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Polymerization of lactams, 95[☆] Preparation of polyesteramides by the anionic polymerization of ε-caprolactam in the presence of poly(ε-caprolactone)

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Abstract

Preparation of polyesteramides–poly[(ε-caprolactam)-*co*-(ε-caprolactone)]s by anionic polymerization of ε-caprolactam in the presence of poly(ε-caprolactone) at 150 °C was studied in this paper. ε-Caprolactam magnesium bromide was used as an initiator of polymerization and polymeric materials containing 5–25 wt% ε-caprolactone units were obtained. Thermal methods (DSC and DMA) were employed for characterization of poly[(ε-caprolactam)-*co*-(ε-caprolactone)]s and their mechanical properties were also evaluated. By introducing the activator with *N*-acyllactam structure, the polymerization rate increased and it was possible to carry out the polymerization at 110 °C. Mechanical properties of polyesteramides were influenced by both the content of ε-caprolactone units incorporated into copolymer and polymerization temperature. The mechanism of incorporation of poly(ε-caprolactone) is discussed. The results show that it is not possible to restrict exchange transacylation reactions, progressing in the course of polymerization, by kinetic tools.

Keywords: Polyesteramides; Mechanical properties; Thermal properties

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1. Introduction

Aliphatic esters, such as poly(ε-caprolactone) (PCLO), represent an important group of biodegradable synthetic polymers [1]. However, relatively low melting temperature of PCLO (~60 °C) bounds the application possibilities of this polymer. On the other hand, due to high concentration of hydrogen bonds and, consequently, high crystallinity, aliphatic polyamides, such as poly(ε-caprolactam) (PCLA), are renowned construction plastics, resistant toward biodegradation [2].

Thanks to the variation of the type and content of the ester and amide components in the polymer chains, poly(esteramides) represent a group of polymer materials with broadly varying physico-chemical properties and sensitivity toward biodegradation. Poly[(ε-caprolactam)-*co*-(ε-caprolactone)] [P(CLA-*co*-CLO)] could thus come under a new group of biodegradable commodity plastics. P(CLA-*co*-CLO) can be obtained by an anionic copolymerization of ε-caprolactam (CLA) and ε-caprolactone (CLO), initiated by basic initiators (Na, K) [3]. When initiated by less basic initiators, such as ε-caprolactam magnesium bromide (CLAMgBr) [4], the resulting copolymer shows a higher melting temperature than materials prepared by Na or K initiators which gives evidence of certain differences in the structure of these materials [5].

P(CLA-*co*-CLO) can be prepared also by polymerization casting method in static molds with sodium ε-caprolactamate (CLANa) or CLAMgBr as initiators. At suitably chosen experimental conditions, the degree of monomer conversion is higher than 97%, both comonomers being almost incorporated into the copolymer.

The mechanism of the copolymer formation is not simple, as one could expect. Thus, by analogy, CLO could be considered to act as a classical activator of the anionic polymerization of CLA, such as γ-butyrolactone [6]; Eqs.

[☆] Part 94: cf. Ref. [13].

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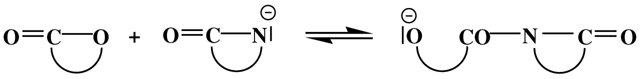
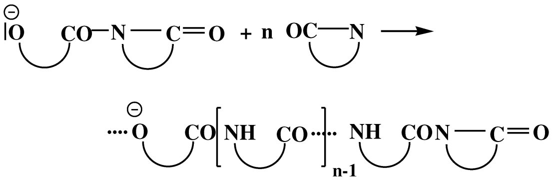
(1) and (2):



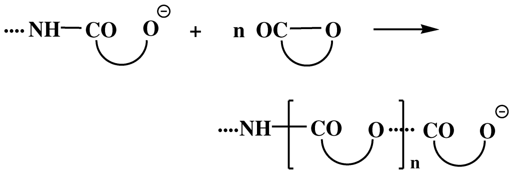
(1)



(2)

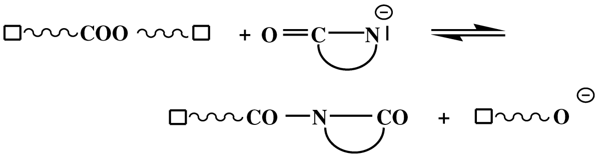
Concentrations of N and O anions are given by fast proton exchange with amide NH donors.

