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ORIGINAL PAPER

Activated anionic ring-opening polymerization of ε-caprolactam with magnesium di(ε-caprolactamate) as initiator: effect of magnesium halides

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Abstract The activated anionic ring-opening polymerization of ε-caprolactam initiated by 0.35 mol% of combined initiator, i.e., equimolar mixture of magnesium di(ε-caprolactamate) (CL_2Mg) with magnesium halides ($MgCl_2$, $MgBr_2$, and MgI_2) as well as of ε-caprolactam magnesium bromide (CLMgBr) in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam as an activator has been investigated in the temperature range 140–200 °C. It was found that the reaction rate increased while the apparent activation energy decreased in the following series: $CL_2Mg/MgCl_2 < CL_2Mg/MgBr_2 \sim CLMgBr < CL_2Mg/MgI_2$. In addition, the poly(ε-caprolactam)s prepared with CL_2Mg/MgX_2 ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) are characterized by slightly higher thermal stability than polymers obtained with CLMgBr as initiator. These observations were explained in terms of the coordination of Lewis acids (MgX_2, where X = Cl, Br, and I) with imide carbonyl of *N*-acyllactam end groups leading to the increase of their reactivity and stability.

Keywords Ring-opening polymerization · Anionic polymerization · ε-Caprolactam · Poly(ε-caprolactam) · Magnesium di(ε-caprolactamate)

Introduction

Among polymerization of various cyclic amides [1], the anionic ring-opening polymerization (ROP) of ε-caprolactam is one of the most studied processes [1, 2]. The activated anionic ROP of ε-caprolactam is usually started with a two-component

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catalytic system, consisting of lactam anion or their precursor as an initiator and *N*-acyllactam-type activator [1, 2]. The addition of activators with *N*-acyllactam structure, such as either monofunctional *N*-acetyl-ε-caprolactam [3–7] and *N*-benzoyl-ε-caprolactam [8–10] or difunctional *N*,*N*′-isophtaloyl-bis-ε-caprolactam [6, 10] and *N*,*N*′-hexamethylene-bis(carbamoyl-ε-caprolactam) [11–13], is critical for achieving high polymerization rate. This is because of the fact that the nucleophilic attack of the lactam anion on the carbonyl group in the monomer in so-called non-activated ROP of ε-caprolactam is considerably slower in comparison with that to the endocyclic carbonyl group in the activator [1, 2].

Sodium salt of ε-caprolactam (CLNa) or its precursors (sodium hydride, sodium methoxide) are a most used initiator in the (co)polymerization of lactams [7, 9, 11–17]. The main disadvantages of this initiator are rather high content of cyclic oligomers [18–20] in obtained polymers and relatively low thermal stability [5] of resulting polyamides.

ε-Caprolactam magnesium bromide (CLMgBr) in a combination with *N*-acyllactam activators represents another very active in the ROP of ε-caprolactam initiating system [6, 8–10, 21–24]. Due to the fast reaction rate (equilibrium content of polymer [17] is achieved for 5–10 min [25] and even in less than 5 min under optimized polymerization conditions [26]), this initiator was successfully used in the reaction injection molding technology to produce block copolymers of ε-caprolactam with polyethers [25]. Other magnesium salt of ε-caprolactam, magnesium di(ε-caprolactamate) (CL_2Mg), has received insignificant attention as initiator of ε-caprolactam polymerization due to its low activity in comparison with CLMgBr [4, 5, 27–29]. These magnesium salts of ε-caprolactam, in comparison with CLNa, are less sensitive to trace of water in the system [30] and also allow to synthesize polyamides with considerably higher thermal stability (especially in the case of using of CL_2Mg) [5, 29] and lower content of cyclic oligomers [18].

The rate of ε-caprolactam polymerization initiated by CL_2Mg could be significantly increased by the addition to the system of such Lewis acid as $MgBr_2$ [4, 5, 29]. The observed positive effect of this additive was explained by the increase of electrophilicity of imide carbonyl in *N*-acyllactam end groups due to its coordination with $MgBr_2$ (Fig. 1) [4, 5, 29].

