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Block copolymers of hexano-6-lactam with *N*-methylated aliphatic (co)polyamides

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Abstract

Diblock copolymers consisting of poly(hexano-6-lactam) hard blocks and highly *N*-methylated (or *N*-ethylated) softer blocks of poly(dodecano-12-lactam) or poly(octano-8-lactam) were prepared by anionic polymerization of hexano-6-lactam initiated with diacylamine branching sites of multifunctional precursors of polymeric initiators (PPI). The PPI were prepared by the acidolytic copolymerization of the respective *N*-alkyllactams (≥90 mol%), *N*-benzoyllactams (≤5 mol%) and lactams (≤5 mol%). The method provides diblocks accompanied by small amounts of the homopolymers. The PPI and block copolymers were chrraracterized by ^{1}H NMR, imide and carboxyl group analysis, viscosity, SEC, DSC, mechanical properties and water sorption. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Lactam polymerization; *N*-methylated block copolyamides; Physical properties

1. Introduction

Block copolymers with blocks of aliphatic polyamides have been often prepared by anionic polymerization of lactams in the presence of non-polyamide polymeric initiators. The well-known Nylon RIM technology is the application of such preparation method. In our previous paper [1], diblock copolymers consisting of poly(hexano-6-lactam) (PA6) and poly(dodecano-12-lactam) (PA12) blocks were prepared by anionic polymerization of hexano-6-lactam (HL) using PA12 with diacylamine branching sites as precursors (PPI) of polymerization initiator (PI). The initiation function of PPI containing, e.g. three diacylamine sites is shown in Scheme 1. The acyllactam initiators of the subsequent polymerization of HL are formed by the transacylation cleavage of PPI with HL anions.

The PPI resulted from acidolytic copolymerization of dodecano-12-lactam with *N*-benzoyldodecano-12-lactam initiated with benzoic acid [2] via transacylation reactions leading to polymeric *N*-acyl branches [3]. The prepared block copolymer always contains minor parts of PA12 and PA6 homopolymers, the amount of which as well as other characteristics of the product are dependent on the PPI characteristics. Some special features concerning the crystallization behavior and morphology of the block copolymers were observed [4] in comparison with the

PA6–PA12 blends. However, the PA12 blocks cannot substantially modify physical properties of PA6 because both polyamides do not differ much in melting temperature, T_m, degree of crystallinity, and other properties. This has been the reason why we extended our method in the present study to block copolymers where crystalline PA6 blocks are combined with amorphous or low-melting blocks of aliphatic polyamide, mainly with the blocks of poly(*N*-methyldodecano-12-lactam) (MePA12).
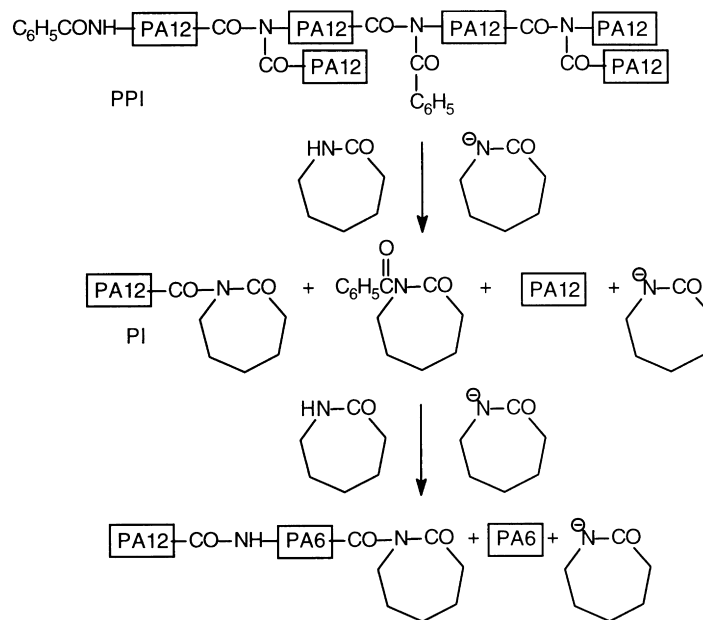
2. Experimental

2.1. Chemicals

N-methyldodecano-12-lactam (MeDL), *N*-methyloctano-8-lactam (MeOL), and *N*-ethyl-dodecano-12-lactam (EtDL) were obtained by rearrangement of the corresponding *O*-alkyllactims prepared from lactams and dialkyl sulfates [5,6] and purified by vacuum rectification through a 25 cm column packed with stainless-steel spirals. They were characterized by boiling points and GLC purity: MeDL 150°C/14 Pa, >99.9%; MeOL 116°C/26 Pa, >99.9%; EtDL 120°C/1.3 Pa, >99.3%. For purification and provenience of hexano-6-lactam (HL), dodecano-12-lactam (DL), benzoic acid, *N*-benzoylhexano-6-lactam (BHL) and *N*-benzoyldodecano-12-lactam (BDL), see Ref. [1]. Octano-8-lactam (OL) (BASF, Germany) was three times crystallized from acetone and once from benzene, m.p.

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C_6H_5CONH—[PA12]—CO—N—[PA12]—CO—N—[PA12]—CO—N—[PA12]

PPI

[PA12]—CO—N—CO + $C_6H_5\overset{O}{C}N$—CO + [PA12] + N—CO

PI

[PA12]—CO—NH—[PA6]—CO—N—CO + [PA6] + N—CO

Scheme 1.

74.0–74.5°C; for preparation of *N*-benzoyloctano-8-lactam (BOL), see Ref. [3].