However, as was already suggested by Goodman and Vachon [3] and confirmed by us [5], CLO, due to its enormous polymerizing activity, is converted into the polyester as soon as it is dissolved in CLA (at 90 °C) during the preparation of the polymerization feed; Eq. (3).



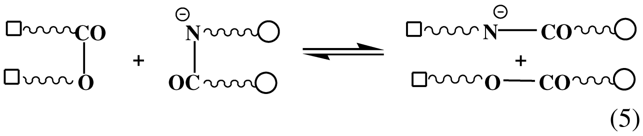
(3)

In addition to the reaction of the lactam anion with CLO, also the reaction of this anion with the ester group of the polyester chain gives rise to the propagation centers—which is an analogy with the activation of the anionic polymerization by low-molar-mass esters [6]; Eq. (4).



(4)

The incorporation of the CLA units into the copolymer structure then proceeds at higher temperatures (150 °C) according to Eqs. (1) and (2). Simultaneously with this propagation reaction, a number of transacylation reactions occur in the system, being catalyzed by the polymerization initiator present; Eq. (5).



(5)

As was described in the literature [3,7–9], the copolymer prepared by the copolymerization of CLA and CLO to high degrees of conversion had a random structure.

Notch impact strength of these materials increases with increasing fraction of the CLO structural units incorporated, while modulus of elasticity decreases. The copolymers prepared show a single melting endotherm; the NMR spectra also suggest a rather random nature of the copolymer [3,5].

Thermal properties of P(CLA-*co*-CLO) (prepared with CLAMgBr as initiator) were investigated by HiRes™ TGA and the degradation products identified by FTIR and mass spectroscopy [10]. The TGA measurements have suggested that the mechanism of the degradation of poly(ε-caprolactam) involves both an 'unzipping' depolymerization leading to the formation of ε-caprolactam and random chain scission through the amide group pyrolysis. Since the PCLO and PCLA blocks are degraded at well separated temperature regions, the presence in the thermograms of degradation steps in a close vicinity of their respective degradation temperatures supports the assumption that the copolymer chain contains parts (blocks) which are at least enriched with the CLO or CLA components.

It is the aim of this work to study the synthesis of P(CLA-*co*-CLO) by anionic polymerization of CLA in the presence of PCLO which was prepared beforehand as a 'polymeric activator'. This process models the mentioned above rapid formation of PCLO at the beginning of polymerization. Materials thus prepared were further characterized and their physico-chemical properties compared to those of copolymers obtained by simultaneous copolymerization of CL and CLO.

2. Experimental

2.1. Chemicals

ε-Caprolactam (CLA) (DSM) was used as obtained and stored in a dessicator over P_2O_5, water content 65 ppm.

ε-Caprolactone (CLO) (Fluka) was purified by distillation under reduced pressure over powdered calcium hydride, water content 17 ppm.

ε-Caprolactam magnesium bromide (CLAMgBr) concentrate (from DSM) was stored in a round-bottom flask under protective atmosphere of argon. Content of Mg^{2+} was 1.06 mol kg^{-1} (determined by chelatometric titration).

2.2. Preparation of poly(ε-caprolactone)

Poly(ε-caprolactone) was prepared in aluminum mold with wall thickness of 4 mm and internal cavity of $140 \times 150 \times 4$ mm, sealed with a gasket of heat-cured silicon rubber. The polymerization mixture was prepared under protective atmosphere of argon in a glass flask. The initiator CLAMgBr was dissolved in CLO at room temperature in an ultrasonic bath. After dissolution the polymerization mixture was transferred into a mold heated to 60 °C immersed in silicon-oil bath. After 30 min of polymerization the plaque was removed, desintegrated and extracted with methanol at room temperature. Yield of polymer 80%; $M_n = 24,500$ g mol^{-1}, $M_w = 55,300$ g mol^{-1} (SEC analysis, universal calibration PCLO—PS/THF was used).

2.3. Preparation of poly[(ε-caprolactam)-co-(ε-caprolactone)]

The copolymer samples have been synthesized by the anionic ring-opening polymerization of CLA at a temperature ranging from 90 to 180 °C in the presence of PCLO and 0.5 or 1.0 mol% ε-caprolactam magnesium bromide (CLAMgBr) in the same mold described above. PCLO was dissolved in a glass flask under dry argon at 80 °C in CLA. Then a solid concentrate of CLAMgBr in CLA was introduced and after dissolution (max. 3 min) the polymerization mixture was transferred immediately to a mold heated to the polymerization temperature. The mold was kept for 1 h in the bath and then slowly cooled by standing at room temperature. After demolding, test specimens have been prepared and a part of the crude polymer was disintegrated by special rasp for the determination of polymer yield by hot-water extraction.

