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Role of magnesium complexes in the anionic polymerization of hexano-6-lactam

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Abstract: The course of anionic hexano-6-lactam polymerization initiated with magnesium compounds differs in some parameters from that initiated with lactam alkali salts. This may be attributed to the coordination of magnesium compounds with functional groups on polymer chains. Supposed coordination effects were proved on model compounds of N-ethylacetamide and N-butyryl-hexano-6-lactam with magnesium bromide. Based on interpretation of Raman and NMR spectra, the interaction between magnesium bromide and both types of ligands as an electron donating coordination of carbonyl groups was proposed. N-butyryl-hexano-6-lactam is more distinctly coordinated to magnesium atom through the carbonyl group located in the cyclic constitution unit.

Introduction

Magnesium salts of lactams are well known initiators of the anionic polymerization of lactams [1, 2]. Besides alkaline salts (Na, K) of lactams magnesium salts belonged for a long period of time among “exotic” initiators. The importance of the magnesium compounds as initiators of polymerization sharply increased only with the application of the anionic polymerization of hexano-6-lactam (HL) in the Reaction Injection Moulding (RIM) technology. The magnesium salt of HL (HL_2Mg) is a very low efficient initiator [3] comparing to ethylmagnesium bromide (EtMgBr) or hexano-6-lactam magnesium bromide [4] (HLMgBr). The high rate of HL polymerization initiated by EtMgBr or HLMgBr is explained as a consequence of the coordination of these compounds, or $MgBr_2$ as a product of their disproportion reaction, to the growth centers of the polymerization [5]. Due to this coordination the electrophilicity of the carbon atom in the imide carbonyl end group is increased and this facilitates the addition of lactam anion to the growth center in the propagation step.

The common characteristic of non-activated anionic polymerizations of HL (i.e. polymerization mixture consisting of HL and initiator only) initiated by magnesium compounds is the indistinct dependence of the polymerization rate on the initiator concentration [6,7]. The limiting, maximum achievable polymer content of these polymerizations is lower than that which corresponds to the equilibrium composition of the polymerization product at the given temperature. The interesting characteristic of activated [7] and also non-activated [8] anionic polymerizations of HL initiated by magnesium compounds is marked suppression of cyclization reactions in the course of polymerization comparing to the polymerization initiated with sodium salt of hexano-6-lactam. The formation of cyclic dimer is suppressed particularly strongly. The functional groups of linear molecules taking part in cyclization reactions, however, are identical regardless to initiator type used. The explanation of the suppressed formation of cyclic oligomers in the presence of magnesium compounds may be due to the coordination of these compounds with functional groups of linear molecules. It can be assumed that this coordination could discriminate the occurrence of chain conformation of poly(hexano-6-lactam) necessary for the formation of cyclic oligomers. The existence of complexes of magnesium compounds with low molecular model compounds which contain identical functional groups like linear molecules formed in the course of the anionic polymerization of HL may serve as an indirect evidence of this explanation.

It has been proved that magnesium bromide forms a complex with six HL molecules. In this complex all the six molecules of HL have almost exactly equivalent positions, the carbonyl oxygen atoms forming coordination bonds to the magnesium atom and the amide protons being bound by predominantly electrostatic bonds to the bromine atoms [9]. Similarly, octano-8-lactam differed from HL by the occurrence of *cis* as well as *transoid* conformation of the amide group [10-12], forms a highly symmetrical complex [13] with $MgBr_2$.

This paper is focused on the study of the coordination of magnesium bromide with N-ethylacetamide simulating *trans* amide groups in polyamide chains and also with N-butyryl-hexano-6-lactam as a model of imide groups, the growing centres of anionic lactam polymerization.

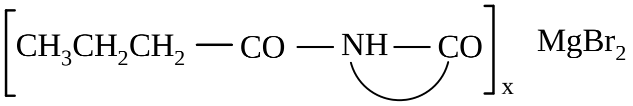
Results and discussion

Synthesis of the N-ethylacetamide / $MgBr_2$ complex (I)

$$\left[CH_3 - CO - NH - CH_2CH_3\right]_4 MgBr_2 \qquad \text{(I)}$$

The coordination compound of N-ethylacetamide (N-EAA) with magnesium bromide (I) was prepared according to the procedure described elsewhere [9]. The complex of N-EAA with $MgBr_2$ is a crystalline and strongly hygroscopic compound with a light yellow colour. The elemental analysis (C, H, N, Br) proved that the molar ratio of N-EAA and $MgBr_2$ in the complex is 4:1.