2.2. Precursors of polymeric initiators (PPI)

The PPI and the model homopolymer of MeDL were prepared in ampoules sealed under vacuum, under conditions given in Table 1. The viscous amorphous polymers of MeDL and MeOL were spread on a polyethylene film, allowed to crystallize in part, cut into pieces, extracted three times by refluxing in anhydrous diethyl ether, cooling and decantation, and dried in vacuum at 13 Pa and room temperature. The copolymer of MeOL and OL was similarly extracted under cooling below 0°C.

The unreacted monomers in the extract were determined by GLC using a 2 m (i.d. 2 mm) stainless-steel column
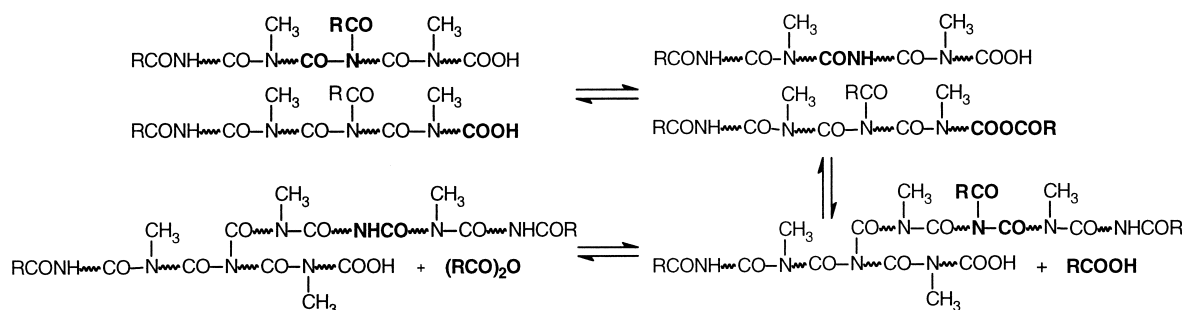
Table 1
Synthesis and composition of precursors of polymeric initiators (PPI) based on branched copolymers of *N*-methyllactams, MeL (MeDL = *N*-methyldodecano-12-lactam, MeOL = *N*-methyloctano-8-lactam, EtDL = *N*-ethyldodecano-12-lactam), *N*-benzoyllactams, BL (BDL = *N*-benzoyldodecano-12-lactam, BOL = *N*-benzoyloctano-8-lactam), and lactams, L (DL = dodecano-12-lactam, OL = octano-8-lactam)

PPI	Components (mol%)					Time (h)	Temp. (°C)	Unreacted $[MeL]/[MeL]_0$	PPI composition (mol %)		
	$[MeL]_0$	$[BL]_0$	$[L]_0$	[BzOH]	[AlCl$_3$]				$[MeL]_p$	$[BL]_p$	$[L]_p$
	MeDL	BDL	DL								
A1	90.89	5.01	2.00	1.98	0.34	50	180	0.031	90.63	5.15	2.06
A2	89.41	5.15	4.17	1.03	0.73	40	180	0.031	89.11	5.30	4.29
A3	88.87	5.20	5.21	0.56	0.47	96	180	0.054	88.31	5.46	5.47
A4	89.35	4.97	4.97	0.55	0.48	114	180	0.075	88.58	5.33	5.32
A5	89.30	4.96	4.98	0.66	0.30	133	180	0.354	84.34	7.26	7.29
A6	89.24	5.01	5.01	0.60	0.39	144	180	0.166	87.38	5.88	5.88
A7	87.47	4.88	4.87	2.78	0.00	150	180	0.728	65.55	13.42	13.40
A8	89.52	4.98	4.98	0.40	0.37	120	180	0.541	79.70	9.65	9.64
A9	29.92[a]							0.740[a]	18.76[a]		
	60.24[b]	4.63	4.63	0.56	0.03	50	200	0.604[b]	57.53[b]	11.17	11.17
	MeOL	BOL	OL								
A10	89.02	5.25	5.07	0.47	0.56	153	180	0.209	86.52	6.45	6.23
MeDL homopolymer for polymerization blending											
Lin	96.78	–	–	3.22	–	64	240	0.222	100	0	0

(MeL_0, MeL—initial and final concentrations of MeL; MeL_p, BL_p, L_p—concentrations of monomer units in PPI, BL_p includes imide branching units.)
[a] EtDL.
[b] MeDL.

CH₃ RCO CH₃
RCONH∿CO–N∿CO–N∿CO–N∿COOH

CH₃ RCO CH₃
RCONH∿CO–N∿CO–N∿CO–N∿COOH

⇌

CH₃ CH₃
RCONH∿CO–N∿CONH∿CO–N∿COOH

CH₃ RCO CH₃
RCONH∿CO–N∿CO–N∿CO–N∿COOCOR

CH₃ CH₃
CO∿N–CO∿NHCO∿N–CO∿NHCOR
CH₃
RCONH∿CO–N∿CO–N∿CO–N∿COOH + (RCO)₂O
CH₃

⇌

CH₃ RCO CH₃
CO∿N–CO∿N–CO–N–CO∿NHCOR
CH₃
RCONH∿CO–N∿CO–N∿CO–N∿COOH + RCOOH
CH₃

Scheme 2.

packed with 5% Carbowax 20M on Chromosorb W; column temperature 180°C; carrier gas nitrogen, 40 cm³ min⁻¹; FID; HL as an internal standard.

The concentrations of COOH end-groups and imide branching sites I were determined by conductometric titration in propan-2-ol/water solutions using 0.1 M sodium 2-propoxide in propan-2-ol for the direct titration of COOH and in excess for the alkaline hydrolysis of imide (60°C/30 min) and the back titration with 0.1 M aqueous HCl.

The concentration of pendent benzoyl groups B was determined by aminolysis in benzene as described earlier [1].

Viscometric average molecular weight of PPI was determined in THF solutions at 25°C using the published Mark–Houwink parameters for the MeDL homopolymer [7].