2.4. Thermal analysis

The DSC measurements were performed using a DSC 2920 Modulated DSC (TA Instruments) in the temperature range 20–250 °C with a constant heating rate of 10 °C min^{-1} and nitrogen purge (50 $\text{cm}^3\ \text{min}^{-1}$).

For the DMA measurements, specimens having dimensions of 2 × 4 × 30 mm were prepared. For these measurements, we used dry samples or samples conditioned at 52% humidity at 23 °C for 110 days. The DMA DX04T tester (RMI, Czech Republic) was used, the measurements being performed in a temperature range between −100 and 250 °C at a heating rate of 3 °C min^{-1}. Bending mode Single Cantilever with a constant deformation of ±0,2 mm and sinusoidal force at a frequency of 1 Hz was used.

2.5. Mechanical properties

Tensile tests were carried out with beam-shaped specimens of cross-section dimensions 2 × 4 mm on an Instron instrument at a clamp distance of 100 mm and a displacement rate of 1 mm min^{-1}. Notched impact strength (a_k) was measured with the Charpy pendulum on specimens of dimensions 50 × 20 × 4 mm with the average notch depth of 1 mm at −20 or +23 °C. The distance of supports was 40 mm and the pendulum velocity at impact was 2.9 m s^{-1}.

3. Results and discussion

3.1. Preparation of poly[(ε-caprolactam)-co-(ε-caprolactone)]

3.1.1. Polymerization initiated by CLAMgBr

The polymerization of CLA, initiated by 1 mol% CLMgBr and performed at 150 °C in presence of 5–25 wt% of PCLO ($M_n = 24,500\ \text{g mol}^{-1}$), was investigated in detail. The results are given in Tables 1 and 2. The incorporation of the CLO units from a polymerization feed containing up to 15 wt% of PCLO into the copolymer did not affect the content of water-extractable fractions; ranged up to about 3% and was roughly equal to that of low-molecular-weight fractions — similarly to the CLA homopolymer. For 25 wt% of PCLO the extractable fraction increased to 6%.

The thermal properties of the materials prepared are of prime importance. The DSC curves of the unextracted (virgin) samples showed always a single melting endotherm. This single melting temperature and its distinct decrease with increasing initial PCLO concentration suggest that a copolymer with distinct random structure is formed. Similarly, enthalpy of melting was decreasing, too; if we make an assumption that the enthalpy of melting would be given only by the lactam sequences (190 kJ g^{-1}), the crystallinity should decrease from the initial 52 to 25% for the highest content of PCLO (see Table 1). Hence, it can be stated that, with increasing content of the ester units incorporated, the content of the crystalline phase decreases (the degree of the ordering of the system distinctly decreases).

T_g can more sensitively be determined by DMA. The dependence of the tangent of the loss factor (tg δ) of 'dry' samples shows two distinct maxima (Fig. 1). The first one (tg δ_1) is located at −55 °C for the unmodified PCLA, and shifts to −70 °C for the material with 25 wt% of PCLO. This can be assigned to the well-known β-transition of polyamide chains caused by the enhanced mobility of the –CO–NH– bonds in the polymer. The other one (tg δ_2), referred to as the α-transition, varied in the range of 97 °C (for unmodified PCLA) to 31 °C (for material with 25 wt% of PCLO) and corresponded to the T_g of polyamide 6 and copolymer. This dependence affirms that the CLO units, when incorporated into the copolymer, act as a plasticizer,

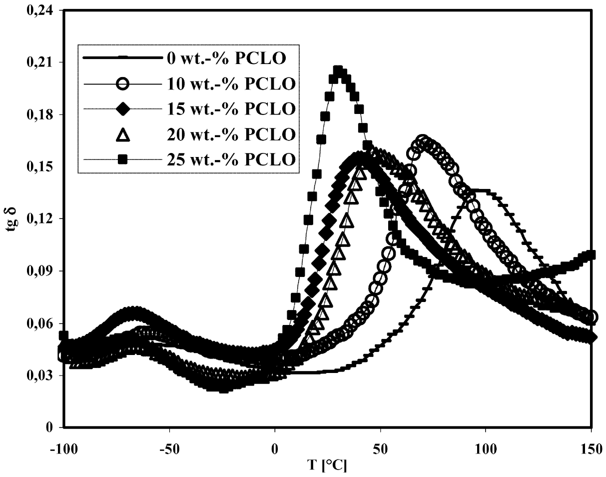


Fig. 1. Dynamic-mechanical spectra of dry samples of poly[(ε-caprolactam)-*co*-(ε-caprolactone)] copolymers prepared by the anionic polymerization of ε-caprolactam in the presence of poly(ε-caprolactone).