The formation of the similar complex (see Fig. 1) was also claimed for the polymerization of ε-caprolactam initiated by CLMgBr, in this case $MgBr_2$ was

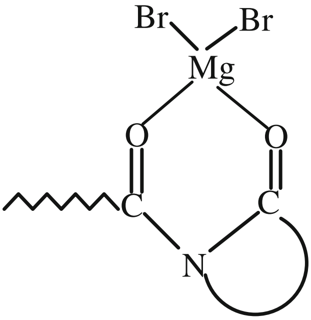


Fig. 1 Possible coordination of $MgBr_2$ with growing chain ends

generated in situ due to the disproportion reaction of CLMgBr in the reaction mixture (Eq. 1) [4, 5, 25, 29]:

$$2\text{CLMgBr} \leftrightarrows \text{CL}_2\text{Mg} + \text{MgBr}_2. \quad (1)$$

Finally, the formation of the complexes of $MgBr_2$ with ε-caprolactam [31] and various model compounds [32, 33] has unambiguously been proven by different analytical techniques. Evidently, the change of the nature of added salt ($MgBr_2$) would influence the reactivity of growing species as well as the reaction rate significantly. In this article, we report the effect of magnesium halides (MgX_2, X = Cl, Br, and I) on the activated anionic ROP of ε-caprolactam initiated by CL_2Mg and the thermal stability of obtained polyamides.

Experimental

Materials

ε-Caprolactam (JSC "Grodno Azot") was purified by double vacuum distillation followed by recrystallization from absolute benzene and stored under argon atmosphere. Benzene, 1,4-dioxane, and diethyl ether (Sigma-Aldrich) were dried by refluxing with Na/benzophenone ketyl, distilled, and stored under dry argon atmosphere. 1-Chlorobutane, 1-bromobutane, and 1-iodobutane (Sigma-Aldrich) were dried with $CaCl_2$ and then distilled with CaH_2 under argon atmosphere. Acetic anhydride (Sigma-Aldrich) was dried with sodium acetate and distilled in argon atmosphere. *m*-Cresol (Sigma-Aldrich) and magnesium chips (Sigma-Aldrich) were used as received.

N-acetyl-ε-caprolactam was synthesized according to known procedure [34] by refluxing of ε-caprolactam (1.15 mol) with an excess of acetic anhydride (3.9 mol) for 4 h followed by double vacuum distillation; the fraction boiling at 81–83 °C/1.5 mmHg was collected, and the purity was checked by ^1H NMR (Fig. S1).

CLMgBr was prepared following described procedure [35] by the reaction of equimolar quantities of butyl magnesium bromide with ε-caprolactam in diethyl ether. The solvent was evaporated under reduced pressure, and the resulting solid substance was dried in vacuum at 45–50 °C for 3 h. Analytical composition of initiator: Mg 11.1% (theor. 11.2%), Br 35.0% (36.9%). CL_2Mg–magnesium halide combined initiators were synthesized through the disproportionation of corresponding butyl magnesium halides by 1,4-dioxane followed by the addition of ε-caprolactam to resulting Bu_2Mg/MgX_2 mixture (X = Cl, Br, or I) as described in [27, 28]. Then, solvent was evaporated under reduced pressure, and the resulting solid substance was dried in vacuum at 80–100 °C for 3 h. As an example of typical procedure, the synthesis of $MgCL_2/MgI_2$ is presented in detail. The solution of butyl magnesium iodide in diethyl ether (3.2 M) was prepared by the reaction of magnesium (1 g, 4.2×10^{-2} M) with 1-iodobutane (4.7 mL, 4.2×10^{-2} M). Then, a solution of 1,4-dioxane (4.8 mL, 5.6×10^{-2} M) in diethyl ether was dropwise added within 10 min to the ethereal solution of butyl magnesium iodide to synthesize $MgBu_2/MgI_2$ mixture. The reaction was completed by refluxing for

30 min. After that, the ethereal solution of $MgBu_2/MgI_2$ (16.9 mL, 0.77 M) was added dropwise to the suspension of ε-caprolactam (3 g, 2.7×10^{-2} M) in diethyl ether (10 mL), and reaction mixture was stirred vigorously during 30 min. Then, the solvent was removed under vacuum at room temperature, and solid substance was dried in vacuum at 80–100 °C for 5 h. Analytical composition of initiator: Mg 8.6% (theor. 9.2%), I 44.9% (48.2%).