Number- and weight-average molecular weights were determined by SEC using a H-P 1090 chromatograph, H-P 1037A differential refractometer, 600 mm × 7.5 mm column with PL-gel 10 μm MIXED (Polymer Laboratories), THF as a mobile phase and calibration with polystyrene standards.

2.3. Anionic polymerization of HL with PPI

Polymerizations were carried out either in glass ampoules or in an aluminum mould as described in Ref. [1]. Sodium hexano-6-lactamate and magnesium hexano-6-lactamate bromide polymerization catalysts were prepared by the addition of sodium *tert*-butoxide in THF [1] and ethyl magnesium bromide in diethyl ether [8], respectively, to an excess of HL and evaporation in vacuum. The polymer blend consisting of PA6 and MePA12 was prepared similarly with BHL added as an initiator instead of PPI.

The portions of the polymerization products non-extractable with boiling water or ethanol were determined by three successive extractions (150 ml solvent/0.5 g copolymer shavings) and drying at 60°C/130 Pa for 24 h. HL was determined in the collected ethanolic extracts by HPLC [1].

Poly(MeDL-*co*-DL) copolymer, separated from the block copolymer by extraction with ethanol, was characterized in some cases by SEC as described above for PPI.

The ¹H NMR spectra were recorded on a Bruker AC-F-300 spectrometer at 300.1 MHz with 10% (w/v) solutions of extracted polymers in formic acid–D₂O (9:1 (v/v)) and HMDS as an internal standard.

DSC (first runs from −20 to 250°C at 10°C min⁻¹) and water sorption measurements were performed with water-extracted samples, while mechanical properties with non-extracted dry samples under the conditions described earlier [4].

3. Results and discussion

3.1. Precursors of polymeric initiators (PPI)

It is known that acidolytic and cationic polymerizations of *N*-methyl derivatives of higher lactams, viz. *N*-methyldodecano-12-lactam (MeDL), proceed faster than that of the corresponding nonsubstituted lactams [9]. However, in contrast to DL and OL, the polymerization cannot be further accelerated by the addition of *N*-acyllactams. Such an acceleration is based on the very fast polymerization of *N*-acyllactam and a fast transacylation of lactam with *N*-acylamide monomer units of the polymer formed [2], which is excluded with *N*-methyllactams. For this reason, the acidolytic polymerization was accelerated by the addition of AlCl₃ as an efficient cationic catalyst [10,11].

The desired structure of PPI with polymeric diacylamine branching sites can be theoretically obtained in the copolymerization of *N*-acyllactam with *N*-methyllactam, e.g. of *N*-benzoyldodecano-12-lactam (BDL) with MeDL, only at the expense of an increasing molecular weight of the copolymer and formation of the low-molecular weight anhydride (benzoic anhydride) (Scheme 2) by the exchange of acyls between *N*-acyllactam monomer units of the chain and terminal carboxyls via anhydride. However, this is not very effective because the reverse reaction has obviously the same chance to occur. Therefore, the unsubstituted lactam DL was added as further comonomer in order to introduce more amide groups on which the acylation can proceed and thus attain the transacylation equilibrium between benzoyls and long-chain acyls. For the composition of copolymerization mixtures, polymerization conditions, and the calculated concentration of individual monomer units in the resulting PPI, see Table 1.

Table 2
Characteristics of PPI

PPI	[I]^a (mmol g^{-1})		[COOH]^b (mmol g^{-1})		[B]^c (mmol g^{-1})	$\bar{M}_n{}^d$ $\times 10^{-3}$	$\bar{M}_v{}^e$ $\times 10^{-3}$	$\bar{M}_{gpc}{}^f$ $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	i^g	$\bar{M}_{(b+h)}{}^h$ $\times 10^{-3}$
	Detd.	Calcd.	Detd.	Calcd.							
MeDL											
A1	100	99	114	115	–	8.8	8.4	9.5	2.9	**0.86**	**4.7**
A2	–	203	–	86	–	11.7	11.8	–	–	**2.36**	**3.5**
A3	–	256	–	51	–	19.7	–	11.7	4.9	**5.01**	**3.3**
A4	224	249	52	52	10.4	19.3	–	15.3	2.9	**4.31**	**3.6**
A5	197	340	63	66	9.5	15.3	11.6	11.4	3.7	3.13	3.7
A6	118	275	51	55	12.7	18.4	10.8	19.0	3.1	2.31	5.5
A7	152	652	338	372	111	2.8	4.8	3.8	2.7	0.45	1.9
A8	208	445	48	69	43.7	14.5	11.9	9.0	3.1	4.33	2.73
EtDL/MeDL											
A9	–	509	–	94	36.6	15.5	–	–	–	**7.83**	**1.8**
MeOL											
A10	–	312	–	80	–	12.5	–	–	–	**4.90**	**2.1**
MeDL homopolymer for polymerization blending											
Lin	0	0	155	161		6.3	10.2	12.3	2.0		

^{a} Imide branching sites (titrimetrically and calculated from PPI composition).
^{b} Carboxylic end groups.
^{c} Pendent imide benzoyls in PPI.
^{d} Calculated.
^{e} THF, 25°C (for Mark–Howing parameters, see Ref. [6]).
^{f} GPC (polystyrene standards).
^{g} Number of imide groups per PPI macromolecule, $i = [BL]/([BzOH] + 3AlCl_3])$.
^{h} Estimated average molecular weight of MeL blocks and homopolymer $\bar{M}_{(b+h)} = \bar{M}_n/(i + 1)$ (figures in bold are derived from calculated values of [I]).

The yield of MeDL incorporated in the copolymer is 27–97%, whereas DL and BDL were copolymerized quantitatively. In contrast to PPI based on the non-*N*-substituted DL, the resulting copolymers are soluble in common polar solvents and can be better characterized.

