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Polymerization of lactams, 96[☆] anionic copolymerization of ε-caprolactam with ω-laurolactam

Jan Budín *, Jiří Brožek, Jan Roda

Department of Polymers, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

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Abstract

Poly[(ε-caprolactam)-*co*-(ω-laurolactam)] was prepared at two different experimental arrangements — pseudoadiabatically and isothermally. Polymerization activity of two initiators ε-caprolactam magnesium bromide (CLMgBr) or sodium salt of ε-caprolactam (CLNa) in combination with *N*-benzoyl-ε-caprolactam (BzCL) was compared. The copolymerizations were carried out in the whole concentration scale of both monomers and in the temperature range from 120 to 240 °C. Prepared materials were evaluated by means of polymer yield, DSC, DMA and WAXS. The results have shown fundamental differences between both initiators. Copolymers prepared by initiation with CLNa have random character, one melting endotherm and display one crystalline form opposite copolymers prepared by initiation with CLMgBr having heterogeneous character proved especially by two melting endotherms (∼140 and ∼210 °C) and two types of crystalline form (α and γ).

Keywords: Copolyamides; Anionic polymerization; Thermal properties

1. Introduction

Polyamide 6 (PA6) or poly(ε-caprolactam) (PCL) is synthesized by polymerization of cyclic monomer ε-caprolactam (CL) [1–4]. This plastic has been usually used for the preparation of high-quality fibers but one-third of production finds the use as a construction material.

The transformation of monomer (CL) into polymer is possible by all known reaction mechanisms. The most widely used one is hydrolytic polymerization [5–7]. Fast anionic polymerization [8] has been also used in industry. Cationic polymerization [9] was studied only from theoretical aspects.

PCL teems not only with a lot of outstanding properties but also some disadvantages as low impact strength under minus temperatures which restricts its application possibilities. For further expansion of PCL application it is necessary to modify its properties. There are several well known ways of modification: physical [10,11] and chemical modification which include copolymerization and preparation of random or block copolymers by different procedures and mechanisms.

Significant changes of polyamide properties can be also achieved by copolymerization of lactams with different ring size, i.e. with different number of methylene groups in lactam rings. The size of lactam cycle does not determine only its stress but also conformation of amide bond and consequently its interaction with acidic or basic part of initiation system, too. ω-Laurolactam (LL) is the only one industrially supplied copolymerization partner of ε-caprolactam (CL). Copolymerization of these two lactams can fit together their advantages and suppress their disadvantages [12–19]. Polyamide 6 exhibits relatively high-moisture absorption, melting temperature about 220 °C, very good mechanical properties as modulus, tensile strength, etc. [20]. Polyamide 12 (PA12)/poly(ω-laurolactam)/(PLL) has low-moisture absorption, lower melting point ∼174 °C and chemical resistance [20].

Fast activated anionic polymerization has been successfully used for polymerization casting [16,21–23] or RIM technology [24] of lactams mentioned. Most authors have used for the initiation of polymerization sodium hydride (NaH) [11,16,19,22–27] or sodium salt of ε-caprolactam (CLNa) [15,18,21] and only several authors have mentioned the use of magnesium compounds like ethyl magnesium bromide (EtMgBr) [12] and ε-caprolactam magnesium bromide (CLMgBr) [13]. The required high polymerization rate of the anionic polymerization is achieved by introducing a so called activator, which is the compound containing or forming in situ

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[☆] Part 95: cf. Ref. [39].

* Corresponding author. Tel.: +420 2 2044 3190; fax: +420 2 2044 3175.
E-mail address: jan.budin@vscht.cz (J. Budín).

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N-acyllactam structure. Some typical activators are *N*-acetyl-ε-caprolactam [18,19,27], *N*-benzoyl-ε-caprolactam [12,25], *N*,*N*′-hexamethylene-bis(carbamoyl-ε-caprolactam) [21], *N*,*N*′-isophtaloyl-bis-ε-caprolactam [12,13], 2,4(6)-diisocyanatotoluene [24]. The choice of the initiation system (combination of initiator and activator) and polymerization conditions have fundamental influence on polymerization rate, polymer yield, structure and properties of resulting materials.

PCL and PLL are semicrystalline polymers. Methylene groups and amide groups in PCL chains are in trans conformation and the chains are arranged in antiparallel position; this alignment is designated as α-form [19]. PLL possesses all methylene groups in trans conformation but amide groups are shifted from the plane and chains are not fully expanded in parallel arrangement; this alignment is denoted as γ-form [28]. γ-Form is preferred in random PA6/12 copolymers containing about 50 or less mol% CL [26]. Thermal or mechanical treatment can lead to changes of crystalline form to less stable structure of γ-form in the case of PCL [29–31] and α-form in the case of PLL [32–34].