Polymerization

The polymerization mixture was prepared by mixing of ε-caprolactam (25 g), appropriate initiator (7.5×10^{-4} mol), and *N*-acetyl-ε-caprolactam (7.5×10^{-4} mol) at 90 °C under argon atmosphere and then charged into glass test tubes (~2.5 g of reaction mixture). Then, the tubes were immediately immersed into another bath at 140, 160, 180, or 200 °C for polymerization. After predetermined time, the polymerization was terminated by cooling the tubes in water (15 °C). The polymer yield was determined gravimetrically after two times successive extraction by boiling water for 2 h and drying at 70 °C up to constant weight as a ratio of sample weight after and before monomer extraction.

Polymer characterization

The content of Mg and halogen in the synthesized initiators was determined by chelatometric and Volhard's titrations, respectively. ^1H NMR spectra were recorded on a Bruker AC-400 spectrometer at 25 °C in $CDCl_3$. The intrinsic viscosity of the obtained polymers was measured in *m*-cresol at 25 ± 0.1 °C using an Ubbelohde viscosimeter. The viscometric-average molecular weights (M_v) were calculated using the following equation: $[\eta] = 7.44 \times 10^{-4} \times M_v^{0.745}$ [5, 36]. Thermogravimetric analysis (TGA) was performed on a TGA51 TA Instruments apparatus between 20 and 550 °C under nitrogen with a heating rate 10 °C min^{-1}.

Results and discussion

The initiator represents a key component for the anionic ROP of ε-caprolactam and, therefore, influences significantly on the polymerization kinetics and the properties of obtained polymers [5, 18, 25, 28–30]. The results of the comparative study on the activity of CL_2Mg (in the presence of magnesium halides) and widely used CLMgBr in the activated anionic polymerization of ε-caprolactam are presented below.

Magnesium di(ε-caprolactamate)

The activated ROP of ε-caprolactam was firstly investigated using CL_2Mg/MgX_2 ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) as initiators in the presence of *N*-acetyl-ε-caprolactam as activator in a temperature range 140–200 °C.

$CL_2Mg/MgCl_2$ as initiator

The rate of the polymerization of ε-caprolactam with *N*-acetyl-ε-caprolactam/$CL_2Mg/MgCl_2$ initiating system increased with increasing reaction temperature achieving the equilibrium monomer yield in less than 10 min at 180 and 200 °C (see ESM, Fig. S2). The dependences of polymer yield on the polymerization time (Fig. S2) are linear at least up to 80–85% of the monomer conversion indicating that the polymerization of ε-caprolactam exhibits zero-order kinetics in respect of the monomer concentration under investigated conditions.

According to [15, 16, 23], the rate of activated anionic polymerization of ε-caprolactam exhibiting zero-order kinetics could be expressed by following equations:

$$-\frac{d[M]}{dt} = k_{p\,\mathrm{app}} \tag{2}$$

$$[M]_0 - [M] = k_{p\,\mathrm{app}} \cdot t \tag{3}$$

where $[M]_0–[M] = [\mathrm{M}]_0 \times$ yield, $k_{p\ \mathrm{app}}$—the apparent rate constant and t—polymerization time.

As shown in Fig. 2, the zero-order plots are linear up to high monomer conversions (80–85%) and pass trough the origin. The apparent rate constants calculated from the initial slopes of the above-mentioned plots (Fig. 2) were used to construct an Arrhenius plot (see ESM, Fig. S3). The apparent activation energy of polymerization of ε-caprolactam with *N*-acetyl-ε-caprolactam/$CL_2Mg/MgCl_2$ initiating system was calculated from the slope of Arrhenius plot ($E_{a\ \mathrm{app}} = 45.3$ kJ mol^{-1}). This value is comparable with one reported for the ε-caprolactam polymerization with *N*-acetyl-ε-caprolactam/CLMgBr initiating system [25].

