL, *N*-benzoyl-12-dodecanelactam

[b] Fraction of non-polymerized 12-dodecanelactam

[c] Content of imide groups in the extracted PPI

[d] Calculated from equation (3)

[e] $\bar{P}_n = 52$ determined by viscometry

served for the separate preparation of the solution of the sodium 6-hexanelactamate catalyst by reaction with sodium t-butoxide[11]. Both solutions were thoroughly mixed at 90–100°C and transferred under inert gas either to the ampoule, which was then immersed in a 180°C salt bath, or into the mould preheated to 170°C in a silicone-oil bath.

Anionic homopolymerization of HL in the presence of PA12 leading to blends was carried out in the same way. BHL was added as an initiator instead of PPI.

The extractable portion in the copolymerization product was determined by three successive extractions with boiling ethanol and drying at 60°C/130 Pa for 24 h. HL was determined in the extract by h.p.l.c. (conditions as stated above for DL, DL was an internal standard).

Number-average molecular weights of the extracted block copolymers PA6-*block*-PA12 or PA6–PA12 blends were determined from their intrinsic viscosity $[\eta]$ calculated from one viscosity measurement[12] (*m*-cresol, $c = 0.4\,g\,dl^{-1}$, 25°C) using the Mark–Houwink equation for PA6 (equation (6) in ref. 13).

The content of PA12 homopolymer in extracted PA6-*block*-PA12 was estimated by t.l.c.: 1 mg copolymer was dissolved in 0.1 ml 100% formic acid and 2 μl of the solution (20 μg sample) was applied as a spot ~4 mm in diameter on a 0.2 mm layer of Kieselgel G (Merck) on a $5 \times 25\,cm^2$ glass plate. Standard spots of the defined amount of PA12 homopolymer (0.2–2 μg) dissolved in formic acid/toluene (3/1 v/v) were applied at both sides. The plate was dried, developed with formic acid/water (25/10 v/v), thoroughly dried and visualized in iodine vapour. The PA12 homopolymer remains on the start, whereas the block copolyamide forms a 1.5–2.2 cm long spot with the centre at R_F 0.63–0.68. For estimation, the colour intensities of spots on the start were compared.

Competitive acylation with model imide

The reaction of *N*-butyryl-*N*-benzoylethylamine with the potassium salt of HL (KL) was carried out in tetrahydrofuran (THF) under the conditions described in ref. 14. Samples were withdrawn into THF containing an excess of acetic acid on KL and *N*,*N*-diphenylacetamide as an internal standard for h.p.l.c. analysis (for h.p.l.c. conditions, see model aminolyses). The ratio of KL benzoylation to butyrylation was calculated from the amounts of consumed model imide and formed *N*-ethylbenzamide.

RESULTS AND DISCUSSION

The poly(12-dodecanelactam) precursors of polymeric initiators (PPI)

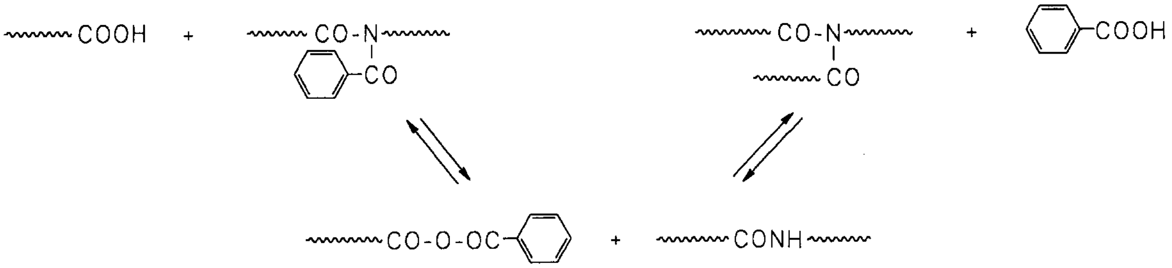
The PPI (*Table 1*) were synthesized by copolymerization of 12-dodecanelactam (DL) and *N*-benzoyl-12-dodecanelactam (BDL) with benzoic acid (A) as an initiator. The analyses of polymer extracts proved that BDL is completely incorporated into the polymer. For simplicity, we assumed a complete utilization of benzoic acid in the initiation and a negligible equilibrium concentration of anhydrides (*Scheme 3*). Fast transacylations shown in this scheme can acylate any of the chain amide groups during copolymerization and lead to the random distribution of imide groups and to substitution of most of the imide benzoyls with long branches of PA12 acyls. The resulting average molecule of PPI can be characterized by the following:

(1) Average number of imide groups i. Since every molecule of benzoic acid initiates the propagation of one polymer molecules[5,15]:

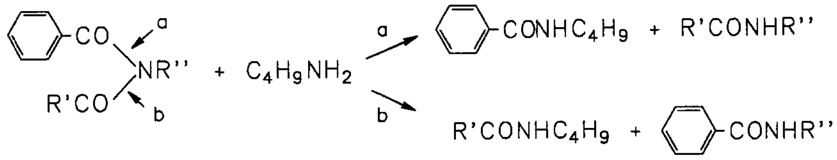
$$i = [BDL]_0/[A]_0 \qquad (1)$$

where $[BDL]_0$ and $[A]_0$ are the initial molar concentrations of BDL and A, respectively.

(2) Residual fraction of benzoyl imides μ, which is largest in non-equilibrium samples obtained at short polymerization times and low temperatures. We determined μ as *N*-butylbenzamide formed by aminolysis of PPI with butylamine under the conditions when only one acyl of diacylamine moiety is split off[16] (*Scheme 4*). In our case, one acyl is benzoyl and the other is derived from a long aliphatic carboxylic acid. The aminolysis of model *N*-acyl-*N*-alkyl benzamides (*Table 2*) revealed that there is no preference in the reaction of benzoyl or aliphatic acyl with butylamine in *N*-alkyl-*N*-acylbenzamides having longer acyls than acetyl. The acetyl derivative is an exception in which the acetyl splitting is favoured. Hence, the value of μ is twice as high as the yield of *N*-butylbenzamide found in the aminolysis of PPI.



Scheme 3



Scheme 4

Table 2 Aminolysis of the model imides $C_6H_5CON(R'')COR'$ with butylamine in benzene at 50°C

R'	R''	c_{imide} (mol l^{-1})	t (h)	$C_6H_5CONHBu$/ $R'CONHBu$ (mol/mol)
CH_3	C_2H_5	0.050	50	28/72
			100	29/71
			150	21/79
C_3H_7	C_2H_5	0.045	50	51/49
			100	51/49
			150	51/49
C_3H_7	C_8H_{17}	0.047	50	50/50
			100	47/53
			150	48/52

Table 3 Characteristics of PPI

No.	i^a	μ^b	i'^c	s^d	$\bar{P}_s^e$
A1	2.00	0.016	1.99	4.95	10.6
A2	2.01	0.024	1.99	4.93	9.2
A3	2.03	0.146	1.94	4.59	2.1
A4	2.26	0.000	2.26	5.52	15.7
A5	3.36	0.085	3.28	7.27	3.5
A6	3.75	0.063	3.68	8.12	4.6
A7	10.00	0.019	9.94	20.70	8.5

[a] Calculated number of imide branching sites per macromolecule (equation (1))

[b] Determined fraction of benzoyl imides in total imides

[c] Number of imides available for the initiation of PA6 blocks per macromolecule (equation (5))

[d] Number of PA12 segments (equation (2))

[e] Number-average degree of polymerization of a segment (equation (4))

(3) Number of PA12 branches and segments between imide groups:

$$s = i(2 - \mu) + 1 \qquad (2)$$

(4) Number-average degrees of polymerization of PPI molecule $\bar{P}_n$ and of its PA12 segment $\bar{P}_s$:

$$\bar{P}_n = ([DL]_0 - [DL] + [BDL]_0)/[A]_0 \qquad (3)$$

where $[DL]_0$ is the initial molar concentration of DL and $[DL]$ is the molar concentration of residual DL monomer. Consequently:

$$\bar{P}_s = \bar{P}_n/s \qquad (4)$$

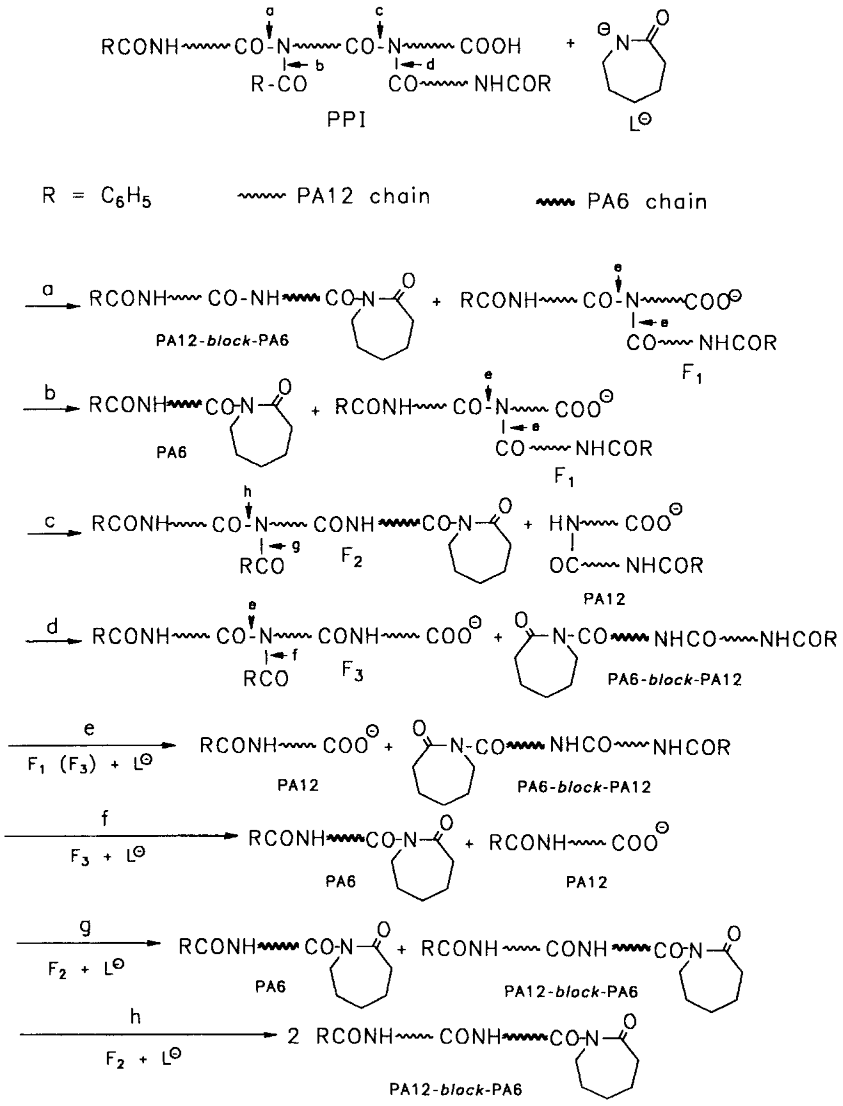
The basic characteristics of PPI are summarized in *Tables 1* and *3*.

Anionic block copolymerization of HL with PPI

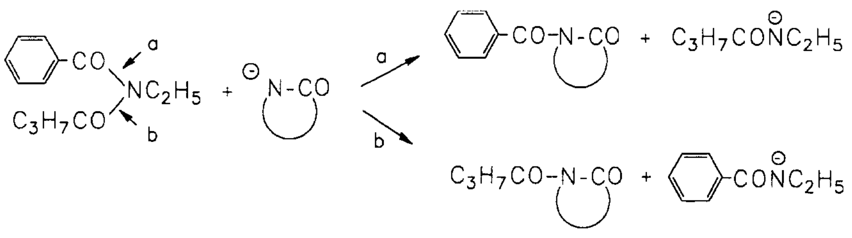
The amount of PA12 in the product of polymerization is limited by the solubility of PPI in HL. This solubility decreases with the increasing molecular weight of PPI. Because only temperatures up to about 100°C can be used for mixing of the components to avoid a premature onset of polymerization, we succeeded in using up to 20 wt% PPI. The polymerizations were completed below the melting temperature of the polymers. Polymerization time in glass ampoules was always longer than required for the crystallization and shrinking of the product. The conditions of polymerization are summarized in *Table 4*. As PPI always contains a known amount of carboxylic end-groups that need to be neutralized, the concentration of the basic catalyst (Na salt of HL) in the copolymerization mixture was correspondingly increased.