The authors of papers [25,35,36] reported that all synthesized CL/LL copolymers were random regardless of the polymerization mechanism used. The character of copolymers was determined by means of ^{13}C NMR.

The submitted paper compares initiation activity of CLNa and CLMgBr in the anionic copolymerization of ε-caprolactam and ω-laurolactam and attempts to explain extraordinary behavior of magnesium initiator.

2. Experimental

2.1. Materials

ε-Caprolactam (CL, Bayer) and ω-laurolactam (LL, ATO-Chemie) were used as received and were stored in desiccator over phosphorous pentoxide. Initiators ε-caprolactam magnesium bromide (CLMgBr, DSM) 1.06 mol/kg and sodium salt of ε-caprolactam (CLNa, Bruegemann) 1.3 mol/kg were supplied in sealed plastic bags as concentrate in CL and were stored in flask under argon. Activator *N*-benzoyl-ε-caprolactam (BzCL) was prepared by reaction of *N*-benzoylchloride (Fluka) with CL in benzene (Penta Chrudim) and pyridine (Fluka). Product was repeatedly crystallized from cyclohexane; melting temperature 73 °C (DSC).

2.2. Copolymerization in test tubes

Copolymerizations of CL with LL were performed in glass test tubes with inner diameter 2 cm. The monomer ratios were from 100:0; 90:10 up to 3:97 CL:LL (mol%). The mixture of monomers was melted in temperature range 110–160 °C depending on its composition. Activator 0.5 mol% BzCL was added immediately after melting of mixture and then 0.5 mol% CLNa or CLMgBr was dosed and dissolved in CL/LL mixture. Polymerization was carried out in silicon or salt bath. The polymerization was stopped by cooling the test tube at −78 °C. The test tube was broken to separate the copolymer sample which was immediately placed into a desiccator over P_2O_5 to avoid moisture absorption.

2.3. Polymerization casting

The monomer mixture was melted at 120–150 °C in a round bottomed flask under argon atmosphere. Then activator (BzCL) and initiator (CLMgBr or CLNa) were added, respectively. Thus formed monomer feed was transferred into aluminum mold (internal cavity 160×140×2 mm) preheated at polymerization temperature 150–170 °C. After 5 h of polymerization the mold was cooled at room temperature. The plaques were, after demolding, immediately placed into desiccator over P_2O_5 to avoid moisture absorption.

2.4. Polymer characterization

A part of the sample was disintegrated and extracted three times with cold methanol for the determination of polymer yield. The samples were dried at room temperature under reduced pressure (30 Pa) to constant weight.

DSC measurements were carried out on DSC 2920 (TA Instruments). The weight of extracted sample was about 5–7 mg. Measurements were performed from room temperature to 240 °C under nitrogen purge and a heating rate of 10 °C min^{-1}.

The content of incorporated CL and LL units was calculated from the nitrogen content (elemental analysis on PE 2400).

The degree of crystallinity and its type of extracted samples was determined by means of wide angle X-ray scattering (WAXS) on Difractometer D8 Bruker with Cu K_α radiation in the range of diffraction angels (2θ) from 5 to 35° at a speed 2° min^{-1} (voltage 40 kV and current 30 mA).

For the DMA measurements, specimens having dimensions of 2×4×30 mm were prepared from virgin samples. The DMA DX04T tester (RMI, Czech Republic) was used, the measurements being performed in a temperature range −100 and 150 °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.

3. Results

3.1. Effect of the initiator type

Basic experiments in test tubes were carried out at equimolar composition of monomer feed and the polymerization proceeded under pseudoadiabatic conditions. The increase in temperatures varied from 5 to 45 °C depending on the rate of polymerization process, composition of polymerization feed and mold geometry. The concentration of both activator (BzCL) and initiator (CLNa or CLMgBr) was 0.5 mol%. The polymerization time was 30 min and polymerization temperature 150, 180 and 210 °C. The polymerization temperature 150 °C was designed below the both melting temperatures of corresponding homopolymers poly(ε-caprolactam) — PCL ($T_m = 220$ °C) and poly(ω-laurolactam) — PLL ($T_m = 170$ °C),

Table 1
Influence of initiator type on the anionic copolymerization of equimolar mixture of ε-caprolactam (CL) and ω-laurolactam (LL), activator *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%), initiator sodium salt of ε-caprolactam (CLNa, 0.5 mol%) or ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%), polymerization time 30 min

T_{p1} (°C)	T_{p2} (°C)	CLNa		CLMgBr	
		k_m (%)	T_m (°C)	k_m (%)	T_m (°C)
110	150	70.7	139	69.0	136; 214
110	180	72.7	150	70.1	138; 199
110	210	90.6	127	68.4	138

T_{p1}, temperature of polymerization mixture preparation; T_{p2}, polymerization temperature; k_m, polymer yield, extraction with cold methanol; T_m, melting endotherm of extracted copolymer.

the polymerization temperature 180 °C below the melting temperature of PCL and above the melting temperature of PLL, the polymerization temperature 210 °C above the melting temperature of PLL and close to the melting temperature of PCL.

