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# Kinetic investigation and regularities during the synthesis of Poly(ε-caprolactam-co-ε-caprolactone) and Poly(ε-caprolactam-co-δ-valerolactone) biodegradable copolymers

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## Summary

Large diversity of tailor-made poly[(ε-caprolactam)-co-(ε-caprolactone)] P[(CLA)-co-(CLO)] and poly[(ε-caprolactam)-co-(δ-valerolactone)] P[(CLA)-co-(VLO)] copolymers have been obtained via activated anionic polymerization of ε-caprolactam (CLA) with sodium caprolactam (NaCL) as a basic initiator. In the present study several poly(ε-caprolactones) (PCLOs) and poly(δ-valerolactone) polyols were employed as effective bifunctional polymeric activators (PACs) and suitable comonomers of CLA. The obtained poly(esteramides) PEAS were isolated and their structure was confirmed by the $^1$H NMR and FTIR spectroscopy. The influence of the molecular weight and type of the PACs, the CLA/PAC ratio and polymerization conditions on the conversion, intrinsic viscosity and polymerization kinetic was explored. The results demonstrated that the use of the PACs reduces the polymerization time to several minutes and polymerization process proceeds without induction period at low energy of activation and high yield of copolymers. Evaluation of the PACs activity and the activation energy confirmed that the PACs are highly active compounds efficient to CLA features modification.

## Introduction

Nowadays, the environment pollution becomes very significant ecological problem. The biodegradable polymers belong to the well known eco-polymers and their use in the technique and industry is of great importance. Therefore, a main research tendency is to combine higher sensitivity toward biodegradation with better mechanical and physical properties.

The aliphatic poly(amides) as polyamide-6 (PCLA) are attractive because of their properties: excellent load bearing (strength and stiffness), work capabilities at elevated temperatures, good chemical and abrasion resistance, low coefficient of friction and impact resistance [1]. Nevertheless, the modification of some PCLA features, particularly the toughness and the biodegradability has been a challenge for a long time [2-4]. The poly(lactones) are suitable comonomers for modification of poly(amides) [5, 6]. The latter improve elastomeric properties, the compatibility to other polymers and the sensitivity to biodegradation of poly(amides). In this way, the poly(esteramides) (PEAS) successfully combine the excellent mechanical and physical properties of the nylons, and represent the transition materials from non-biodegradable to biodegradable ones [7-10]. The PEAS are preferentially synthesized via anionic ring opening polymerization. Different lactone-based comonomers and catalytic systems are reported in the literature. Goodman et al., synthesize PEAS on the base of CLA and CLO in the presence of NaCL [11]. Roda et al., copolymerize the CLA with high molecular PCLO in the presence of ε-caprolactam magnesium bromide (CLAMgBr) [12]. All of these copolymers exhibited increased mechanical properties. Gonsalves et al., Nakayama et al., Tokiwa et al., and Roda et al., realize the biodegradation of PEAS mainly by means of the enzyme lipase (Rizopus arrizus) or fungi treatment: (Fusarium moniliforme, Aspergillus niger, ligholitic fungi – Irpex Lacteus) [13-15].

One of the most efficient methods of preparation of tailor-made PCLA copolymers is the introduction of various segments as bifunctional PACs via anionic polymerization of CLA [16-17]. Applying similar approach for synthesizing of PEAS it could be possible to prepare a diversity of copolymers with central (elastomeric and biodegradable) poly(lactone) blocks - (B) and terminal (hard) poly(amide) blocks - (A). In such manner the degree of elastification and the sensitivity toward biodegradation of PEAS can be successfully varied. Several poly(ε-caprolactones) and poly(δ-valerolactone) telechelic polyols were chosen as precursors for the preparation of effective PACs. In the literature there are no data about copolymerization of CLA with aforementioned types of polyols applied as PACs.

This work is focused on PEAS synthesizing by ring opening polymerization of CLA, using new effective PACs on the base of telechelic PCLOs and PVLO polyols. Detail investigation of the influence of the type, content, and molecular weight of the central PAC blocks on the polymerization kinetics, the structure and the molecular weights of the obtained copolymers was performed.