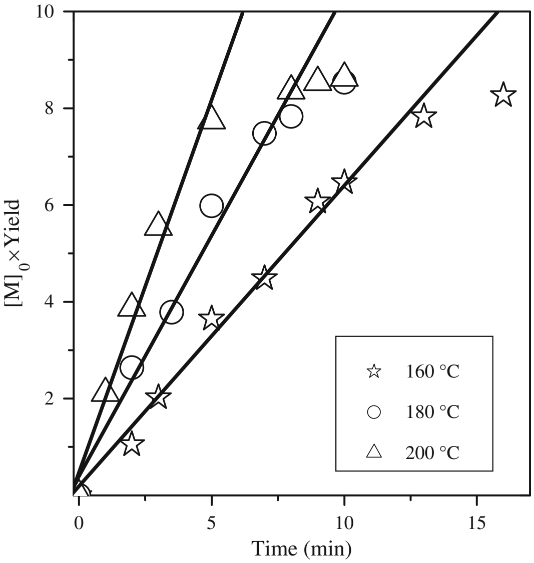


Fig. 2 Zero-order plots for ε-caprolactam polymerization initiated with 0.35 mol% of equimolar $CL_2Mg/MgCl_2$ mixture in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam at different temperatures

Fig. 3 Viscometric-average molecular weight versus yield dependences for ε-caprolactam polymerization initiated with 0.35 mol% of equimolar $CL_2Mg/MgCl_2$ mixture in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam at different temperatures

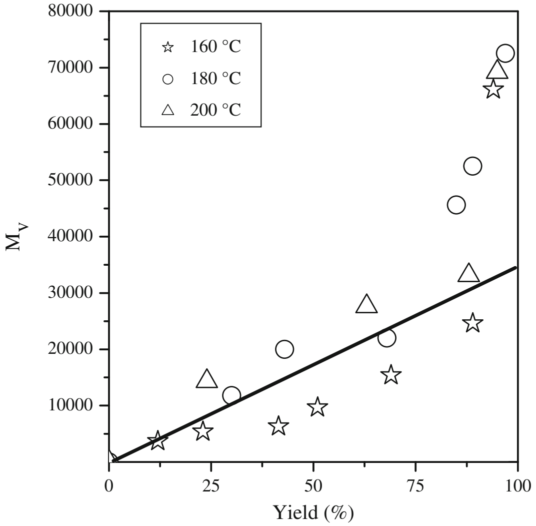


Figure 3 shows viscometric-average molecular weight (M_v) versus yield dependences for ε-caprolactam polymerization using *N*-acetyl-ε-caprolactam/ $CL_2Mg/MgCl_2$ initiating system at different temperatures. Note, that viscometric-average molecular weight was determined using relationships derived for the anionic poly(ε-caprolactam) and calibrated as a number-average by membrane osmometry [5, 36]. Therefore, assuming the similar molecular weight distribution for poly(ε-caprolactam)s prepared in this study, we can conclude that M_v is close to number-average molecular weight (M_n).