The results are summarized in Table 1. The polymer yields were higher for materials prepared by the initiation with CLNa, moreover, increased with an increase of polymerization temperature than CLMgBr which were temperature independent.

The results of DSC were surprising, since the extracted copolymers prepared by the initiation with CLMgBr at polymerization temperature 150 and 180 °C exhibited two well distinguished melting endotherms (∼140 and 200 °C), Fig. 1. The lower endotherm is in the range of the melting temperature of a copolymer prepared by initiation with CLNa (∼140 °C) and could correspond to random copolymers prepared by the initiation with sodium salts of lactam [25,35]. The higher endotherm could correspond to homopolymer PCL, resp. copolymer with prevailing content of CL units.

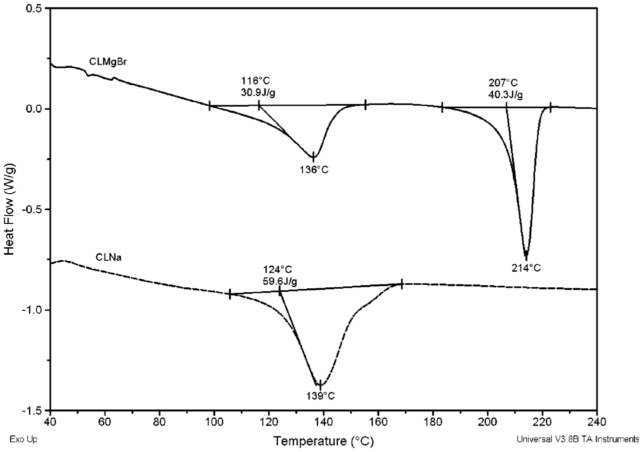


Fig. 1. Thermal properties (DSC) of copolymers prepared from equimolar mixture of ε-caprolactam (CL) with ω-laurolactam (LL) activated with *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%) and initiated either with ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%) or with sodium salt of ε-caprolactam (CLNa, 0.5 mol%) at 150 °C, polymerization time 30 min.

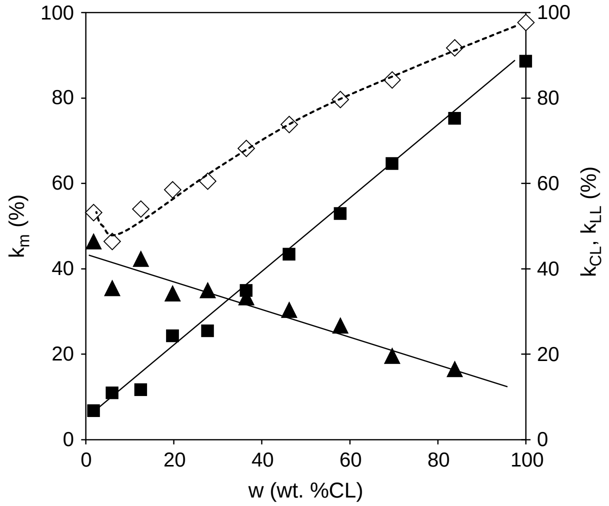


Fig. 2. Influence of polymerization feed composition on polymer yield (◇ k_m) and content of incorporated ε-caprolactam (CL) (■ k_{CL}) or ω-laurolactam (LL) units (▲ k_{LL}); copolymerization of ε-caprolactam (CL) with ω-laurolactam (LL) activated with *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%) and initiated with ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%) at 150 °C, polymerization time 30 min.

3.2. Influence of the composition of the polymerization mixture

As mentioned above, the extracted copolymers prepared by initiation with CLMgBr exhibit two separated melting endotherms. This phenomenon has not been published yet and therefore we have studied the copolymerization of CL with LL in details.

The copolymerizations were carried out in the whole concentration range of monomer feed composition under the same experimental conditions and two initiators (CLMgBr or CLNa) were used for a comparison. We have chosen the polymerization temperature 150 °C and polymerization time 30 min. The results are summarized in Tables 2 and 3.

The yield of copolymer prepared by initiation with CLMgBr decreases with increasing content of LL in the feed (Fig. 2). The copolymer composition was derived from the content of nitrogen in a copolymer determined by elemental analysis (x_{CL}, Table 2). The dependence of incorporated CL related to the monomer feed composition is near to diagonal (Fig. 2) and more than 90% of initial CL content is incorporated into copolymer during 30 min of polymerization in all cases. LL does not show such activity and maximum 45% of LL related to its initial amount is incorporated into copolymer during 30 min of polymerization. This is in accordance with published data [37] that the monomers differ in their reactivity, dielectric constant, etc.