Mechanism of block copolymerization. The PPI starts the anionic polymerization of HL by acylation of an HL anion (activated monomer L^-) with one of its imide acyls, creating an *N*-acyl-6-hexanelactam propagation centre (*Scheme 1*). The acylation with a PA12 acyl leads to the block copolymer whereas the benzoylation leads to PA6 homopolymer. Various ways in which the multifunctional PPI can be transferred to monofunctional polymeric initiators are shown in *Scheme 5*. The formation of the propagating diblock copolymer PA6-*block*-PA12 or PA6 homopolymer and the residual PA12 homopolymer fragment is indicated for the original PPI macromolecule (acylations *a*–*d*) and subsequently for its fragments F_1, F_2, F_3 (acylations *e*–*h*).

It is evident that only half of the reactions indicated are realized because only one of two acyls in the imide



Scheme 5



Scheme 6

groups reacts. It is necessary to estimate the probability of their reaction. After all the imide groups of PPI are transformed to amide, a molecule of PA12 homopolymer results.

Fraction of PA6 homopolymer. In principle, aliphatic acyls of both the branches and the main chain acylate L⁻ with the same probability and start the formation of the block copolymer. On the other hand, the acylation capacity of pendent benzoyls could be different and cannot be derived from the competitive aminolysis presented above. Therefore, we have carried out the model reaction of *N*-butyryl-*N*-ethylbenzamide with HL anion in THF and estimated the proportion of butyrylation and benzoylation (*Scheme 6* and *Table 5*).

It turned out that butyrylation is highly favoured at the beginning of reaction and that it is never lower than about 70%, even at high conversions (up to the complete consumption of *N*-butyryl-*N*-ethylbenzamide). This means that only up to 30% of branching sites containing the benzoyl group will form the PA6 homopolymer. Hence, the maximum fraction of copolymerized HL incorporated in the PA6 homopolymer is 0.3μ, i.e. 4 wt% in our case.

Taking into account this upper limit of benzoyl initiation, the number of remaining branching sites

Table 4 Conditions of HL polymerization in the presence of PPI or linear PA12

No.	PA12[a] no.	wt%	$[\mathrm{I}]^b$ (mol%)	$[\mathrm{NAL}]^b$ (mol%)	Method[c]	t (min)	EP[d] (wt%)	HL[e] (wt%)
1	A1	9.2	0.21	0.29	G	20	17.1	16.0
2	A1	15.0	0.37	0.44	G	20	9.7	–
3	A1	15.0	0.37	0.50	G	61	2.8	–
4	A2	5.0	0.13	0.30	M	30	5.4	–
5	A2	10.0	0.28	0.45	M	30	3.8	–
6	A2	15.0	0.44	0.68	M	30	5.2	–
7	A2	20.0	0.62	0.70	M	30	5.6	–
8	A3	9.1	1.00	1.00	G	15	4.4	3.0
9	A4	9.1	0.13	0.20	G	40	4.0	3.8
10	A4	15.1	0.24	1.05	G	60	6.9	4.8
11	A5	9.4	0.70	0.91	G	30	4.0	2.3
12	A6	9.1	0.54	0.60	G	40	3.6	2.5
13	A6	15.0	0.94	0.94	G	30	4.7	3.0
14	A7	10.2	0.36	0.50	G	30	4.7	3.2
15	A7	15.0	0.56	0.70	G	30	5.5	3.2
16	–	0	0.40	0.40	M	30	2.7	–
17	Lin	5.0	0.40	0.40	M	30	2.8	–
18	Lin	10.0	0.40	0.40	M	30	2.9	–
19	Lin	15.0	0.60	0.60	M	30	2.4	–

[a] PPI or PA12 homopolymer used in the polymerization mixture; for PPI number see *Table 1*

[b] Concentration of initiator groups [I] and catalyst [NaL] (Na salt of HL) relative to $[\mathrm{HL}]_0$

[c] G, in glass ampoule, 180°C; M, in metallic mould, 170°C

[d] Portion extractable in ethanol

[e] Residual HL determined by h.p.l.c.