Synthesis of the N-butyryl-hexano-6-lactam / $MgBr_2$ complex (II)



$$\left[CH_3CH_2CH_2 - CO - NH - CO\right]_x MgBr_2$$

(II)

The reaction of N-butyryl-hexano-6-lactam (N-BtHL) with magnesium bromide has been carried out at ambient temperature. The product of this reaction, a white powdery substance, is also very hygroscopic in nature. The results of elemental analysis have revealed a non-integral value of the coordination number of N-BtHL between 1 and 2. This may give evidence to the heterogenity of the reaction product. The result of chelatometric titration of magnesium content leads to similar conclusion.

It can not be excluded that traces of moisture present in the reaction mixture may affect the coordination degree of N-acyllactam to $MgBr_2$. If there any hydration of the complex occur the following hydrolysis of imide structure is very probable.

Thermal analysis

According to DSC analysis the melting temperature of the complex of N-EAA with $MgBr_2$ (I) lies in the temperature range of 95 – 99°C and that of the complex of N-BtHL with $MgBr_2$ (II) lies in the temperature range of 128 – 132°C. TGA analysis showed the stability of the complex (I) (Fig. 1) upto temperature around 110°C. Thereafter a three-stage decomposition became distinct. The first decomposition stage, in the range of 110 – 250°C, probably corresponds to the detachment of two molecules of N-EAA (weight loss of 38.5 w% theory). The remaining two molecules of N-EAA are detached in the temperature range of 250 – 350°C.

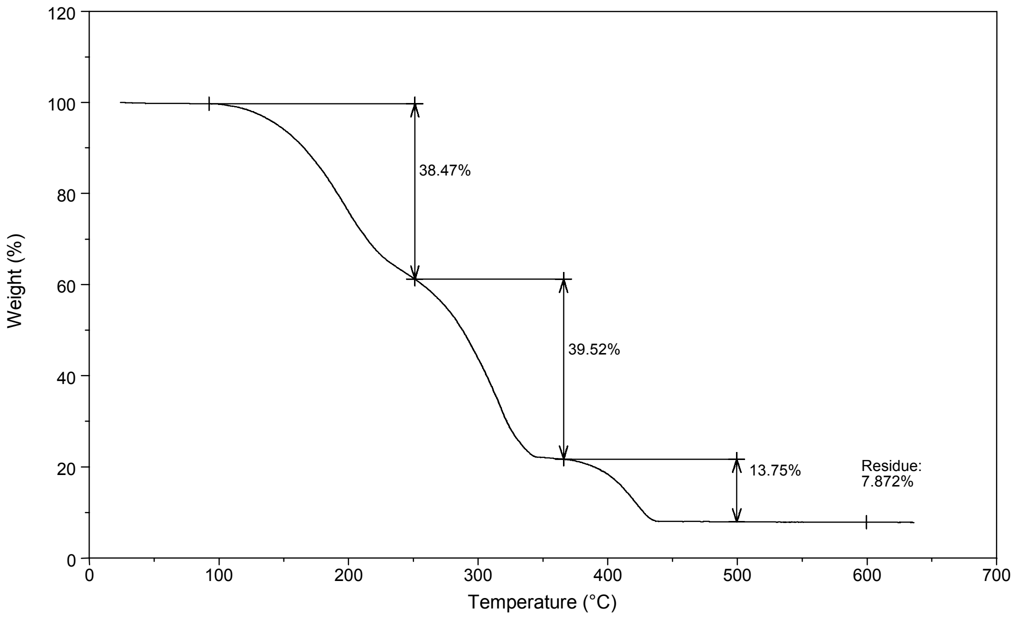


Fig. 1. TGA thermogram of the complex, $MgBr_2(N\text{-}EAA)_4$.

The final product of the thermal decomposition is MgO, as was found in the case of complexes of magnesium bromide with HL [9] or with octane-8-lactam [10].