All copolymers prepared from monomer feed containing 30–70 mol% CL showed after extraction two melting endotherms (Fig. 3). The enthalpy of fusion of lower melting endotherm (130–140 °C) slightly increases with a decrease of incorporated CL (Table 2). On the other hand, higher melting endotherm slightly decreases with a decrease of incorporated CL.

For the comparison, the same experiments were carried out by initiation with CLNa at 150 °C. The results are shown in

Table 2
Influence of polymerization feed composition on the anionic copolymerization of ε-caprolactam (CL) and ω-laurolactam (LL), activator *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%), initiator ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%) at 150 °C, polymerization time 30 min

y (mol% CL)	k_m (%)	x_{CL} (mol%)	w_{CL} (wt%)	K_{CL} (%)	K_{LL} (%)	T_m (%)	ΔH_M (J/g)
100	97.7	–	–	–	–	220	89
90	91.7	89	82	90	–	217	84
80	84.2	85	77	93	65	216	70
70	79.6	78	66	91	63	131; 217	14; 60
60	73.8	71	59	94	57	134; 214	12; 46
50	68.2	65	51	96	53	137; 213	20; 38
40	60.5	56	42	92	49	140; 212	25; 31
30	58.5	55	42	–	43	139; 210	41; 5
20	54.0	33	22	94	48	150	53
10	46.2	35	23	–	38	161	59
3	53.2	20	13	–	47	174	74

y, content of CL in polymerization feed; k_m, polymer yield, extraction with cold methanol; x_{CL}, number of incorporated CL units determined by elemental analysis; w_{CL}, weight amount of incorporated CL units determined by elemental analysis; K_{CL}, relative amount of incorporated CL related to the initial CL content; K_{LL}, relative amount of incorporated LL related to the initial LL content; T_m, melting endotherm of extracted polymer; ΔH_M, enthalpy of fusion.

Table 3
Influence of polymerization feed composition on the anionic copolymerization of ε-caprolactam (CL) and ω-laurolactam (LL), activator *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%), initiator sodium salt of ε-caprolactam (CLNa, 0.5 mol%) at 150 °C, polymerization time 30 min

y (mol% CL)	k_m (%)	x_{CL} (mol%)	w_{CL} (wt%)	K_{CL} (%)	K_{LL} (%)	T_m (°C)	ΔH_M (J/g)
100	96.3	–	–	–	–	220	86
90	92.1	88	80	88	–	210	76
80	86.9	82	72	90	81	201	51
70	78.8	76	64	87	67	183	38
60	73.7	66	53	84	65	156	47
50	70.7	61	47	91	59	139	57
40	69.6	52	38	97	59	134	53
30	65.7	46	33	–	55	140	53
20	60.8	28	18	87	57	153	48
10	53.0	27	17	–	47	164	54
3	60.9	12	7	–	58	174	62

y, content of CL in polymerization feed; k_m, polymer yield, extraction with cold methanol; x_{CL}, molar fraction of incorporated CL units determined by elemental analysis; w_{CL}, weight fraction of incorporated CL units determined by elemental analysis; K_{CL}, relative amount of incorporated CL related to the initial CL content; K_{LL}, relative amount of incorporated LL related to the initial LL content; T_m, melting endotherm of extracted polymer; ΔH_M, enthalpy of fusion.

Table 3 and Fig. 3. The polymerization activity evaluated by k_m of both initiators used is not significantly different. Nearly the same content of CL (∼90% of initial amount) is incorporated into copolymers after 30 min by using both initiators. LL is incorporated into copolymer with higher rate by using CLNa. There is essential difference in their thermal properties. Copolymers prepared by initiation with CLNa have only one melting endotherm (Fig. 4) and they are obviously random [18,21]. An eutectic minimum of melting endotherm was achieved at 40 mol% CL in monomer feed, see Table 3, which is in agreement with published data [16,26].

3.3. Effect of polymerization temperature

The polymerization temperature has a significant influence on the polymerization course and also on the properties of resulting material. The influence of the polymerization temperature (varied in interval from 120 to 240 °C) was studied for equimolar composition of a monomer feed, the concentration of BzCL and CLMgBr 0.5 mol% and the polymerization time 30 min, see Table 4. At polymerization temperatures 150–210 °C polymer yield was 70% though the equilibrium was not reached and the molar fraction of polymerized lactams was constant, 60 mol% CL and 40 mol% LL. Materials prepared in polymerization temperature interval 150–180 °C exhibit two melting endotherms, Fig. 5. From the change of peak area it is obvious that the increase of polymerization temperature caused a decrease of the area of higher temperature peak.