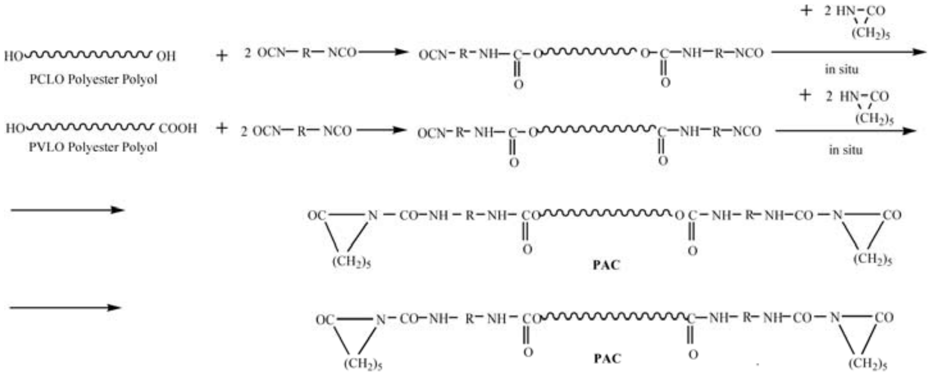
## Experimental

### *Materials*

The monomer ε-caprolactam (CLA; Merck) was dried in a vacuum oven, over $P_2O_5$ at 60°C for 5 days. The initiator sodium caprolactam (NaCL) was synthesized and purified according to ref. [18]. Isophorone diisocyanate (IF; Merck), sulfuric acid ($H_2SO_4$; Merck, 96 %) and chloroform ($CHCl_3$; Merck) utilized for extraction of the obtained copolymers, were used as received. Toluene ($C_7H_8$; Merck) was purified by distillation, which was followed by drying over sodium. Commercial grade poly(ε-caprolactone) polyols, CAPA$^{®}$2054, CAPA$^{®}$2125, CAPA$^{®}$2205, CAPA$^{®}$2304 (Solvay Caprolactones) were chosen as precursor for PACs. The bifunctional telechelic PVLO oligomer was prepared according to ref. [19]. The synthesis conditions and characterization of the PACs were reported in our previous work [20].

### *Synthesis*

The synthesis of P[(CLA)-co-(CLO)] and P[(CLA)-co-(VLO)] copolymers was performed using the ampoule technique [17]. The process was carried out in bulk at



**Scheme 1.** PACs formation.

temperature 180°C, as described elsewhere [20]. The diisocyanate end-capped polyols, dried monomer CLA, and the ampoules were added to a glass reactor in nitrogen atmosphere and were molten at 100°C with continuous stirring for 20 min, a requisite for *in situ* formation of PACs (Scheme 1).

The reaction temperature was raised to 130÷140°C and initiator (NaCL) was added under vigorous stirring. The polymeric mixture was forced into ampoules with $N_2$. The copolymers containing 2, 5 and 10 wt % PAC were prepared with a constant

**Table 1.** Codes of the PACs and corresponding PEAS obtained by anionic polymerization of CLA.

| № | PAC Code[a] | Copolymers Code[b] | PAC Content (wt %) |
|---|---|---|---|
| 1 | $PAC_{PVLO3200IF}$ | $PCLA/PAC_{PVLO3200IF}$ | 2 |
| 2 | | | 5 |
| 3 | | | 7 |
| 4 | | | 10 |
| 5 | $PAC_{PCLO3000IF}$ | $PCLA/PAC_{PCLO3000IF}$ | 2 |
| 6 | | | 5 |
| 7 | | | 10 |
| 8 | $PAC_{PCLO2000IF}$ | $PCLA/PAC_{PCLO2000IF}$ | 2 |
| 9 | | | 5 |
| 10 | | | 10 |
| 11 | $PAC_{PCLO1250IF}$ | $PCLA/PAC_{PCLO1250IF}$ | 2 |
| 12 | | | 5 |
| 13 | | | 10 |
| 14 | $PAC_{PCLO550IF}$ | $PCLA/PAC_{PCLO550IF}$ | 2 |
| 15 | | | 5 |
| 16 | | | 10 |

[a] The nomenclature of the used polymeric activators is consisted of abbreviations and digits. The abbreviation PAC originates from polymeric activator, the abbreviations PCLO and PVLO derives from poly(ε-caprolactone) and poly(δ-valerolactone), respectively. The digits indicate the molecular weight $M_n$ (g.mol$^{-1}$) of the used poly(lactone) polyol before functionalization, and the abbreviation IF (isophorone diisocyanate) denotes the functionalizing agent;

[b] The nomenclature of the copolymers is consisted of the abbreviation of poly(ε-caprolactam) PCLA and the corresponding PACs code.

initiator concentration of 1 mol % to the monomer quantity. The obtained copolymer samples were extracted with $CHCl_3$ for 8 h in a Soxhlet apparatus and dried in vacuo at 60°C until constant weight was reached. The specific codes of the PACs used in this study and the corresponding copolymers with CLA are given in Table 1.
Different feed compositions were polymerized (at 180°C and NaCL 1 mol %) in order to compare the activity of the new synthesized PACs to another commonly used lactone-based comonomers and catalytic systems concerning CLA (Table 2).