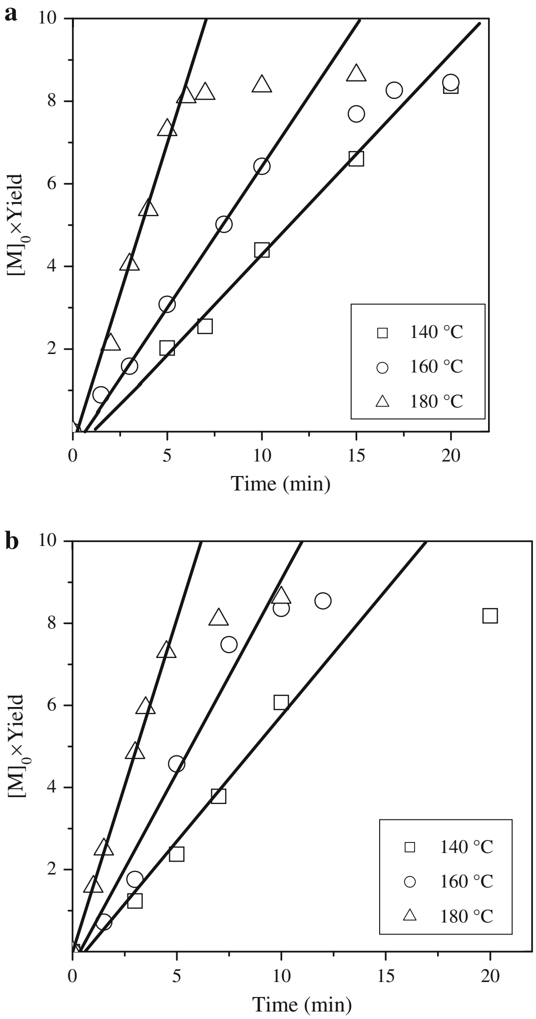
The viscometric-average molecular weight increased with increasing monomer conversion irrespective of polymerization temperature, while the experimental values of M_v correlated moderately with the theoretical line (constructed assuming that one molecule of activator (*N*-acetyl-ε-caprolactam) generated one polymer chain) up to 85–90% of monomer conversion (Fig. 3). This indicates that the anionic polymerization of ε-caprolactam proceeded in a controlled fashion under investigated conditions. However, an exponential increase of M_v at high monomer conversions is observed at all investigated temperatures and could be attributed to known Claisen type condensation reactions leading to the decrease of the growing chains concentration and the formation of "coupled" or even branched macromolecules [16, 25].

$CL_2Mg/MgBr_2$ and CL_2Mg/MgI_2 as initiators

The polymerization of ε-caprolactam with *N*-acetyl-ε-caprolactam/$CL_2Mg/MgBr_2$ and *N*-acetyl-ε-caprolactam/$CL_2Mg/MgBr_2$ initiating systems was then studied at three different reaction temperatures, i.e., 140, 160, and 180 °C. It was found that reaction rate increased in the following order: $CL_2Mg/MgCl_2 < CL_2Mg/MgBr_2 < CL_2Mg/MgI_2$ (see ESM, Figs. S2, S4, and S5). In addition, the polymerization of ε-caprolactam with *N*-acetyl-ε-caprolactam/$CL_2Mg/MgBr_2$ and *N*-acetyl-ε-caprolactam/CL_2Mg/MgI_2 initiating systems also exhibits zero-order kinetics in respect of the monomer concentration, since the dependences of polymer yield on the reaction time (Fig. 4a, b) are linear up to high monomer conversions (~85%). Importantly, the polymerization of ε-caprolactam with CL_2Mg/MgI_2 as an initiator is characterized by lower value of the apparent activation energy ($E_{a\ app} = 38.6$ kJ mol^{-1}, Fig. S6) in comparison with the mixtures of CL_2Mg with $MgBr_2$ ($E_{a\ app} = 41.7$ kJ mol^{-1}, Fig. S7) or $MgCl_2$ ($E_{a\ app} = 45.3$ kJ mol^{-1}, Fig. S3).

The viscometric-average molecular weight of poly(ε-caprolactam)s synthesized with $CL_2Mg/MgBr_2$ and CL_2Mg/MgI_2 as initiators increased in direct proportion to monomer conversion and experimental values of M_v correlated well with theoretical line (Fig. 5) indicating that the polymerization proceeded in a controlled fashion. The correlation between experimental and theoretical values of M_v is considerably better in the case of using $CL_2Mg/MgBr_2$ or CL_2Mg/MgI_2 in comparison with

Fig. 4 Zero-order plots for ε-caprolactam polymerization initiated with 0.35 mol% of equimolar **a** $CL_2Mg/MgBr_2$ and **b** CL_2Mg/MgI_2 mixtures in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam at different temperatures