Table 1
DSC and DMA analysis of polyesteramides prepared by the polymerization of ε-caprolactam in the presence of poly(ε-caprolactone) (PCLO) initiated with 1 mol% ε-caprolactam magnesium bromide, polymerization time 1 h, polymerization temperature 150 °C

PCLO (wt%)	y_w[a] (%)	ΔH_m[b] (J g^{-1})	T_m[c] (°C)	Max (tg δ)$_1$[d] (°C)	Max (tg δ)$_2$[d] (°C)	E_f (23 °C)[e] (GPa)	Max (tg δ)$_1$[d,f] (°C)	Max (tg δ)$_2$[d,f] (°C)	Max (tg δ)$_2$[d,f] (°C)	E_f (23 °C)[e,f] (GPa)
0	97.5	96	217	−55	97	1.2	−67	20	82	0.9
5	97.1	89	206	−58	70	1.3	−72	15	75	0.5
10	97.3	85	195	−62	71	1.0	−68	14	75	0.2
15	96.8	76	184	−63	52	0.9	−71	9	67	0.1
20	95.8	60	177	−65	47	0.7	−67	3	65	0.1
25	93.4	45	156	−70	31	0.3	−72	−3	–	0.1

[a] y_w, Polymer content determined by extraction of polymerizate with hot water.
[b] ΔH_m, Entalpy of fussion of nonextracted sample.
[c] T_m, Melting temperature of nonextracted sample.
[d] Max (tg δ)$_{1,2}$, temperature corresponding with local maxima of tg δ dependence (from DMA).
[e] E_f, Flexural modulus from DMA.
[f] Samples conditioned at 52% relative humidity at 23 °C for110 days.

i.e. they lower T_g of the material. This confirms the validity of the relation:

$$1/T_{g,copol} = w_a/T_{g,a} + w_b/T_{g,b}$$

$$\textit{for } T_g(\textit{PCLO}) = 213 \text{ K and } T_g(\text{PCLA}) = 370 \text{ K}$$

In case of conditioned samples (52% relative humidity, 110 days), three maxima appear on the DMA curve (Fig. 2 and Table 1). In the region of the β-transition caused by the kink motion of amide bonds, the maximum decreases for dry copolymers with increasing content of the built-in ester units; also the maximum of tg δ_2 distinctly decreases. In contrast, with the conditioned samples, the values of temperatures corresponding to the β-transition remain constant at about −70 °C and are lower than those of dry materials. Surprisingly, the α-transition is split which may suggest the presence of two non-crystalline phases — one being less plasticized than the other one, wherein the intensity of the former is very low (its intensity corresponds to β-transition); the difference between the peaks pertaining to these two phases is constant (60 ± 2 °C, see Fig. 2).

Mechanical properties were measured for dry samples only. At −20 °C, as well as at 23 °C, the copolymers prepared show higher notch impact strength than pure PCLA (Table 2). This quantity increases with increasing PCLO content but this increase manifests itself distinctly only at as high content of incorporated PCLO as 20 wt%. Relative tensile modulus of elasticity, expressed as a relative change with respect to pure PCLA, as well as tensile strength at yield decrease with increasing PCLO content. The samples show a relatively high elongation (deformation at break), which is, for 25 wt% of PCLO, higher than 350%.

In Table 3, selected properties of polyesteramides, prepared by a polymerization of CLA in the presence of PCLO, as described in the present paper, are compared to those of the materials prepared by a copolymerization of CLA with (monomeric) CLO [5]. In this comparison, values of the polymer content, melting temperature and notch

Table 2
Mechanical properties of poly(esteramide)s prepared by the polymerization of ε-caprolactam in the presence of poly(ε-caprolactone) (PCLO), polymerization conditions see Table 1

PCLO (wt%)	a_k[a] (kJ m^{-2})				E_t/E_{to}[b]		σ_s[c] (MPa)		ε_r[d] (%)	
	−20 °C	s[e]	23 °C	s[e]		s[e]		s[e]		s[e]
0	–	–	3	0.7	1.0	–	88	0.5	12	4.0
5	3	0.2	4	0.7	0.8	0.06	71	1.8	5	0.7
10	4	0.6	5	0.6	0.7	0.05	69	0.8	25	2.6
15	4	0.3	8	0.3	0.5	0.03	56	1.9	35	1.8
20	5	0.3	11	0.4	0.3	0.01	41	1.1	40	4.2
25	11	1.7	NB[f]	–	0.1	0.01	21	8.3	>350	–