**Table 2.** Codes and compositions of the different CLA polymerization systems.

| Code | Type of Comonomer | Content of Comonomer (wt %) | Type of Activator |
|---|---|---|---|
| PCLA/$PAC_{PCLO3000IF}$ | $PAC_{PCLO3000IF}$[a] | 2 | $PAC_{PCLO3000IF}$ |
| PCLA/PCLO3000/NAcCL | PCLO3000[b] | 2 | NAcCL[c] |
| PCLA/PCLO3000 | PCLO3000[b] | 2 | - |
| PCLA | - | - | - |

[a] The used $PAC_{PCLO3000IF}$ possesses dualistic function: as activator and comonomer;
[b] The code PCLO3000 designates poly(ε-caprolactone) polyol with Mn=3000 (g.mol$^{-1}$);
[c] The concentration of NAcCL is 0.5 mol %.

### *Instruments and Methods*

#### *$^1$H NMR spectroscopy*

The $^1$H NMR spectra were recorded with a Bruker AM400 spectrophotometer operating at 400 MHz in the mixture of HCOOH:$CDCl_3$ (1:1 v/v). The HCOOH was used as an internal standard.

#### *FTIR spectroscopy*

The FTIR spectra were recorded with a Perkin-Elmer 1600 (FTIR) over the range 450÷4500 cm$^{-1}$ at a resolution of 1 cm$^{-1}$, using the thin melted films of the copolymers.

#### *Degree of Conversion*

The degree of conversion of the copolymers was followed by interruption of the polymerization process at a certain stage and removal of the both by-products and unreacted monomers by the extraction following the standard procedure as described above.

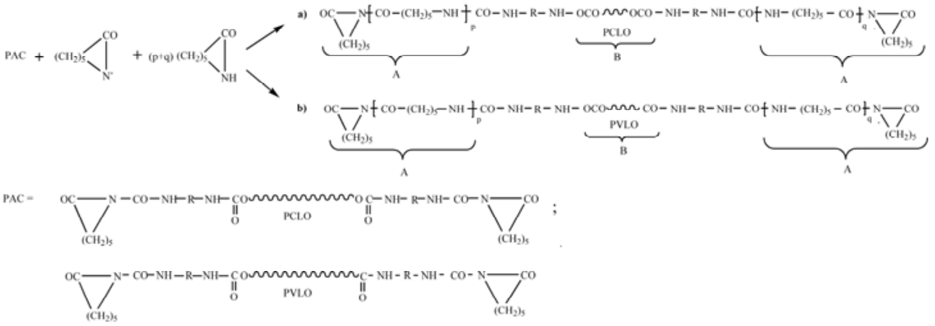
#### *Viscosimetric Molecular Weight*

The intrinsic viscosities ([η]) of the copolymers were obtained in sulfuric acid (96 %). The average viscosimetric molecular weights ($M_v$) were calculated by the Mark-Houwink relationship according to ref. [1]. All samples contain very small gel fraction, sometimes less than 1 wt %. The soluble fraction was used for further viscosimetric investigations.

## Results and discussion

### *Synthesis of the P[(CLA)-co-(CLO)] and P[(CLA)-co-(VLO)] copolymers*

The activated anionic polymerization of CLA was used for synthesis of P[(CLA)-co-(CLO)] and P[(CLA)-co-(VLO)] copolymers. The polymerizations were initiated by NaCL as basic initiator and activated by PACs on the base PCLO or PVLO polyols. The amount of the PACs was varied in order to change the number of active centers and to achieve different ratio between (A) segments and (B) blocks. The mechanism of the copolymers formation for both general types of copolymers is shown in Scheme 2a and b, respectively.