3.4. Polymerization casting

Plaques of dimensions 160×140×2 mm have been prepared by polymerization casting procedure. Such a mold shape could guarantee isothermal polymerization conditions. The copolymerizations were performed in the whole concentration range of both comonomers at 150–170 °C. The concentrations both activator BzCL and initiators (CLMgBr or CLNa) were 0.5 mol%. The polymerization time was 5 h in order to approach the equilibrium polymer yield. The results are summarized in Table 5.

3.4.1. Initiation with CLMgBr

The polymer yield of copolymers prepared by initiation with CLMgBr decreased with a decrease of CL content in monomer

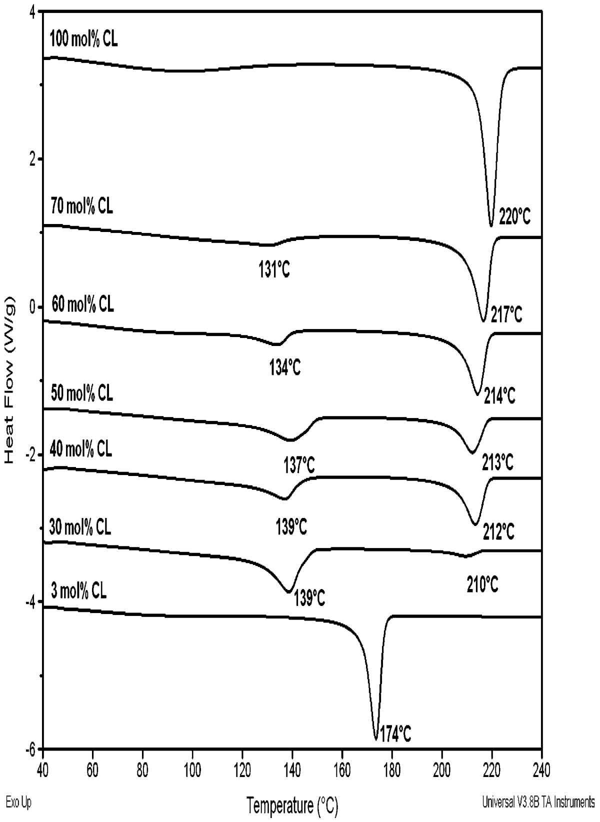


Fig. 3. Influence of polymerization feed composition on thermal properties (DSC) of materials prepared by copolymerization of ε-caprolactam (CL) with ω-laurolactam (LL) activated with *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%) and initiated with ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%) at 150 °C, polymerization time 30 min.

feed in similar trend as in the case of copolymers prepared in glass test tubes, compare Tables 2 and 5. The lowest polymer yield (81%) was reached for copolymers prepared from polymerization feed containing higher content of LL and confirms already approved lower polymerization activity of LL. DMA analyses of nonextracted (virgin) samples of copolymers are disturbed by the presence of unreacted monomers.

Glass transition temperatures (DMA) in the range of 80–20 mol% of CL in monomer feed decrease from 52 to 39 °C for CLMgBr and from 58 to 45 °C for CLNa and they are affected by unreacted monomers acting as softener (plasticizer). The flexural modulus from DMA at 23 °C decreases with increasing content of LL in the monomer feed, Table 5.

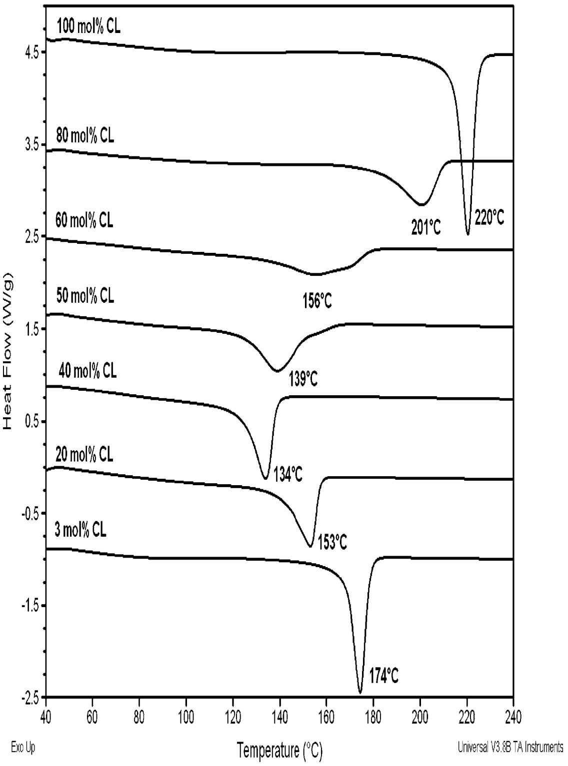


Fig. 4. Influence of polymerization feed composition on thermal properties (DSC) of material prepared by copolymerization of ε-caprolactam (CL) with ω-laurolactam (LL) activated with *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%) and initiated with sodium salt of ε-caprolactam (CLNa, 0.5 mol%) at 150 °C, polymerization time 30 min.