A typical TGA trace of the complex (II) is shown in Fig. 2. A moderate increase of the complex weight upto 90°C was observed. This may be due to the sorption of water contained in nitrogen which is used as the purge gas. It is then understandable that water sorbed by the complex may have influence on mechanism of the thermal decomposition. Considering the results of elemental analysis, showing that analyzed complex is not a uniform chemical individual, an interpretation of thermal decomposition stages is rather difficult. Nevertheless the TGA record clearly shows a significant decomposition of the complex in the temperature range of 150 – 280°C. A complete decomposition is recorded in the temperature range of 280 – 450°C. The final product of the thermal decomposition is MgO.

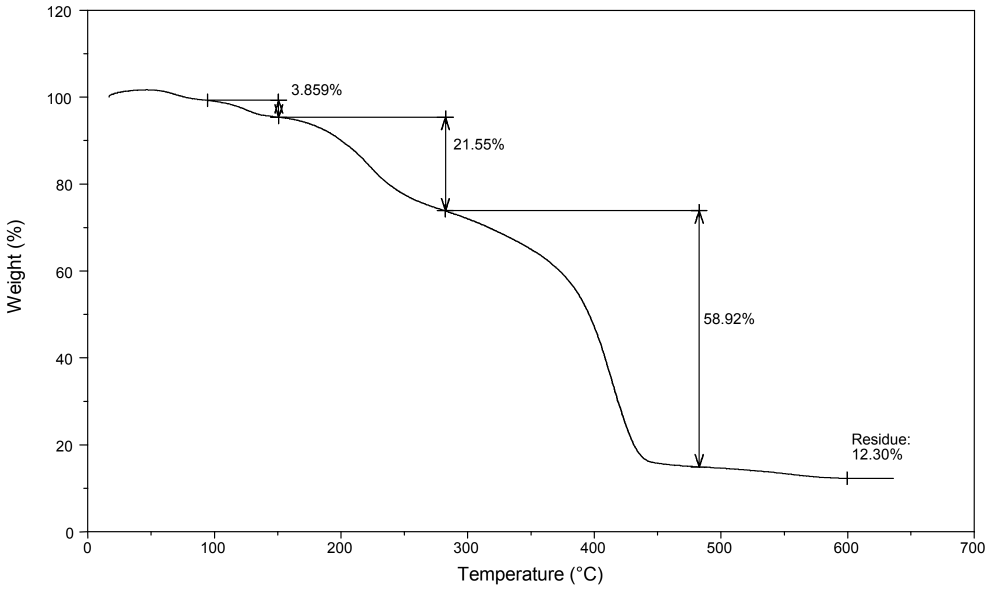


Fig. 2. TGA thermogram of the complex, $MgBr_2(N\text{-}BtHL)_{1\text{-}2}$.

Raman spectra

Raman spectra of N-ethylacetamide and its complex with $MgBr_2$ are shown in Fig. 3. It is evident that the characteristic carbonyl stretching vibration of N-EAA, ν(C=O) 1650 cm^{-1}, splits into three bands 1683, 1638 and 1568 cm^{-1} in the complex, indicating an interaction of the carbonyl group of N-EAA with $MgBr_2$. The –NH- vibration at 3270 cm^{-1} of N-EAA is shifted to 3267 cm^{-1} in the complex. This is very probably the consequence of the intensification of hydrogen-bonded bridges.

Also in the case of the complex of N-butyro-hexano-6-lactam with $MgBr_2$ (Fig. 4) the characteristic carbonyl stretching vibration of N-BtHL, ν(C=O) 1697 cm^{-1} belonging to both carbonyl groups of N-acyllactam, splits into three bands 1731, 1625 and 1587 cm^{-1}. This also indicates the existence of an interaction between carbonyl groups of N-BtHL with magnesium bromide.

NMR spectroscopy

^{13}C NMR spectra of 5 wt% solutions of free N-EAA and N-BtHL in $CDCl_3$ were measured at 300 K. As we did not find suitable solvents in which corresponding complexes with $MgBr_2$ remains stable, required NMR spectra were measured in solid state. Signal assignment of the resulting solution and solid-state ^{13}C NMR spectra are presented in Figures 5 and 7. Signal of carboxyl group of N-EAA in the complex is significantly shifted to lower field (170.92 ppm) compared with free N-EAA (169.16 ppm), which reflects substantial decrease in electron density around carboxyl carbon (Fig. 5). Electrons are rather localized around oxygen and double bond in carboxyl group and are weakened as a consequence of their coordination with $MgBr_2$ through oxygen atom.