**Scheme 2.** Mechanism of copolymers formation for both general types of copolymers.

According to the generally accepted mechanism of the activated anionic polymerization of lactams the reaction starts with two component catalyst system, composed of lactamate-anions and activating compounds. The addition of activators in the system is essential because the nucleophilic attack of the lactam anion on the carbamoyl group in the monomer proceeds more slowly than that to the endocyclic carbonyl group in the activators. The propagation step is also composed of similar nucleophilic attack to the N-acyllactam type growing chain ends and the proton transfer. Therefore, if there were no side reaction during the polymerization of lactams, the growing chain ends should be always the corresponding N-acyllactams, and the number of the resulting poly(amide) chains should be equal to that of the activator (PAC) concentration.

The formation of the copolymers was proved by analysis of the isolated final products. The $^1$H NMR spectra (Fig. 1a and b) show peaks characteristic for the PCLA, PCLO or PVLO sequences and confirmed the successful PACs incorporation: the peak at 3.3 ppm has been assigned to the ε-$CH_2$ protons from PCLA block; the signal at 4.1 ppm characterize the ε-$CH_2$ protons from PCLO or δ-$CH_2$ protons from PVLO blocks.

The FTIR spectra were also used for characterization of the copolymers. The absorption peaks at 3000÷3300 cm$^{-1}$ and 1500÷1650 cm$^{-1}$ regions, and the peak at 1260 cm$^{-1}$ due to γ-$CH_2$ can be considered of well established assignment for PCLA block. The last vibration is overlapped with δ(CONH, amide III) vibrations. The strong carbonyl band at 1734 cm$^{-1}$ characterizes the ester carbonyl group from PCLO or PVLO blocks.

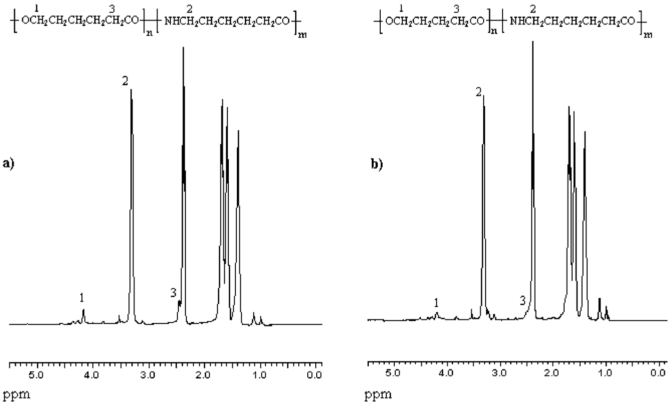


**Figure 1.** $^1$H NMR spectra of a) P[(CLA)-co-(CLO)] and b) P[(CLA)-co-(VLO)] copolymers.

It was suggested that at the first stage of the polymerization process proceeded the exhaustion of the PAC and through the time of polymerization the copolymer becomes richer in A (PCLA) segments. The $^1$H NMR and FTIR spectra of the unreacted compounds (extracted with chloroform in Soxhlet apparatus) confirm the proposed copolymerization reaction mechanism. No characteristic bands of PCLA or PVLO units were observed. The spectra have shown only presence of the CLA monomer and oligomers.

*Kinetic and regularities of the copolymerization process*

Different copolymer structures and properties were achieved varying the molecular weights and content of the PACs. The effect of the PACs incorporation on the polymerization process is demonstrated on Figure 2 a÷d and a'. The degree of monomer conversion ($X_n$) and the variation of the viscosimetric molecular weight ($M_v$) of the copolymers were explored with the reaction time (t). Obviously, $X_n$ and $M_v$ are proportional to the polymerization time until the monomer-polymer equilibrium was reached. Thus the pseudo-living character of the polymerization is proved.

The influence of the PCLA/PAC ratios on the course of the polymerization process is also depicted in the figures. At higher concentrations of PACs the $X_n$ and the rate of copolymerization slightly decrease due to the well known side-reactions between the comonomers [12]. This regularity is most pronounced in the presence of $PAC_{PCLO550IF}$ macromere.

The intrinsic viscosity studies of PEAS have revealed that the copolymerization process of CLA in the presence of PACs proceeds without formation of significant amount of gel fraction or networks. This phenomenon is much strongly expressed after the optimum degree of conversion is reached. Predominately, the building of the linear and branching copolymer structures is estimated.