The DSC measurements confirmed formation of the two melting endotherms for copolymers prepared from monomer feed containing 30–70 mol% CL and significant decrease in the total enthalpy of fusion of copolymers prepared by polymerization casting in comparison with polymerization in glass test tubes, compare Tables 2 and 5. Also the values of melting endotherms are shifted to the lower values. The degree of crystallinity was determined from the enthalpy of fusion, related to value of model mixture of PLL and PCL composed of equimolar mixture of both structural units ($0.5\times 190+0.5\times 220=205$ J/g). The values 190 J/g for PCL and 220 J/g for PLL 100% crystalline polymers were taken from Ref. [17].

The degree of crystallinity determined by WAXS measurement reaches the minimum for copolymer prepared from 40 mol% of CL in the monomer feed in accordance with published literature [16]. On the other hand, the degree of crystallinity determined by means of DSC does not follow the same trend (Table 5) and decreases with increasing content of LL in monomer feed and does not reach minimum (each method is sensitive in different way on arrangement of the system). WAXS also provided information about a crystalline form of copolymers (Fig. 6). The copolymers with prevailing CL units have α-form, while copolymers with prevailing LL units have γ-form with accordance with the literature [29]. Copolymers containing 50–60 mol% incorporated CL units contain both α and γ-form. The α-form could be related to the part with melting endotherm about 210–213 °C and with high content of incorporated CL. We suppose, the γ-form could be related to the part with endotherm of melting about 126–152 °C and high content of incorporated LL.

3.4.2. *Initiation with CLNa*

The copolymerizations initiated with CLNa were carried out at lower polymerization temperature 150 °C than in the copolymerizations initiated with CLMgBr except boundary LL/CL ratio in monomers feed (20/80, 80/20). From comparison with the data in Table 5, it is evident that CLNa

Table 4
Influence of polymerization temperature on the anionic copolymerization of equimolar mixture of ε-caprolactam (CL) and ω-laurolactam (LL), activator *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%), initiator ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%), polymerization time 30 min

T_p (°C)	k_m (%)	x_{CL} (mol%)	w_{CL} (wt%)	K_{CL} (%)	K_{LL} (%)	T_m (°C)	ΔH_M (J/g)
120	26.8	94	90	66	4	209–219	91
140	46.9	81	71	92	21	213	70
150	69.0	62	48	92	56	139; 213	19; 33
160	69.1	62	48	92	56	133; 213	29; 20
170	68.8	56	42	80	63	135; 214	37; 5
180	70.1	63	49	95	56	138; 199	53; 1
210	68.4	57	44	82	60	138	58
240	58.9	62	49	78	48	144	68

T_p, polymerization temperature; k_m, polymer yield, extraction with cold methanol; x_{CL}, molar fraction of incorporated CL units determined by elemental analysis; w_{CL}, weight fraction of incorporated CL units determined by elemental analysis; K_{CL}, relative amount of incorporated CL related to the initial CL content; K_{LL}, relative amount of incorporated LL related to the initial LL content; T_m, melting endotherm of extracted polymer; ΔH_M, enthalpy of fusion.

has higher polymerization activity than CLMgBr, especially for higher initial content of LL in monomer feed.

DMA measurements provided values of T_g which vary in range from 45 to 58 °C, Table 5. In comparison with copolymers prepared by initiation with CLMgBr the flexural modulus is lower in the whole range of composition of feed. The presence of copolymer with the melting endotherm about 200 °C probably causes the higher flexural modulus of copolymers prepared by the initiation with CLMgBr.

All copolymers prepared in the presence of CLNa showed only one melting endotherm that confirms their random character. The lowest value of melting endotherm was reached for copolymer prepared from equimolar feed of monomers. Copolymers prepared by initiation with CLNa have lower enthalpy of fusion than copolymers prepared by initiation with CLMgBr (Table 5).

The degree of crystallinity determined from DSC measurement under the same assumption (see above) was lower for copolymers prepared with CLNa compared with CLMgBr (Table 5). The degree of crystallinity determined by means of WAXS has minimum at equimolar composition of monomer feed and there is no crystalline arrangement in the system (Fig. 6). On the other hand, DSC measurement registered some regular phase. WAXS measurements showed that if the content of incorporated CL prevails, α-form of crystal phase is presented and if the content of incorporated LL prevails, γ-form of crystal phase is presented.