Table 5 Reaction of model imide $C_6H_5CON(C_2H_5)COC_3H_7$ with potassium salt of 6-hexanelactam in THF (molar ratio of components 1:1, $c_0 = 1.5 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$, 25°C)

Time (s)	Imide conversion (%)	Acylation ratio[a] C_3H_7CO/C_6H_5CO
29	2	100/0
170	25	96/4
317	41	73/27
2750	100	69/31

[a] From the molar ratio of the imide consumed to $C_6H_5CONHC_2H_5$ formed

available for the initiation of the PA6 block in the diblock copolymer is:

$$i' = i(1 - 0.3\mu) \qquad (5)$$

Length of PA12 blocks and fraction of PA12 homopolymer. Considering all acylation combinations, the length l_B of the PA12 blocks in the copolymer expressed as the average number of segments can range from 1 to i', whereas the length l_H of the residual PA12 homopolymer varies from 2 to $(i' + 1)$. The probability that the acyl chain formed in one of $2^{i'}$ possible acylation events has length k is $2^{(i'-k)}(k+1)$. Hence, the mean length of the remaining PA12 homopolymer is:

$$\bar{l}_H = 2(i'+1)2^{-i'} + \sum_{k=1}^{i'-1}(k+1)2^{-k} \qquad (6)$$

whereas the mean length of the PA12 block is:

$$\bar{l}_H = (2i' + 1 - \bar{l}_H)/i' \qquad (7)$$

This consideration neglects the predetermined way of acylation with 0.7μ sites containing benzoyls, but the resulting error will be small. For non-integer i', $\bar{l}_H$ was obtained by polynomial interpolation between the values calculated in the chosen interval of i' (in our case, $2 < i' < 10$).

The corresponding number-average degrees of polymerization of PA12 block and PA12 homopolymer are:

$$\bar{P}_B = \bar{l}_B\bar{P}_s \quad \text{and} \quad \bar{P}_H = \bar{l}_H\bar{P}_s \qquad (8)$$

respectively. The fraction of PPI present as PA12 homopolymer in the product is then:

$$\bar{l}_H/(i'\bar{l}_B + \bar{l}_H) \qquad (9)$$

Characterization of the copolymerization product. The portion extractable in ethanol and the residual HL were determined and number-average molecular weights $\bar{M}_v$ were calculated from intrinsic viscosity using the relationship for PA6. The amount of PA12 homopolymer was roughly estimated by t.l.c. These characteristics are shown in *Table 6* together with the calculated fractions of PA12 (equation (9)) and PA6 homopolymers, number-average molecular weights of PA6 blocks and homopolymer chains (calculated as $113.1([\mathrm{HL}]_0 - [\mathrm{HL}])/[\mathrm{BDL}]_0 + 105$), number-average molecular weights

Table 6 Characteristics of PA6-*block*-PA12 and PA6–PA12 blends obtained by HL polymerization

No.	ΣPA12[a] (wt%)	PA6[b] (wt%)	Block copolym.[b] (wt%)	PA12[b] (wt%)	Mol. wt × 10^{-4} $\bar{M}_6$[c]	$\bar{M}_\Sigma$[d]	$\bar{M}_v$[e]	$\bar{M}_{12B}$[f]	$\bar{M}_{12H}$[f]
1	9.6	0.4	94.1	5.5	4.29	4.56	5.26	0.27	0.53
2	16.6	0.4	91.8	7.8 (<10)	2.68	2.95	3.07	0.27	0.53
3	15.0	0.4	94.5	5.1 (~3)	3.02	3.29	3.36	0.27	0.53
4	5.3	0.7	96.7	2.7	8.30	8.54	8.78	0.24	0.46
5	10.1	0.7	94.3	5.1	4.13	4.37	4.67	0.24	0.46
6	15.8	0.6	91.5	7.9	2.46	2.70	3.36	0.24	0.46
7	21.2	0.6	88.8	10.6	1.72	1.96	2.29	0.24	0.46
8	9.5	4.0	91.2	4.8 (~1)	1.05	1.11	1.53	0.06	0.11
9	9.5	0	95.6	4.4 (<5)	7.35	7.76	8.35	0.41	0.81
10	16.2	0	94.5	5.5 (~5)	3.98	4.39	4.72	0.41	0.81
11	9.7	2.3	94.1	3.6 (~2)	1.52	1.63	–	0.11	0.20
12	9.4	1.7	95.1	3.1 (~2)	2.10	2.24	3.16	0.14	0.27
13	15.7	1.6	90.5	7.9 (~4)	1.13	1.27	2.01	0.14	0.27
14	10.7	0.5	98.0	1.5	2.99	3.30	3.28	0.31	0.51
15	15.9	0.5	91.6	8.0	1.90	2.21	2.79	0.31	0.51
16	0	100	0	0	6.20	–	–		
17	5.1	94.9	0	5.1	5.15	–	–		
18	10.3	89.7	0	10.3	3.94	–	–		
19	15.4	84.6	0	15.4	3.61	–	–		