[a] a_k, Notched impact strength at -20 °C and 23 °C
[b] E_t/E_{to}, Relative tensile modulus (E_{to} ~2.8 GPa)
[c] σ_s, Tensile strength at yield
[d] ε_r, Deformation at break
[e] s, Standard deviation
[f] NB, no break

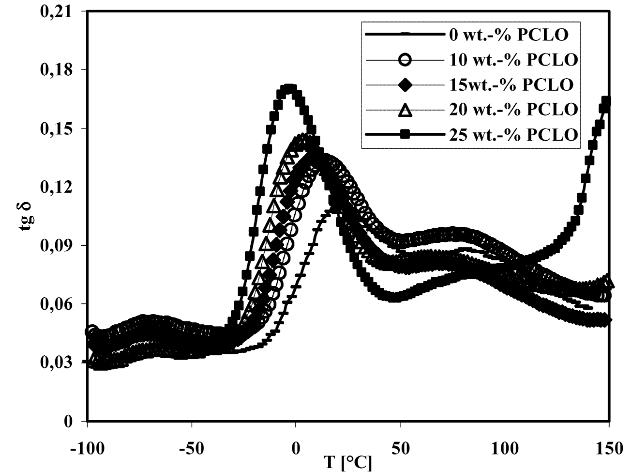


Fig. 2. Dynamic-mechanical spectra of conditioned samples (52 rel% humidity, 20 °C, 110 days) of poly[(ε-caprolactam)-*co*-(ε-caprolactone)] copolymers prepared by the anionic polymerization of ε-caprolactam in the presence of poly(ε-caprolactone).

impact strength are very close for samples having the same ratio of the built-in CLO and CLA units. These phenomena support the mechanism of copolymer formation and significant role of transacylation reactions. Small differences can be explained by a different concentration and type of the initiator applied (CLAMgBr or ethyl magnesium bromide [5]). It can be deduced from Table 3 that there is no substantial difference in properties and structure between materials prepared by polymerization of CLA in presence of PCLO and those synthesized by a copolymerization of CLA and CLO. In both cases similar structures of copolymers were obtained.

3.1.2. Polymerization initiated by CLAMgBr and activated by N-acyllactams

Taking all this data into account, it can be concluded that anionic polymerization initiated by CLAMgBr in presence of PCLO, as well as CLO, yields — after one-hour propagation at 150 °C — an essentially random copolymer, though a certain indication of short blocks can be seen from our thermal measurements [10]. This was confirmed also by an analysis of the NMR spectra [5], showing a certain deviation from random statistics (Table 4). To make the formulation more rigorous, we can state that the structure of the CLO/CLA copolymers obtained using the initiation by ethyl magnesium bromide is close to random.

Obviously, most processes leading to 'random' copolymers (materials) mentioned above are rapid, be it the cleavage of the PCLO chains, Eq. (4), or exchange reactions, Eq. (5). Materials having other structure could in principle be obtained by changing the rate of the individual reactions. Naturally, this can be achieved by changing temperature, which controls the rate of polymerization as well as the exchange reactions. The drop of the polymerization temperature below 150 °C causes a substantial decrease of the polymerization activity of CLA [11]: then, in order to enhance the rate of the CLA polymerization process, it is possible to apply a classical *N*-acyllactam activator [4] showing a distinctly higher activity than CLO or PCLO. Supposedly, *N*-acyllactam activators could cause such a rapid formation of the PCLA chains that the block character of the copolymer could be enhanced by lowering the probability of the random copolymer formation (exchange reactions).