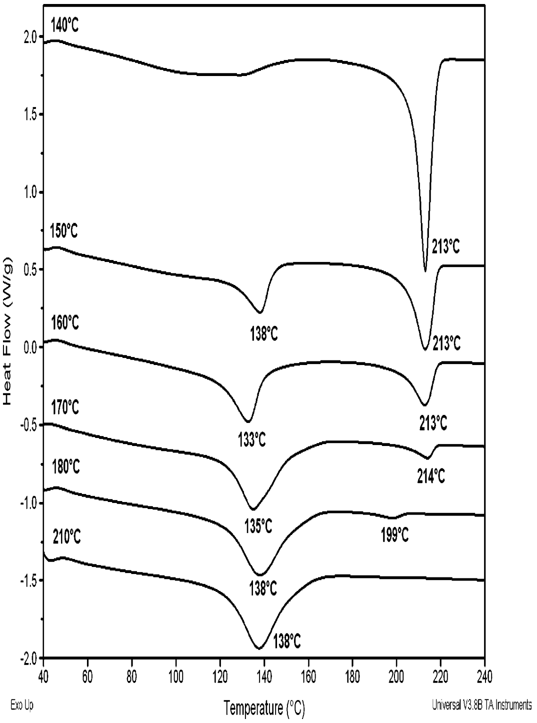


Fig. 5. Influence of polymerization temperature (on the left side of the curve) on thermal properties (DSC) of materials prepared by copolymerization of equimolar amount of ε-caprolactam (CL) with ω-laurolactam (LL) activated with *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%) and initiated with ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%), polymerization time 30 min.

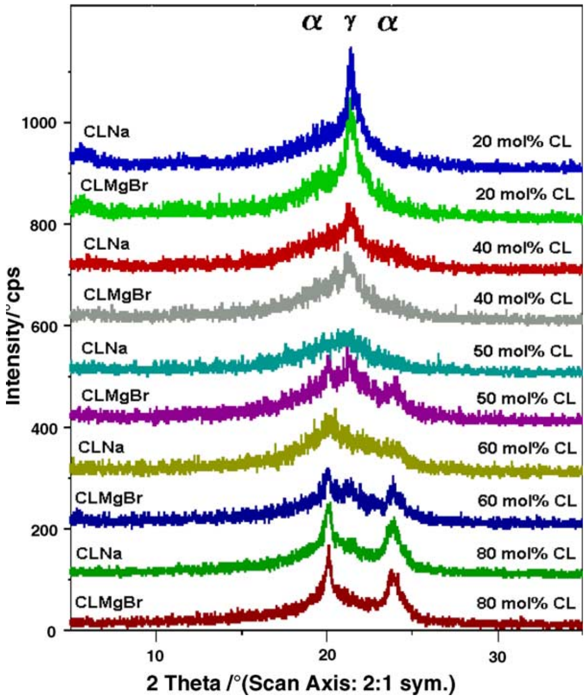


Fig. 6. WAXS traces of materials prepared by mold casting of polymerization feed of ε-caprolactam (CL) and ω-laurolactam (LL) (composition indicated on curves) activated with *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%) initiated either with ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%) or with sodium salt of ε-caprolactam (CLNa), polymerization time 5 h at 150–170 °C (Table 5).

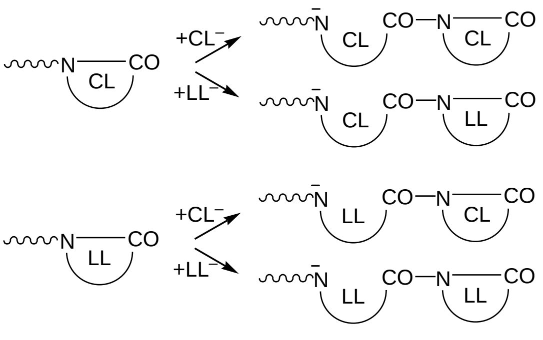
Table 5
Influence of polymerization feed composition on copolymerization of ε-caprolactam (CL) and ω-laurolactam (LL), activator *N*-benzoyl-ε-caprolactam (BzCL, 0.5 mol%), initiators ε-caprolactam magnesium bromide (CLMgBr, 0.5 mol%) or sodium salt of ε-caprolactam (CLNa, 0.5 mol%); mold casting procedure, polymerization time 5 h

Initiator	y (mol% CL)	T_p (°C)	k_m (%)	T_g (°C)	T_m (°C)	ΔH_M (J/g)	E_f (MPa)	α_α (%)	α_γ (%)	α_c (%)	α_{DSC} (%)
CLMgBr	80	170	97.1	49	209	55	1050	24	0	24	26
	70	160	96.7	52	116; 221	5; 55	1150	23	0	23	29
	60	160	93.5	44	126; 213	8; 36	1050	16	4	20	21
	50	160	91.4	48	129; 210	34;18	900	6	3	9	25
	40	160	89.7	44	131; 210	43; 0.3	750	0	9	9	21
	30	160	86.1	39	139; 211	41; 0.3	800	0	15	15	20
	20	160	80.9	40	149	43	750	0	22	22	21
CLNa	80	160	99.4	58	195	62	1150	26	0	26	30
	60	150	98.9	48	138	25	850	9	0	9.0	12
	50	150	94.9	52	125	39	650	0	0	0	19
	40	150	97.9	49	133	35	750	0	11	11	17
	20	160	91.8	45	152	41	850	0	19	19	20