The molecular weights ($M_v$) of the copolymers slightly diminish after the equilibrium degree of conversion for the investigated CLA/PAC ratios (Figure 2 a÷d and a'). This could be explained with appearance of side-reactions such as trans-amidation, backbiting, Claisen-type condensation, branching and degradation [4]. It has been

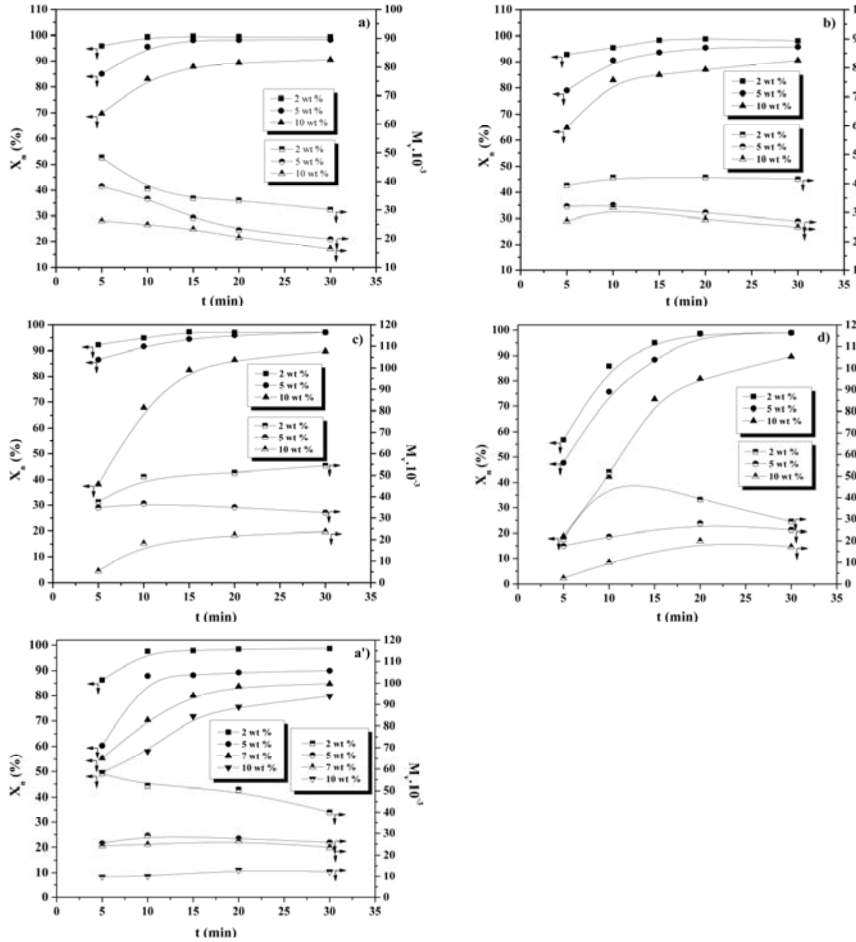
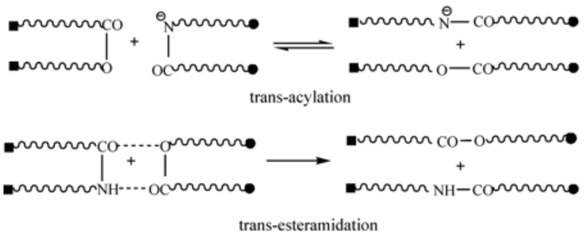


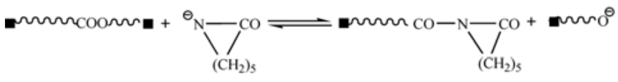
**Figure 2.** The $X_n$ and $M_v$ versus polymerization time (t) in dependence of the used activators and their concentration: (a) $PAC_{PCLO3000IF}$, (b) $PAC_{PCLO2000IF}$, (c) $PAC_{PCLO1250IF}$, (d) $PAC_{PCLO550IF}$, (a') $PAC_{PVLO3200IF}$.

established that a branched polymer chain has a lower $M_v$ than linear polymer molecules of the same molecular weight. The reactions of trans-acylation and trans-esteramidation also occur in the system in addition to the reaction of trans-amidation, as shown in Scheme 3.



**Scheme 3.**

Simultaneously, with the reaction of the lactam anion with CLA, the reaction of this anion with the ester group could also proceeds according to Scheme 4 [12].



**Scheme 4.**

The above mention side reactions led to the formation of P[(CLA)-co-(CLO)] and P[(CLA)-co-(VLO)] copolymers possessing random distributed blocks.

In order to evaluate the activity of new synthesized activators CLA was polymerized in the presence of different feed polymerization systems (Table 2, Figure 3). In general, without activator (only in the presence of initiator) the polymerization of CLA proceeds with very long induction period (20÷30 min). It was found that the maximum conversion degree and polymerization rate was reached with PCLA/PAC$_{PCLO3000IF}$ polymerization system (Figure 3).