The characteristics of PPI are surveyed in Table 2. Their composition was calculated from the yields of copolymerization. Molecular weights calculated from the concentration of the catalysts used (AlCl$_3$ is considered trifunctional with respect to the initiation of polymer chains), determined viscometrically and by GPC, are reasonably similar in most cases in spite of the limitations given by variations in hydrodynamic properties of differently branched macromolecules and the GPC calibration by polystyrene standards.

It was also possible to determine the contents of carboxyl end groups and imide groups, I, by titration. The majority of I groups are polymer-branching sites, the remaining part are benzoylimides, B. The ratio B/I is largest in non-equilibrium samples obtained with low concentration of AlCl$_3$ catalyst. The mixed anhydride end groups (Scheme 2), if present, are determined as both imide groups (groups easily cleaved by alkaline hydrolysis) and carboxy end groups. The determined *I* values are considerably lower than those calculated from the initial composition of monomers. The loss of imide groups cannot be ascribed to the formation of benzoic anhydride (Scheme 2) because it is not accompanied by a decrease in carboxyls. Moreover, benzoic anhydride was not found by HPLC in the PPI before their extraction.

The titrimetrically determined and calculated concentrations of carboxy end groups are in a good agreement. We assume that the presence of AlCl$_3$ is responsible for at least a part of the imide loss, but the mechanism is not clear. An indirect evidence indicated that the DL-based PPI prepared without AlCl$_3$ had a higher initiation effect in the anionic polymerization of hexano-6-lactam (HL) than the PPI based on MeDL.

3.2. Synthesis of block copolymers

The anionic polymerization of HL proceeds in the presence of PPI, characterized by the number of imide (diacylalkylamine) groups per molecule, *i*, and benzoylimides, *b*, according to Scheme 1, where the indicated PA12 blocks have to be replaced by MePA12-*co*-PA12 blocks. Theoretically, this would result in up to *i* macromolecules of the AB copolymer, up to *b* chains of PA6, and one molecule of low-molecular weight random copolymer MePA12-*co*-PA12, the remaining deacylated segment from PPI.

Polymerization conditions are presented in Table 3. Two types of catalysts were used: magnesium hexano-6-lactamate bromide (MgBrL) successfully replaced sodium hexano-6-lactamate (NaL) where it was difficult to attain low amounts of residual monomer because of a low concentration of the initiating groups, [I], or the polymerization rate reduced by higher dilution with PPI. The higher efficiency of MgBrL is caused by the suppressed side

Table 3

Synthesis of block copolymers poly(hexano-6-lactam)-*block*-poly(*N*-methyllactam(s)-*co*-lactam) by anionic polymerization of hexano-6-lactam (HL) in the presence of PPI and sodium hexano-6-lactamate (NaL) or magnesium hexano-6-lactamate bromide (MgLBr) as a catalyst

Product no.	PPI		Initiation system			Polymerization		Extractables, wt%		$[HL]/[HL]_0(\%)$[a]
	no.	wt%	Imide[b] (mol%)	Catalyst[b]	(mol%)	Method[c]	Time (min)	H_2O	EtOH	
PA6-*block*-poly(MeDL-*co*-DL)										
1	A6	5	0.07	MgLBr	1.0	M	30	4.4	6.1	4.0
2	A6	8.1	0.12	MgLBr	0.8	M	30	6.1	13.1	8.3
3	A2	9	**0.23**	NaL	0.5	G	30		9.0	4.5
4	A5	10	0.25	NaL	1.1	M	30	9.7	16.8	8.8
5	A6	10	0.15	MgLBr	1.0	M	30	4.7	4.6	2.2
6	A6	15	0.24	MgLBr	1.0	M	30	3.3	5.5	2.1
7	A2	15	**0.40**	NaL	0.6	G	30		10.0	1.9
8	A1	15	**0.20**	NaL	0.7	G	30		13.0	2.7
9	A3	15	**0.51**	NaL	0.7	G	30		10.0	1.9
10	A5	20	0.56	NaL	1.1	G	30	3.0	11.2	0.9
11	A5	20	0.56	NaL	1.4	M	30	3.5	12.9	2.3
12	A6	20	0.33	MgLBr	1.0	G	30	10.0	11.7	3.0
13	A6	20	0.33	MgLBr	1.0	M	30	3.0	8.2	1.3
14	A7	25	0.57	MgLBr	1.8	G	15	6.6	21.5	2.7
15	A8	25	0.79	MgLBr	1.0	G	15	4.3	15.7	1.7
16	A3	25	**0.97**	NaL	1.5	G	60		11.0	7.6
17	A4	25	**0.94**	MgLBr	0.9	G	30		15.0	1.7
18	A1	30	**0.48**	NaL	1.0	G	30		17.0	3.8
PA6-*block*-poly(MeOL-*co*-OL)										
19	A10	9	**0.44**	NaL	0.9	G	30		5.0	4.2
PA6-*block*-poly(EtDL-*co*-MeDL-*co*-DL)										
20	A9	20	**0.98**	MgLBr	1.2	G	30		11.0	1.6
Polymerization blend PA6/MePA12										
21	(Lin)	5	0.60[d]	MgLBr	0.6	M	30	7.1	10.5	4.7

[a] Unreacted HL determined by HPLC.

[b] Relative to $[HL]_0$.

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

[d] Initiator *N*-benzoylhexano-6-lactam.

condensation reactions consuming the propagation centers [8].

3.3. Characteristics of block copolymers

Extractable portions. Polymerization products are characterized in Table 3 by portions extractable with boiling water and/or ethanol and by the content of unreacted HL. Water extracts closely relate to the determined unreacted HL also containing cyclic HL oligomers and small amounts of linear HL oligomers.