y, content of CL in polymerization feed; T_p, polymerization temperature; k_m, polymer yield, extraction with cold methanol; T_g, glass transition temperature determined by DMA; T_m, melting endotherm of extracted polymer determined by DSC; ΔH_M, enthalpy of fusion; E_f, flexural modulus determined by DMA; α_α, α_γ, degree of crystallinity, α-form, γ-form; α_c, overall degree of crystallinity determined by WAXS; α_{DSC}, degree of crystallinity determined by DSC.

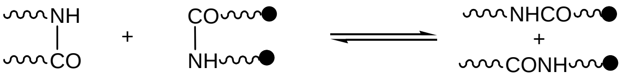
4. Discussion

Two fundamental processes — propagation reactions (1) and exchange reactions (2) (trans reactions versus propagation reactions) play an important role in the synthesis of CL and LL based copolymers. Formation of polymer chains (propagation) of copolymers is actually competitive reaction of CL anion (CL^-) and LL anion (LL^-) with two nonionic growth centers, reactions (1).



(1)

Copolymer structure is further determined by exchange reactions (2).



(2)

Copolymer formation and its composition are therefore influenced by kinetic and thermodynamic effects which involve propagation (1), transacylation (2) and side reactions. The rate of propagation depends on temperature, concentration of lactams, initiator, growth centers and on complex ionic equilibria between the initiator and amide groups of CL, LL, PCL, PLL. These equilibria depend on dissociation constant of initiator, lactam acidities, medium permitivities and temperature. Also, concentration and activity of ions and ion pairs in system are influenced by these facts.

The concentrations of active anions and growth centers decrease in the Claisen type condensations during polymerization. The decay of growth centers is higher in anionic polymerization of LL than CL polymerization [38].

Equilibrium monomer – polymer is established in ring opening polymerization of lactams. In copolymerization the activity of one lactam is lowered by the dilution with the second one. Resulting yield of copolymer is lower compared to yield of homopolymers. These effects are reflected in structure of copolymer CL/LL prepared in presence of both initiators studied.

Copolymerization of CL with LL using CLNa initiator provides random copolymers with single melting endotherms [15,18,21]. It was confirmed also by this study for the temperature interval ranged from 150 to 210 °C, see Table 1 and Fig. 1. CL polymerizes with higher rate than LL [36]. The higher rate of incorporation of CL into (co)polymer would lead to multiblock copolymer with longer PCL segments. Their lengths shorten with the decreasing CL/LL ratio. However, chain amide groups are split by transamidation reactions with a comparable rate irrespective of the monomer segment type. This rate increases significantly with temperature. The splitting leads to a random copolymer.

Similar considerations are valid for initiation with CLMgBr hence the mechanism of CL/LL copolymer formation does not differ significantly. Taking into account the lower CLMgBr basicity and the different temperature dependences, the relations between propagation, exchange and side reactions have to be different. Therefore, in polymerization temperature interval 150–180 °C complex copolymer structures are formed characterized by structural heterogeneity and presence of two melting temperatures.

For more accurate determination of the structure of CL/LL copolymers studied it is necessary to carry out plenty of additional time-consuming experiments for instance determination of consumption of both monomers during polymerization course, material fractionation, NMR, etc. These investigations are now in progress and the results will be included in the forthcoming paper.

5. Conclusions

Copolymers of CL with LL in wide composition range have been prepared in two different arrangements in glass test tubes — pseudoadiabatic experimental conditions and in plague mould — isothermal experimental conditions. Properties of copolymers prepared in two different ways by initiation with corresponding initiators follow generally the same trends.

There are fundamental differences in copolymer properties prepared by initiation both with CLNa and CLMgBr. CLNa exhibits higher polymerization activity especially in copolymerization with higher content of LL and at higher polymerization temperatures. The essential difference is in thermal properties — copolymers prepared by initiation with CLMgBr have two melting endotherms ~140 and ~210 °C in the range from 30 to 70 mol% CL in feed. Copolymers prepared by initiation with CLNa have only one melting endotherm in the whole range of monomers in feed.

WAXS measurements show that copolymers contain the crystal form of prevailed monomer units — in case of CL α-form and in case of LL γ-form, respectively. Copolymers prepared by initiation with CLMgBr from monomer feed containing 50–60 mol% CL displays both α-form and γ-form of crystal phase. On the other hand, copolymer prepared by initiation with CLNa from equimolar content of both comonomers in feed does not show any WAXS crystallinity.

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