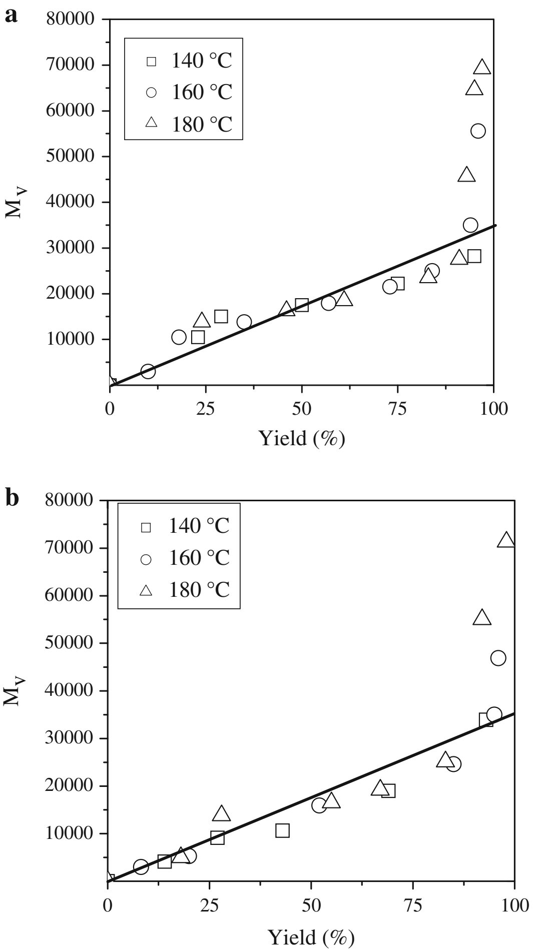


Fig. 5 Viscometric-average molecular weight versus yield plots for ε-caprolactam polymerization initiated with 0.35 mol% of equimolar **a** $CL_2Mg/MgBr_2$ and **b** CL_2Mg/MgI_2 mixtures in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam at different temperatures

$CL_2Mg/MgCl_2$ as an initiator (compare Figs. 3 and 5). This observation points out that the side reactions are suppressed to a higher extent in the presence of $MgBr_2$ and MgI_2 as the additives than with $MgCl_2$. However, the side reactions leading to an exponential growth of M_v are still operated under monomer starved conditions, at least, at high reaction temperatures (160 and 180 °C).

ε-Caprolactam magnesium bromide

In order to compare the results obtained during the investigation of the anionic ROP of ε-caprolactam with CL_2Mg/MgX_2 ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) initiating systems with well-known initiator, the polymerization of ε-caprolactam initiated by CLMgBr was briefly investigated. As shown in Fig. 6a and Fig. S8, the polymerization of ε-caprolactam with *N*-acetyl-ε-caprolactam/CLMgBr initiating system was zero order in monomer concentration. The reaction rates as well as the