Ethanolic extracts are higher than would correspond to the remaining copolymer poly(MeDL-*co*-DL) and correlate with the concentrations of the PPI used. The main part of solids obtained by the extract evaporation is insoluble in THF or MeOH and obviously consists of the block copolymer with shorter blocks of PA6. The MeOH-soluble part was used for the determination of unreacted HL. The THF-soluble part was analyzed by GPC and contained small amounts of low-molecular weight poly(MeDL-*co*-DL), see footnote in Table 4.

Composition of extracted block copolymers is surveyed in Table 4. The content of poly(MeDL-*co*-DL) blocks was calculated from the PPI and $[HL]/[HL]_0$ values (Table 3) as $PPI/[(1 - [HL]/[HL]_0)]$.

The ^1H NMR spectra (Fig. 1) showed three distinct bands in the region of aliphatic CH_2: **A** ($\sigma = 3.0$–3.2 ppm) assigned to CH_2 vicinal to NH and NMe, **B** ($\sigma = 2.0$–2.3 ppm) to CH_2 vicinal to C=O and **C** ($\sigma = 1.0$–1.6 ppm) to the central $(CH_2)_3$ of PA6 block and $(CH_2)_9$ of poly(MeDL-*co*-DL) block. The best results gave the combination of area integrals **B** and **C**. The mole fraction of poly(MeDL-*co*-DL) corresponds to (**C**–3**B**)/6 and was recalculated to the weight fraction using the mean molecular weight of the monomer units MeDL and DL. The difference between the calculated and determined values is small in the samples extracted with boiling water, but considerably lower values than the calculated ones were determined in the samples extracted with boiling ethanol. This complies with the above discussion of the composition of extractables.

The fraction of benzoyl groups in diacylalkylamine branching sites was determined by the aminolysis of PPI as *N*-butylbenzamide [1] formed with the probability of 0.5 (the benzoyl group and long acyl branch have the same chance in the cleavage [1]). The concentration of

Table 4
Characteristics of block copolymers PA6-*block*-poly(MeL-*co*-L)

Copolymer no.	PPI no.	Poly(MeL-*co*-L), wt%		PA6$_{h,max}$[b] wt%	Mol. wt. $\times 10^{-4}$		
		Calculated	^{1}H NMR[a]		$\bar{M}_n$[c]	$\bar{M}_v$[d]	$\bar{M}_{me}$[e]
PA6-*block*-poly(MeDL-*co*-DL)							
1	A6	5.2	5.5	3.1	15.2	12.5	0.55
2	A6	8.7	9.1	3.0	8.6	8.5	0.55
3	A2	9.4	**9.6**	–	4.7	7.7	**0.35**
4	A5	10.9	11.5	1.2	4.1	6.5	0.37
5[f]	A6	10.2	10.1	2.9	7.5	6.6	0.55
6	A6	15.3	14.9	2.6	4.6	4.4	0.55
7	A2	15.3	**11.2**	–	2.8	8.1	**0.35**
8	A1	15.4	**8.9**	–	5.5	11.6	0.47
9	A3	15.4	**12.0**	–	2.1	6.6	0.33
10	A5	20.1	20.3	1.1	2.0	4.4	0.37
11	A5	20.4	19.8	1.1	2.0	3.5	0.37
12[g]	A6	20.5	20.1	2.6	3.3	3.2	0.56
13[h]	A6	20.2	19.9	2.6	3.4	3.2	0.56
14	A7	25.5	24.2	17	1.9	0.7	0.19
15	A8	25.3	24.4	4.7	1.4	1.4	0.27
16	A3	26.5	**25.8**	–	1.1	2.1	**0.33**
17	A4	25.3	**21.6**	1.0	1.2	2.6	**0.36**
18	A1	30.8	**26.3**	–	2.3	9.8	0.47
PA6-*block*-poly(MeOL-*co*-OL)							
19	A10	10.4	–	–	2.5	3.7	**0.21**
PA6-*block*-poly(EtDL-*co*-MeDL-*co*-DL)							
20	A9	20.3	–	1.7	1.1	1.6	**0.18**
Polymerization blend PA6/MePA12							
21	Lin	5.4	4.5	100	1.8	2.2	1.02

[a] Figures in bold were measured with EtOH-extracted samples.

[b] Estimated maximum content of PA6 homopolymer (from the fraction of pendent benzoyls in PPI).

[c] Number-average molecular weight of PA6 blocks calculated from the concentration of initiator groups (propagation centres).

[d] Determined viscometrically as PA6.

[e] Estimated average molecular weight of MeL blocks and homopolymer (see Table 2); figures in bold are derived from the calculated [I]. The values $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the poly(MeDL-*co*-DL) fractions obtained from ethanolic extracts by evaporation, partial dissolution in THF and SEC: [f] 2100, 2.2. [g] 1960, 2.2. [h] 1400, 1.4.

imide benzoyl incorporated in PPI, [B], are included in Table 2. However, utilization of benzoyl groups in the initiation of HL homopolymerization is 30% at the most as it was concluded from model experiments [1]. This makes possible to estimate the maximum possible content of the PA6 homopolymer in the block copolymer as PA6$_{h,max}$ (wt%) = 0.3[B][100 − poly(MeL-*co*-DL)]/[I] (Table 4).