[a] PA12 blocks and homopolymer in the extracted product

[b] Calculated fractions of PA6 homopolymer, PA6-*block*-PA12 and PA12 homopolymer in the product (in parentheses, t.l.c. estimation)

[c] Number-average molecular weight calculated for PA6 blocks and homopolymer

[d] $\bar{M}_\Sigma = \bar{M}_6 + \bar{M}_{12B}$

[e] Determined viscometrically as PA6

[f] Calculated for PA12 blocks and PA12 homopolymer (equation (8))

of PA12 blocks and homopolymer (equations (6)–(8)) and $\bar{M}_\Sigma$ of the product calculated additively from the molecular weights of the components. The values $\bar{M}_\Sigma$ are always somewhat lower than the measured values $\bar{M}_v$. The difference is not large and complies with the fact that the same intrinsic viscosity in *m*-cresol corresponds to much higher molecular weight of PA6 than of PA12. The comparison of measured and calculated $\bar{M}$ values corroborates the plausibility of the proposed mechanism of the anionic polymerization of HL on PA12 initiators formed from PPI.

Anionic polymerizations of HL containing dissolved PA12

The blends of PA6 and PA12 were prepared similarly to the block copolymers by polymerizing HL that contained dissolved linear PA12 with the anionic catalyst and a low-molecular-weight initiator (*Table 4*). The linear PA12 (Lin) was prepared by acidolytic polymerization; its characteristics and preparation conditions are given in the bottom line of *Table 1*.

The differences between the PA12 initiators and linear 'inert' PA12 were already observed in the course of polymerization carried out below the melting temperature of the product. With PPI, the polymerizations proceeded up to a high conversion of HL, giving a transparent homogeneous polymer mixture, which then crystallized in the whole mass. On the other hand, linear PA12 separated during polymerization of HL. The form of separated PA12 (from a uniform turbidity to a rough coagulate) and the conversion of HL at the onset of the separation depended on the initial concentration of PA12. The absence of a compatibilization effect of PA6-*block*-P12 in the case of polymerization blending meant that macroscopically homogeneous products were obtained only with up to 15% PA12.

CONCLUSIONS

Multifunctional precursors of polymeric initiators (PPI) suitable for the anionic block copolymerization of 6-hexanelactam (HL) were prepared by the copolymerization of 12-dodecanelactam (DL) with 2–17 mol% *N*-benzoyl-12-dodecanelactam (DBL) initiated with benzoic acid (A).

As a consequence of transacylation reactions (*Scheme 3*), an average PPI molecule has the structure of PA12 branched on 2–9 imide groups (*Scheme 2*). The branches are formed by PA12 acyls and, to a lesser extent, by the original benzoyl groups. The concentration of benzoyl branches was determined by the aminolysis of PPI using the results of aminolysis of model *N*-benzoylamides.

In the anionic HL polymerization carried out in bulk in the presence of dissolved PPI, the PA12 acyls of imide groups acylate HL anions (L^-) giving monofunctional polymeric initiators. The block copolymer PA6-*block*-PA12 propagates on these initiators (*Schemes 1* and *5*). The acylation of L^- with benzoyl branches gives the propagation centres of PA6 homopolymer. A molecule of PA12 homopolymer remains as a residue from each

PPI molecule after splitting off the acyl branches. The acylation reactivity ratio of benzoyl and aliphatic acyls 30:70 was determined with *N*-butyryl-*N*-benzoylethylamine as a model at 25°C.

The product of copolymerization with 5–21 wt% PPI is a compatibilized mixture of immiscible polyamides PA6-*block*-PA12 (89–98 wt%), PA6 (0–4 wt%) and PA12 (1–11 wt%). The PA6 blocks as well as homopolymer, PA12 blocks and PA12 homopolymer have the ranges $\bar{M}_n = (1-8) \times 10^4$, $(0.5-5) \times 10^3$ and $(1-8) \times 10^3$, respectively.

The blends PA6–PA12 were also prepared by the anionic polymerization of the solution of PA12 in HL for comparison. Owing to the limited solubility, the maximum content of PA12 was only 15% in this case.

Although this study concerns the systems containing PA6 and PA12 components, it is applicable to other combinations of various polyamides and copolyamides[17]. The prepared materials show interesting differences in crystallization behaviour and physical properties, which are discussed in the next paper[18].

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