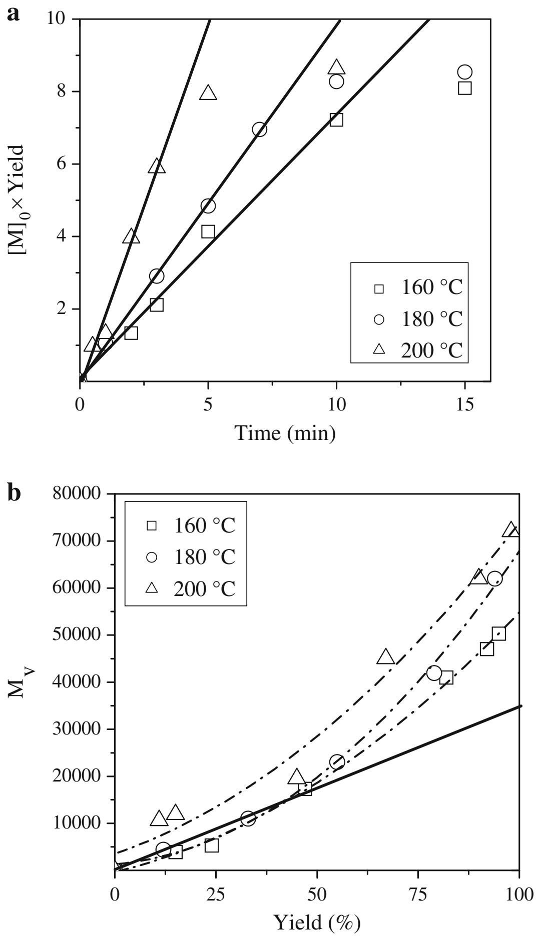


Fig. 6 **a** Zero-order and **b** viscometric-average molecular weight versus yield plots for ε-caprolactam polymerization initiated with 0.35 mol% of ε-caprolactam magnesium bromide (CLMgBr) in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam at different temperatures

apparent activation energy ($E_{\mathrm{a\ app}} = 42.2$ kJ mol^{-1}, Fig. S9) for the ε-caprolactam polymerization initiated by CLMgBr were found to be comparable with those obtained for $CL_2Mg/MgBr_2$ as initiator (vide supra).

As shown in Fig. 6b, the M_vs of obtained polymers increased with increasing polymer yield indicating that polymerization of ε-caprolactam with *N*-acetyl-ε-caprolactam/CLMgBr initiating system proceeded in a controlled fashion. However, in contrast to the polymerization with CL_2Mg/MgX_2 ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) where a good correlation between experimental and calculated values of $M_v s$ was observed up to high monomer conversions (≥85%) (Figs. 3, 5a, b), the $M_v s$ started to deviate from theoretical line at conversions higher than 50% when CLMgBr was used as initiator (Fig. 6b). This observation indicates that the side condensation reactions are suppressed to a lesser extent with CLMgBr as initiator in comparison with a mixture of CL_2Mg with magnesium halides.

Conclusive discussion

Table 1 summarizes the main results from this study in terms of polymerization kinetics for two type of initiators studied, i.e., CL_2Mg/MgX_2 ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) and CLMgBr. As it is evident from Table 1, for the polymerization of ε-caprolactam with CL_2Mg/MgX_2 as initiator, the reaction rate is progressively increased while the apparent activation energy is decreased in the series $MgCl_2 < MgBr_2 < MgI_2$. This row is fully consistent with the decrease of lattice energies of the magnesium halides, $MgCl_2$ (595 kcal mol^{-1}), $MgBr_2$ (571 kcal mol^{-1}), and MgI_2 (545 kcal mol^{-1}) [37], as well as with the increase of their Lewis acidity [38, 39]. In addition, the rate of insertion of magnesium into porphyrins is also increased in the same series: $MgCl_2 < MgBr_2 < MgI_2$ [40]. Taking into account these facts, the observed influence of magnesium halides on the polymerization kinetics could be explained by (and also confirmed) the formation of complex between MgX_2 and growing chain ends (see Fig. 1). The stronger Lewis acids due to the stronger coordination with imide carbonyl of *N*-acyllactam end groups (Fig. 1) increased their reactivity to a higher extent in comparison with weaker Lewis acids that, in turns, leads to the higher reaction rate and lower apparent activation energy with CL_2Mg/MgI_2 as compared with $CL_2Mg/MgBr_2$ or $CL_2Mg/MgCl_2$.

Another interesting observation is that the reaction rates at different temperatures as well as the apparent activation energies are almost similar for the polymerization of ε-caprolactam with CLMgBr and $CL_2Mg/MgBr_2$ as initiators (Table 1). This confirms the accepted point of view that during the polymerization of ε-caprolactam with CLMgBr, the disproportion reaction takes place with the in situ formation of CL_2Mg and $MgBr_2$ [4, 5, 25, 29, 31–33]. On the other hand, an exponential increase of M_v with yield was already observed at moderate monomer conversions (i.e., 50–60%) for CLMgBr (Fig. 6b) in comparison with CL_2Mg/MgX_2 mixtures where deviation of experimental values of M_v from theoretical line starts to occur only at high conversions ≥85% (Figs. 3, 5a, b). In other words, the stabilization of growing species occurs to a lesser extent with CLMgBr as an initiator as compared to CL_2Mg/MgX_2 system that could be connected with the presence in the system of several types of species (CLMgBr, $MgBr_2$, and $MgCL^+$) [4, 29] with different coordination ability to growing chains.