Molecular weight. All copolymers were completely soluble in *m*-cresol. Intrinsic viscosity [η] of their solutions was used for the estimation of number-average molecular weight of PA6 blocks, $\bar{M}_v$, using the Mark–Houwink expression for PA6 homopolymers prepared by the anionic polymerization [12] and neglecting the contribution of poly(MeDL-*co*-DL) blocks, the $\bar{M}_n$ of which being 5–23 times lower. The $\bar{M}_n$ values calculated from the initial concentration of propagation centers corresponding to [I] (mol%) (Table 3) and HL conversion as $\bar{M}_n = 100(1 − HL/HL_0)113.16/[I]$ reasonably agree with the viscometric data for block copolymers prepared with the magnesium hexano-6-lactamate bromide catalyst. On the contrary, the values $\bar{M}_v$ are much higher in

the copolymers prepared using the sodium hexano-6-lactamate catalyst than the calculated values because of the condensation reactions of *N*-acyllactam propagation centers in agreement with our previous results [8]. This means that the coupling of propagating end groups of PA6 blocks may lead to the formation of triblock copolymers with the central PA6 block or also star block copolymers, depending on the further fate of the imide group in the β-ketoimide condensation product shown in Scheme 3.

3.4. Thermal properties and crystallinity

Analogously to PA6-*block*-PA12 copolymers, also the copolymers PA6-*block*-MePA12 consist, in the solid state, of two crystalline phases of PA6 and MePA12, the corresponding amorphous phases, and an amorphous interphase formed from the unequal segments near the bonding sites between blocks. The crystalline MePA12 described by Shalaby [13], consists of two forms differing in packing and thus displaying two melting endotherms in temperature regions 40–48°C and 48–54°C. This agrees with our
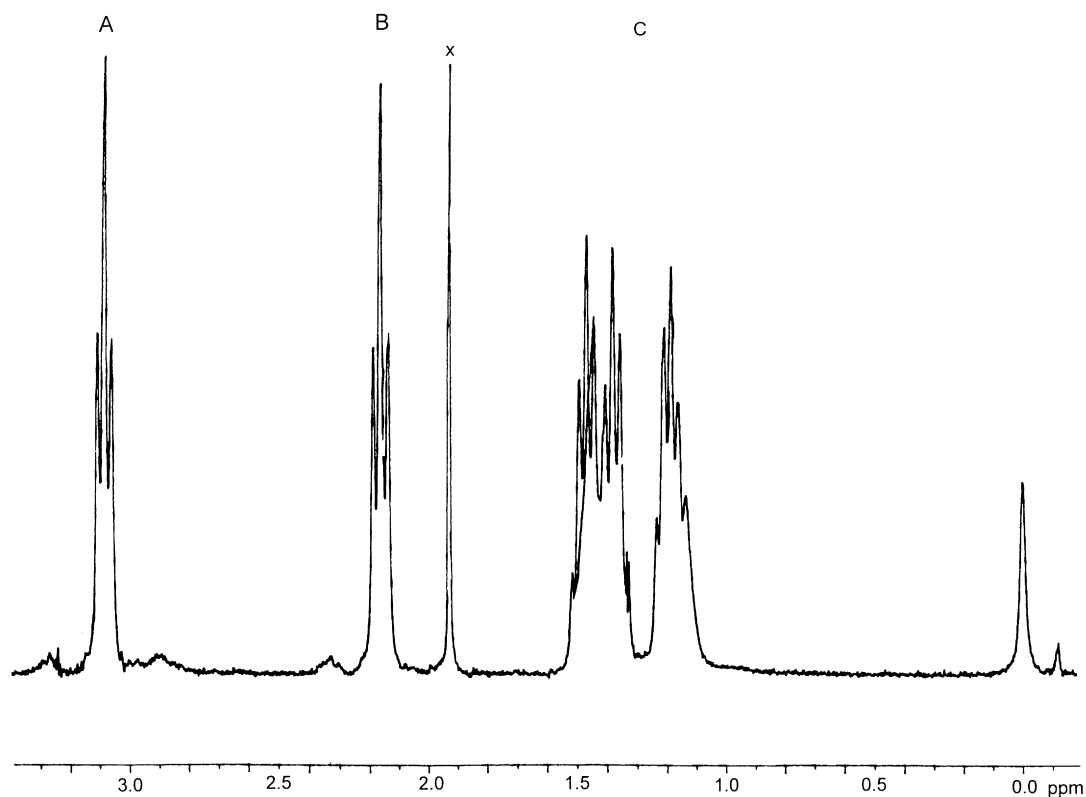
Fig. 1. ^{1}H NMR spectrum of PA6-*block*-poly(MeDL-*co*-DL) in formic acid–D$_2$O (9:1 (v/v)).

observations where DSC of a relatively low-molecular weight linear MePA12, which has been allowed to crystallize at ambient temperature, also showed two endotherms at 53.5 and 60.2°C and the sum of heat effects (heat of fusion) $\Delta H_{f,Me}$ was 71 J g^{-1} (Fig. 2). Our DSC study was carried out with block copolymers prepared with the same MePA12 precursor of initiator (A6, Table 1) in the amount 5–20 wt% in the polymerization mixture. One