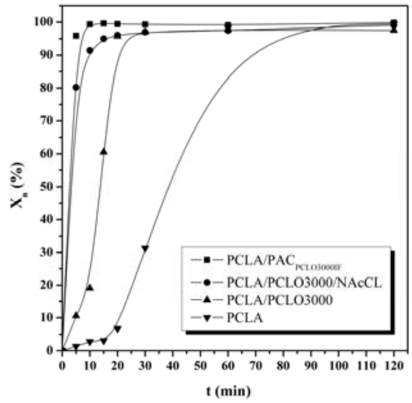


**Figure 3.** The conversion (X$_n$) versus polymerization time (t), explored in different feed CLA polymerization systems.

These experiments have revealed the very high activity of the new synthesized PACs. The latter eliminate the induction period and accelerate the process of polymerization of CLA to several minutes.

The activation energy (E$_a$) for seven feed compositions was estimated, according to the Arenius equation in the 140÷180°C range (Table 3).

The data summarized demonstrate that the use of the PACs is an effective and versatile method to copolymerize CLA at low activation energy, high yield and polymerization rate of the process. The lowest E$_a$ value was achieved with the fifth feed composition. Moreover, the calculated values for the E$_a$ of copolymerization using PACs as activators are much lower in comparison to this calculated to the traditionally used NAcCL (E$_a$ = 55.27 kJ.mol$^{-1}$). These observations on the PACs polymerization activity suggest that they could be successfully used for obtaining of tailored and good-quality PEAS, with activating effect in the following order:

PAC$_{PCLO3000IF}$ $\geq$ PAC$_{PVLO3200IF}$ $\geq$ NAcCL

**Table 3.** The activation energy ($E_a$), maximum polymerization rate ($W_{max}$) and degree of conversion ($X_\infty$) of the obtained PEAS.

| № | Copolymers Code | PCLA/PAC | $X_\infty$ | $W_{max}$ | $E_a$ |
|---|---|---|---|---|---|
| | | (w/w %) | (%)[a] | (%.min$^{-1}$)[b] | (kJ.mol$^{-1}$)[c] |
| 1 | PCLA/PAC$_{PVLO3200IF}$ | 98:2 | 99.80 | 16.33 | 30.19 |
| 2 | | 95:5 | 96.72 | 13.00 | 37.76 |
| 3 | | 93:7 | 92.00 | 10.30 | 38.89 |
| 4 | | 90:10 | 86.77 | 9.75 | 41.16 |
| 5 | PCLA/PAC$_{PCLO3000IF}$ | 98:2 | 99.81 | 16.50 | 29.10 |
| 6 | | 95:5 | 99.43 | 16.33 | 37.43 |
| 7 | | 90:10 | 93.40 | 12.71 | 38.18 |
| 8 | PCLA/PAC$_{PCLO2000IF}$ | 98:2 | 99.43 | 16.33 | - |
| 9 | | 95:5 | 96.60 | 13.71 | - |
| 10 | | 90:10 | 93.88 | 11.12 | - |
| 11 | PCLA/PAC$_{PCLO1250IF}$ | 98:2 | 97.58 | 16.16 | - |
| 12 | | 95:5 | 97.54 | 13.78 | - |
| 13 | | 90:10 | 91.38 | 8.18 | - |
| 14 | PCLA/PAC$_{PCLO550IF}$ | 98:2 | 99.00 | 9.90 | - |
| 15 | | 95:5 | 98.56 | 9.80 | - |
| 16 | | 90:10 | 93.68 | 4.89 | - |

[a] Conversion degree at equilibrium;
[b] Maximum polymerization rate at 180°C;
[c] Activation energy in the 140÷180°C range.

## Conclusions

The novel PACs prepared on the base of telechelic oligomers of PCLO and PVLO with IF were successfully incorporated as soft and biodegradable segments in the main chain of PCLA. The proposed mechanism of the copolymers formation for both general types of copolymers and copolymers structure were confirmed. The influence of the types, the length of the PACs and the PACs concentration, on the polymerization kinetics, molecular weight, and activation energy was established. The activators significantly affect the CLA polymerization rate, the degree of conversion and the molecular weights and were more active in comparison to polymeric systems activated with traditionally used NAcCL. Therefore, the PACs can be used for polyamide-6 features modification and the obtained PEAS could be applied as tailor-made materials including biodegradable construction polymers.

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