3.1.3. Effect of the nature of the activator

To accelerate the polymerization of CLA performed in the presence of PCLO and initiated by 1 mol% CLAMgBr, the following activators were used: *N*-acetyl-ε-caprolactam (AcCLA), *N*-benzoyl-ε-caprolactam (BzCLA), *N*,*N*′-isophthaloyl-bis-ε-caprolactam (IPBCLA). The effect of the

Table 3
Comparison of properties of materials prepared by the polymerization of ε-caprolactam (CLA) in the presence of poly(ε-caprolactone) (PCLO) and copolymerization of ε-caprolactam with ε-caprolactone (CLO) [5]; polymerization time 1 h, polymerization temperature 150 °C

PCLO (wt%)	CLO (wt%)	c_{CLAMgBr}[a] (mol%)	c_{EtMgBr}[b] (mol%)	y_w[c] (%)	ΔH_m[d] (J g^{-1})	T_m[e] (°C)	a_k[f] (kJ m^{-2})	
							−20 °C	23 °C
5	–	1	–	97.1	89	206	3	4
10	–	1	–	97.3	85	195	4	5
15	–	1	–	96.8	76	184	4	8
20	–	1	–	95.8	60	177	5	11
–	5	–	0.5	97.1	84	207	3	4
–	10	–	0.5	97.4	84	194	4	6
–	15	–	0.5	96.6	71	184	4	13
–	20	–	0.5	94.4	50	172	8	NB[g]

[a] c_{CLAMgBr}, Concentration of ε-caprolactam magnesium bromide.
[b] c_{EtMgBr}, Concentration of ethyl magnesium bromide.
[c] y_w, Polymer content determined by extraction of polymerizate with hot water.
[d] ΔH_m, Entalpy of fussion of nonextracted sample.
[e] T_m, Melting temperature of nonextracted sample.
[f] a_k, Notched impact strength at −20 and 23 °C.
[g] NB, no break.

Table 4
Content of dyads in poly(esteramide)s prepared by the copolymerization of ε-caprolactam (a) and ε-caprolactone (o) initiated with 0.5 mol% ethyl magnesium bromide at 150 °C, polymerization time 1 h

$[CLO]_0$[a] (wt%)	$[o]_{ea}$[b] (%)	[o] (%)	[oo] (%)	[ao]	[oa] (%)	[aa] (%)	χ[c]
30	31.7	30.9	6.1	25.0	24.7	44.1	1.16
40	44.8	43.4	13.4	25.7	30.0	32.8	1.13
50	63.1	55.2	26.1	25.2	29.1	19.5	1.10

[a] $[CLO]_0$, Initial concentration of ε-caprolactone in polymerization mixture.

[b] $[o]_{ea}$, ε-Caprolactone content from elemental analysis.

[c] χ, Measure of departure from random statistics.

$$\chi = \frac{[oa]+[ao]}{2[o]\cdot[a]}\cdot 100$$

type of the activator on the course of the anionic polymerization of CLA was tested with the system containing 10 wt% of PCLO. The polymerization process was strongly accelerated by adding 1 mol% of AcCLA, BzCLA or IPBCLA. The degree of the monomer-to-polymer conversion was high and independent of the polymerization temperature and the type of the activator, and ranged at about 97% (Table 5). The copolymers formed at 110–150 °C had virtually equal melting temperatures and similar values of ΔH_m which implies equal content of the crystalline phase. At the polymerization temperature of 150 °C, the copolymers prepared in presence of the activators have a higher melting temperature (ca. 208 °C) than similar systems prepared without any activator (195 °C), cf. Tables 1 and 5. This distinct difference can be assigned to a different arrangement of the copolymer, wherein ΔH_m is the same. It should be stressed that the application of low-molecular-weight activators enhanced the polymerization process rate, which proceeded, in contrast to the previous experiments performed without any activators, 30 min only.

Polymerization with 0.5 mol% IFBCLA and 1 mol% CLAMgBr was studied in more detail (Table 6). Under these conditions, the initiation system is comparable with preceding systems containing AcCLA or BzCLA (because the ratio of initiator and acyl groups is equimolar).

Content of polymer for 10 wt% PCLO is similar for both IPBCLA concentrations used, namely, higher than 97% (cf. Tables 5 and 6). Also, the values of enthalpy of fusion are alike. Removing the water-extractable fractions, that is, the effect of the extraction agent (water) and extraction temperature, may influence the ordering of the material, shifting the melting endotherm maximum toward higher temperatures. Basic mechanical properties (notch impact strength and tensile modulus) do not depend on temperature, whereas for tensile strength at yield and deformation at break a certain temperature dependence can be observed. Within the limits of an experimental error, the comparison of mechanical properties of materials prepared with and without activator at 150 °C suggests that both materials are alike; consequently, the addition of IPBCLA (to speed up the process) does not influence strongly the structure of the material.