PPI should provide the same average length of MePA12 blocks and the same content of both homopolymers. The samples were extracted in boiling water for 3 h and measured in the dry state after several months at ambient temperature, which should also secure an improvement of the crystalline structure of both PA6 and MePA12 blocks (annealing above their T_g). The results are given in Table 5.
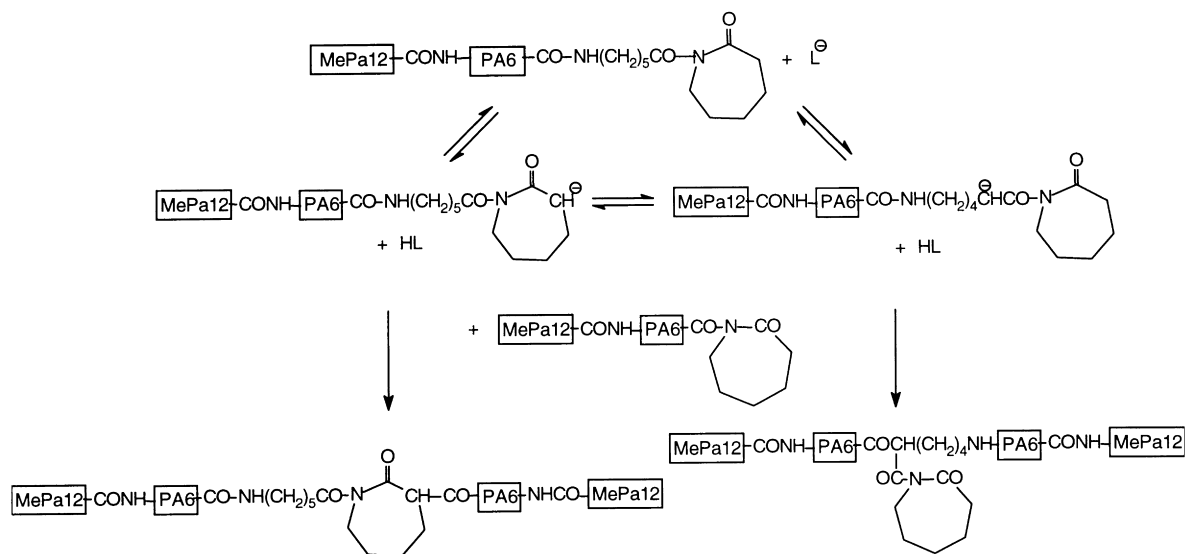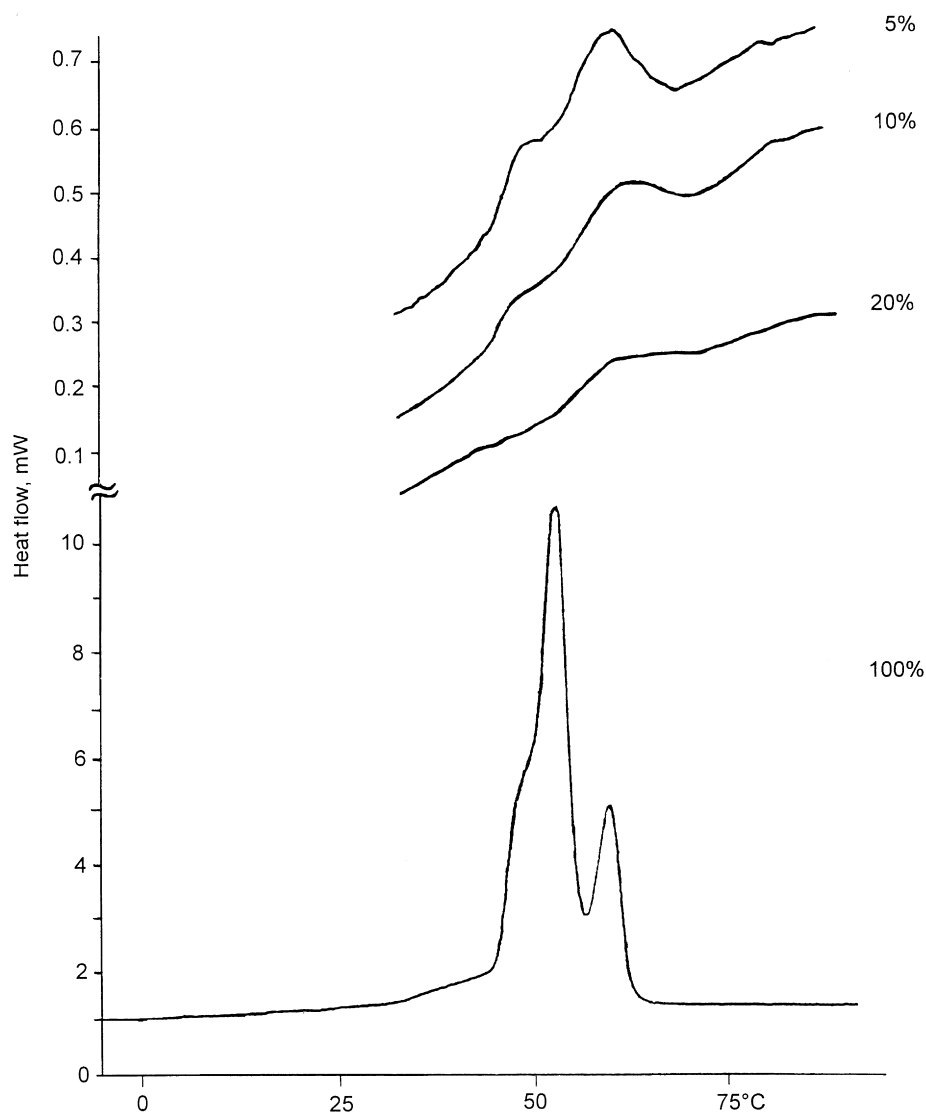

Scheme 3.

Fig. 2. DSC records in the melting region of MePA12: block copolymers containing 5, 10 and 20 wt% poly(MeDL-*co*-DL) blocks (samples 1, 5 and 13, Table 5) and 100% MeDL homopolymer (Lin).