Table 1 The apparent rate constants ($k_{p\ app}$) and apparent activation energies ($E_{a\ app}$) for the anionic polymerization of ε-caprolactam with different initiators (0.35 mol%) in the presence of 0.35 mol% of *N*-acetyl-ε-caprolactam

Initiator	$k_{p\ app} \times 10^2$ (mol kg^{-1} s^{-1})								$E_{a\ app}$ (kJ mol^{-1})
	140 °C	R^2	160 °C	R^2	180 °C	R^2	200 °C	R^2	
$CL_2Mg/MgCl_2$	–	–	1.03	0.993	1.66	0.990	3.06	0.990	45.3
$CL_2Mg/MgBr_2$	0.81	0.995	1.14	0.999	2.34	0.994	–	–	41.7
CL_2Mg/MgI_2	1.02	0.991	1.57	0.996	2.71	0.999	–	–	38.6
CLMgBr	–	–	1.21	0.996	1.94	1.000	3.34	0.993	42.2

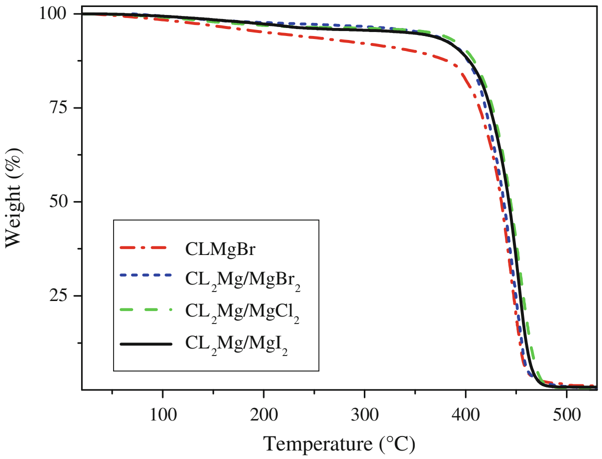


Fig. 7 TGA thermograms of poly(ε-caprolactam)s prepared with different initiators at 160 °C

As we mentioned above, based on the analysis of M_v versus yield plots of poly(ε-caprolactam)s obtained with CL_2Mg/MgX_2 and CLMgBr, the side condensation reactions leading to observed exponential increase of M_v are more pronounced in the case of using of CLMgBr. This, in turn, should influence the thermal stability of obtained polymers. Indeed, as shown in Fig. 7, the poly(ε-caprolactam)s prepared with CL_2Mg/MgX_2 ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) are characterized by slightly higher thermal stability than polymers obtained with CLMgBr as initiator: for example, the loss of weight was 4 and 10% at 360 °C for CL_2Mg/MgI_2 and CLMgBr, respectively. On the other hand, the nature of added salt (MgX_2) does not influence on the thermal stability of polyamides prepared with CL_2Mg/MgX_2 as initiator (Fig. 7). According to Kotelnikov et al. [5], the depolymerization/destruction of poly(ε-caprolactam)s due to the presence of initiators residue in the obtained polymers is responsible for the thermal decomposition. Therefore, the nature of initiator would influence strongly the thermal stability of synthesized poly(ε-caprolactam)s.

Conclusion

In conclusion, we have shown that CL_2Mg in combination with magnesium halides ($MgX_2 = MgCl_2$, $MgBr_2$, and MgI_2) represents an efficient initiator for the activated anionic ROP of ε-caprolactam. The rate of reaction increased while apparent activation energy decreased with the increasing Lewis acidity of corresponding magnesium halide that is consistent with the stronger coordination of stronger Lewis acid with imide carbonyl of *N*-acyllactam end groups leading to the increase of their reactivity. This coordination led also to the suppression of side condensation reactions during the polymerization of ε-caprolactam initiated by CL_2Mg/MgX_2 allowing to synthesize polymers with more controlled molecular weight and better thermal stability in comparison with those prepared with well-known CLMgBr initiator.

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