3.1.4. *Effect of the PCLO concentration and polymerization temperature*

This part of the study was focused on the effect of the PCLO concentration and polymerization temperature on the

Table 5
Polymerization of ε-caprolactam in the presence of 10 wt% poly(ε-caprolactone) initiated with 1 mol% ε-caprolactam magnesium bromide and activated with 1 mol% *N*,*N*′-isophtaloyl-bis-ε-caprolactam (IPBCLA), *N*-benzoyl-ε-caprolactam (BzCLA) or *N*-acetyl-ε-caprolactamem (AcCLA), polymerization time 0.5 h

Activator	T_p[a] (°C)	y_w[b] (%)	ΔH_m[c] (J g^{-1})	T_m[d] (°C)	a_k[e] (kJ m^{-2})				E_t/E_{to}[f]		σ_s[g] (MPa)		ε_r[h] (%)	
					− 20 °C	*s*[i]	23 °C	*s*[i]		*s*[i]		*s*[i]		*s*[i]
IPBCLA	110	96.9	83	207	6	0.1	9	0.7	0.68	0.05	60	7.4	8	1.3
BzCLA	110	96.9	86	205	3	0.5	6	0.7	0.71	0.04	65	2.1	15	4.1
AcCLA	110	97.4	83	205	3	0.1	6	0.6	0.71	0.03	66	4.5	7	2.1
IPBCLA	130	97.3	82	210	7	0.7	12	0.6	0.75	0.05	63	1.8	19	3.4
BzCLA	130	97.1	86	209	3	0.5	6	0.4	0.75	0.03	61	1.8	4.6	0.5
AcCLA	130	96.7	88	209	4	0.2	7	0.3	0.79	0.03	68	2.1	8	2.2
IPBCLA	150	97.1	75	208	7	0.5	11	1.0	0.68	0.03	60	1.5	29	4.9
BzCLA	150	96.9	91	208	2	0.2	7	0.8	–	–	–	–	–	–
AcCLA	150	96.5	86	207	3	0.7	7	1.0	0.75	0.05	63	7.5	9	6.4

[a] T_p, Polymerization temperature.

[b] y_w, Polymer content determined by extraction of polymerizate with hot water.

[c] ΔH_m, Entalpy of fussion of nonextracted sample.

[d] T_m, Melting temperature of nonextracted sample.

[e] a_k, Notched impact strength at − 20 °C and 23 °C.

[f] E_t/E_{t0}, Relative tensile modulus ($E_{t0} \sim 2.8$ GPa).

[g] σ_s, Tensile strength at yield.

[h] ε_r, Deformation at break.

[i] *s*, Standard deviation.

Table 6
Polymerization of ε-caprolactam in the presence of poly(ε-caprolactone) (PCLO) initiated with 1 mol% ε-caprolactam magnesium bromide and activated with 0.5 mol% *N*,*N*′-isophtaloyl-bis-ε-caprolactam, polymerization time 0.5 h

T_p[a] (°C)	PCLO (wt%)	y_w[b] (%)	ΔH_m[c] (J g^{-1})	T_m[d] (°C)	a_k[e] (kJ m^{-2})				E_t/E_{to}[f]		σ_s[g] (MPa)		ε_r[h] (%)	
					−20 °C	s[i]	23 °C	s[i]		s[i]		s[i]		s[i]
110	10	97.1	87	205	5	0.6	5	0.2	0.75	0.07	71	4.0	14	3,5
130	10	97.3	88	207	5	0.2	6	0.2	0.75	0.03	69	1.8	21	9,6
150	10	97.5	81	201	5	0.7	7	0.4	0.64	0.04	63	2.1	32	9,8
110	15	97.2	82	200	5	0.3	9	0.6	0.64	0.02	58	5.3	17	2,5
130	15	96.3	81	201	6	0.6	9	0.4	0.57	0.05	50	3.4	41	11
150	15	95.9	74	194	6	0.3	11	0.6	0.43	0.04	45	3.2	77	30
110	20	97.2	60	184	6	1.4	11	0.5	0.43	0.03	46	2.1	178	71
130	20	96.7	65	188	7	0.3	12	1.2	0.39	0.04	45	5.8	92	60
150	20	95.9	58	185	9	0.4	20	1.5	0.29	0.02	40	1.4	158	58
110	25	96.3	58	170	8	0.6	17	2	0.25	0.02	38	2.0	158	48
130	25	96.1	59	172	9	0.8	NB[j]	–	0.21	0.03	44	7.1	240	39
150	25	95.8	62	167	9	0.8	NB[j]	–	0.14	0.02	41	7.2	>350	–