Table 5
DSC data for selected block copolymers prepared with the polymeric precursor of initiator A6 and for reference samples

Copolymer (no.)	MePA12 (wt%)	$\frac{\bar{M}_{n,PA6}}{\bar{M}_{n,MePA12}}$ [a]	$T_{m,PA}$ (°C)	X [b] (%)	$\frac{\Delta H_{f,PA6}}{PA6}$ (J g^{-1})	$T_{m,MePA12}$ [c] (°C)	$\frac{\Delta H_{f,MePA12}}{MePA12}$ (J g^{-1})
PA6-*block*-MePA12							
1	5.2	28	219.7	49	94	53.7, 61.4	33.7
2	8.7	16	218.2	51	98	51.2, 63.4	21.1
5	10.2	14	216.9	51	97	50sh, 62.8	10.2
6	15.3	8	215.8	54	103	50.9, 63br	5.3
13	20.2	6	216.5	60	114	50.3, 62br	3.2
MePA12 homopolymer							
Lin	100	–	–	–	–	53.5, 60.2	71
PA6/MePA12 blend (95:5)							
21	5.4	2	218.8	55	104	52.1, 64.0	68.9

[a] Ratio of molecular weights of blocks.
[b] Crystallinity of PA6 segments $X = \Delta H_{f,PA6}/(PA6 \times \Delta H_{f,PA6}^0)$; $\Delta H_{f,PA6} = 190$ J g^{-1} [14].
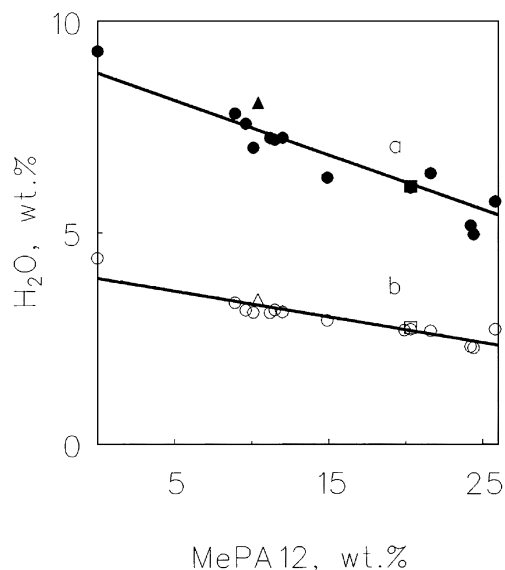[c] sh-shoulder, br-broad.

Fig. 3. Equilibrium content of water absorbed by block copolymers at ~25°C and relative humidity (a) 93% and (b) 65%; (○,●)—copolymers with poly(MeDL-*co*-DL) blocks, (△,▲)—poly(MeOL-*co*-OL) blocks, (□,■)—poly(MeDL-*co*-EtDL-*co*-DL) blocks.

The position of a single melting peak of PA6 shifts only a little to lower T_m with increasing content of MePA12 blocks (i.e. decreasing $\bar{M}_n$ of PA6 blocks) and the heat of fusion relative to the content of PA6 increases slightly.

The calorimetric record of the MePA12 melting endotherm is complicated by a glass temperature transition (T_g) of PA6 which occurs in the same temperature range forming an indistinct peak or shoulder on the DSC curve, as it is shown in an example in Fig. 2. The results are multiple peaks or peaks with shoulders.

Due to this complication, the values of heat of fusion of the crystalline MePA12 fractions shown in Table 5 should be considered only as approximate. Crystallinity of MePA12 blocks strikingly decreases with increasing content of the copolymer being always only a fraction of the corresponding crystallinity of the MePA12 homopolymer.

On the contrary, the PA6/MePA12 blend (95:5 (w/w)), prepared by anionic polymerization of L6 in the presence of a linear MePA12 homopolymer dissolved in the monomer, contained, after the same treatment of the sample, the MePA12 fraction with much higher crystallinity identical with that of the MePA12 homopolymer ($\cong 70$ J g^{-1}). The reason for a suppressed crystallinity of larger fractions of MePA12 blocks could be explained in terms of formation of an amorphous interphase. Because the T_g value of MePA12 is about $-30°C$ (Ref. [13]) and the crystallinity of the blocks is low, the segments formed by MePA12 blocks can be considered soft.

3.5. Mechanical properties

Mechanical properties of the specimens prepared from mould-cast plagues shown in Table 6 differed only slightly from those of PA6 homopolymer and blends of homopolymers.

It has been observed that a monofilament obtained by melt spinning with partial orientation from the 80:20 (w/w) PA6-*block*-MePA12 copolymer exhibited an extensive elastic (reversible) deformation. However, this phenomenon vanished after about a year and the fiber turned brittle. This is obviously caused by the progress in slow crystallization of MePA12 blocks, which reduced the fraction of the MePA12 interphase.

3.6. Sorption of water vapor

The dependence of equilibrium water sorption into block copolymers on the content of MePA12 or other *N*-methyl polyamide blocks is plotted in Fig. 3 for the relative humidities 65 and 93%. A decrease in the absorbed water amount with increasing content of MePA12 can be expected because the sorption of MePA12 is several times smaller than that of PA6. The sorption is also proportional to the fraction of the non-crystalline phase. The linear decrease in the sorption from PA6 to the copolymer containing 25% MePA12 is in agreement with the calculated sorption under the following assumptions:

Table 6
Mechanical properties of PA6-*block*-MePA12 copolymers

Product no.	MePA12 (wt%)	Residual L6 (wt%)	a_K[a] (kJ m^{-2})	Hardness shore D	E[b] (GPa)
Reference PA6 homopolymer					
–	0	2.5	3.4	82	3.6
PA6-*block*-MePA12					
1	5	4.0	4.6	81	3.3
5	10	2.2	3.9	80	3.1
6	15	2.1	3.4	79	2.8
13	20	1.3	3.6	75	2.1
11	20	2.3	3.8	75	2.1
Blend PA6/MePA12					
21	5	4.7	3.6	81	3.3

[a] Notched impact resistance Sharpy (23°C).
[b] Modulus of elasticity calculated from the hardness data.

1. The content of accessible regions of PA6 decreases by 30%, from the extrapolated data of heat of fusion in Table 5.
2. MePA12 absorbs the same amount as unsubstituted PA12, i.e. at 93 and 65% relative humidities, it absorbs 5.1 and 4.4 times less than PA6, respectively [15].

Acknowledgements

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