[a] T_p, Polymerization temperature.
[b] y_w, Polymer content determined by extraction of polymerizate with hot water.
[c] ΔH_m, Entalpy of fussion of nonextracted sample.
[d] T_m, Melting temperature of nonextracted sample.
[e] a_k, Notched impact strength at −20 and 23 °C.
[f] E_t/E_{to}, Relative tensile modulus ($E_{to} \sim 2,8$ GPa).
[g] σ_s, Tensile strength at yield.
[h] ε_r, Deformation at break.
[i] s, Standard deviation.
[j] NB, no break.

preparation of modified PCLA. The polymerization was again initiated by 1 mol% CLAMgBr and activated by 0.5 mol% IFBCLA (to set a molar equivalence of functional groups of the activator and initiator). The PCLO concentration ranged between 10 and 25 wt%. The results are given in Table 6 for three preparation temperatures (110, 130 and 150 °C).

For all the three polymerization temperatures, the polymer content is satisfactory (>96%) and decreases slightly with increasing PCLO content in the feed, as well as with increasing polymerization temperature; the highest polymer content was found for 110 °C, this trend corresponds to the equilibrium CLA-PCLA.

As was already illustrated in Table 1, melting temperatures and melting enthalpies of unextracted materials decrease with increasing content of the PCLO units incorporated in the copolymer (Table 6). The highest values of both quantities were in most cases achieved at the polymerization temperature of 130 °C but the difference is small.

Also mechanical properties were influenced by polymerization temperature. Obviously, notch impact strength a_k increases with increasing PCLO content. The effect of polymerization temperature (110, 130 and 150 °C) on the shape of the dependence of a_k on PCLO content is also distinct. We failed to break the samples with 25 wt% PCLO prepared at 130 and 150 °C.

Tensile modulus of elasticity (E_t) decreases with increasing PCLO content and with increasing preparation temperature (Table 6). Dependence of tensile strength at yield on the PCLO content shows a trend similar to E_t; the lowest values of tensile strength at yield were found for modified polymers prepared at 150 °C. Elongation increases with increasing polymerization temperature; it reaches its maximum value for the material prepared at 150 °C.

Thus, data in Table 6 suggests that, within certain limits, a partial control of properties of copolymers (modified PCLA) by changing temperature and conditions of preparation is possible.

It is interesting to compare melting temperatures of materials prepared at 150 °C using solely CLAMgBr on the one hand and a combination of CLAMgBr and IPBCLA, on the other (cf. Tables 1 and 6). The values of melting temperatures of the products formed by a polymerization with IPBCLA added are in all cases by at least 10 °C higher which demonstrates that properties of these materials can to a larger extent be controlled by a proper choice of the initiation system.

4. Conclusion

In the temperature range of 110–150 °C, we studied anionic polymerization of CLA, initiated by 1 mol% CLAMgBr in the presence of 5–25 wt% PCLO and/or in the presence of 0.5–1.0 mol% *N*,*N*′-isophthaloyl-bis-ε-caprolactam (IPBCLA) in combination with 10–25 wt% PCLO.

It was demonstrated that PCLO acts as a polymeric activator, wherein materials thus obtained have random structure, not differing in their properties from copolymer materials formed under similar conditions by a copolymerization of CLA and CLO. Obviously, PCLO is incorporated into the copolymer chain not only through scission reactions, Eq. (4), but also (and predominantly) through exchange ones, Eq. (5).

Allen and Eaves [12] reported on polyesteramides prepared by NaH-initiated anionic polymerization of CLA in the presence of isocyanato-terminated PCLO ($M_n \sim 2000$ g mol^{-1}). Comparing properties of these copolymers with those described in the present paper, we find that the use of CLAMgBr gives always higher yields of the polymer, approaching the equilibrium content of CLA achieved during the preparation of PCLA. Materials according to Ref. [12] show distinctly higher elongation, as compared to those of ours.

Undoubtedly, the system CLA/PCLO (CLO)/-CLAMgBr/*N*-acyllactam is suitable for the polymerization casting; in contrast, preparation of the material according to a published procedure [12] does not yield a good-quality plastics.

Introducing the *N*-acyllactam activator speeds up the polymerization and enables one to perform a copolymerization at as low temperature as 110 °C, which is unusual with polymerization casting. The effect of the activator (on the rate of the process) manifests itself also in the properties of the product; even at the same composition, the copolymers show melting endotherms at higher temperatures (by 10 °C, at least). Presently, this phenomenon, reflecting a higher degree of ordering of the material, is being intensively investigated.

The polyesteramides prepared were subjected to detailed biodegradation assays, the results of which will be the subject of the forthcoming paper.

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