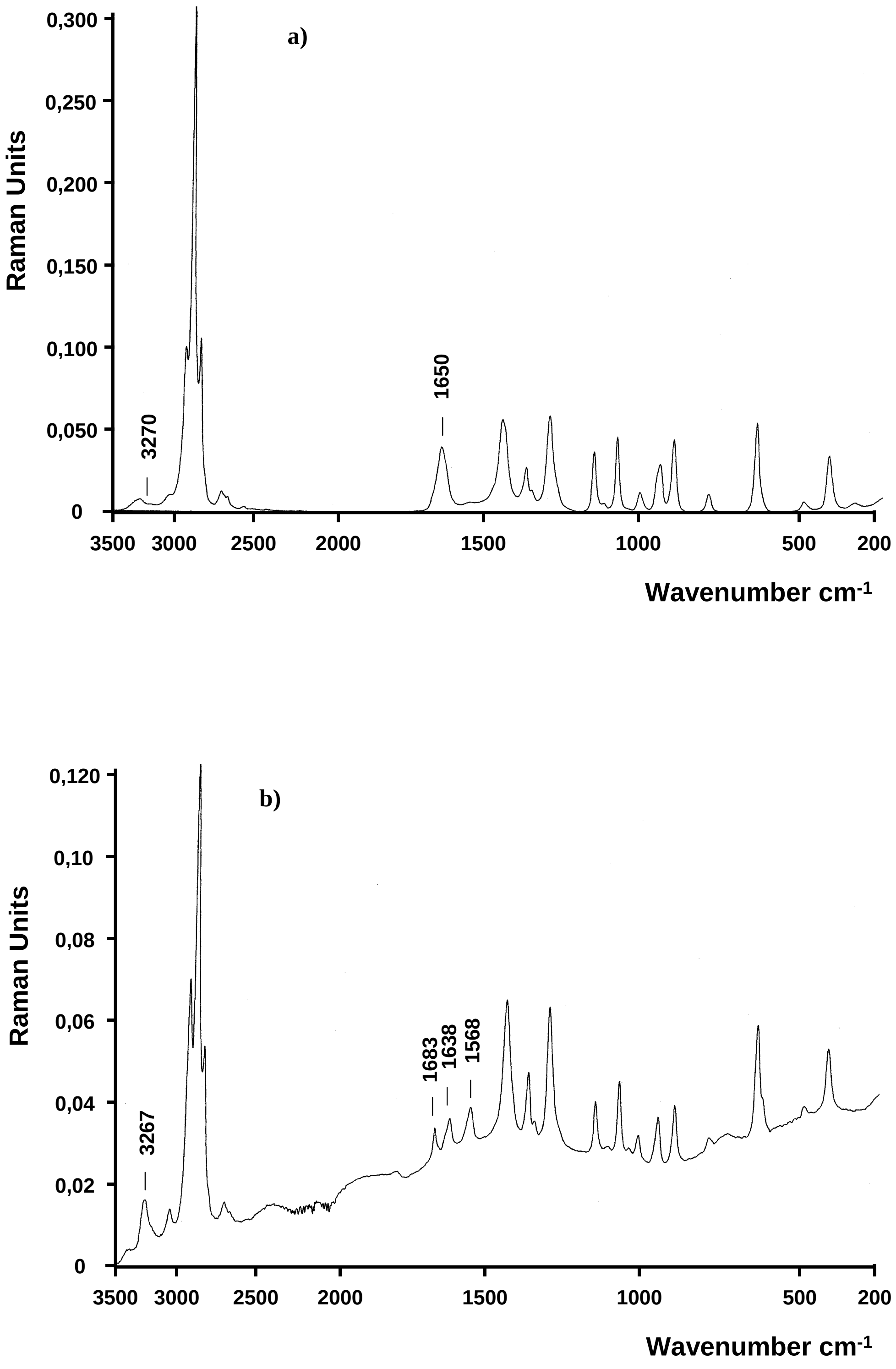


Fig. 3. Raman spectra of N-ethylacetamide (a) and its complex with $MgBr_2$ (b).

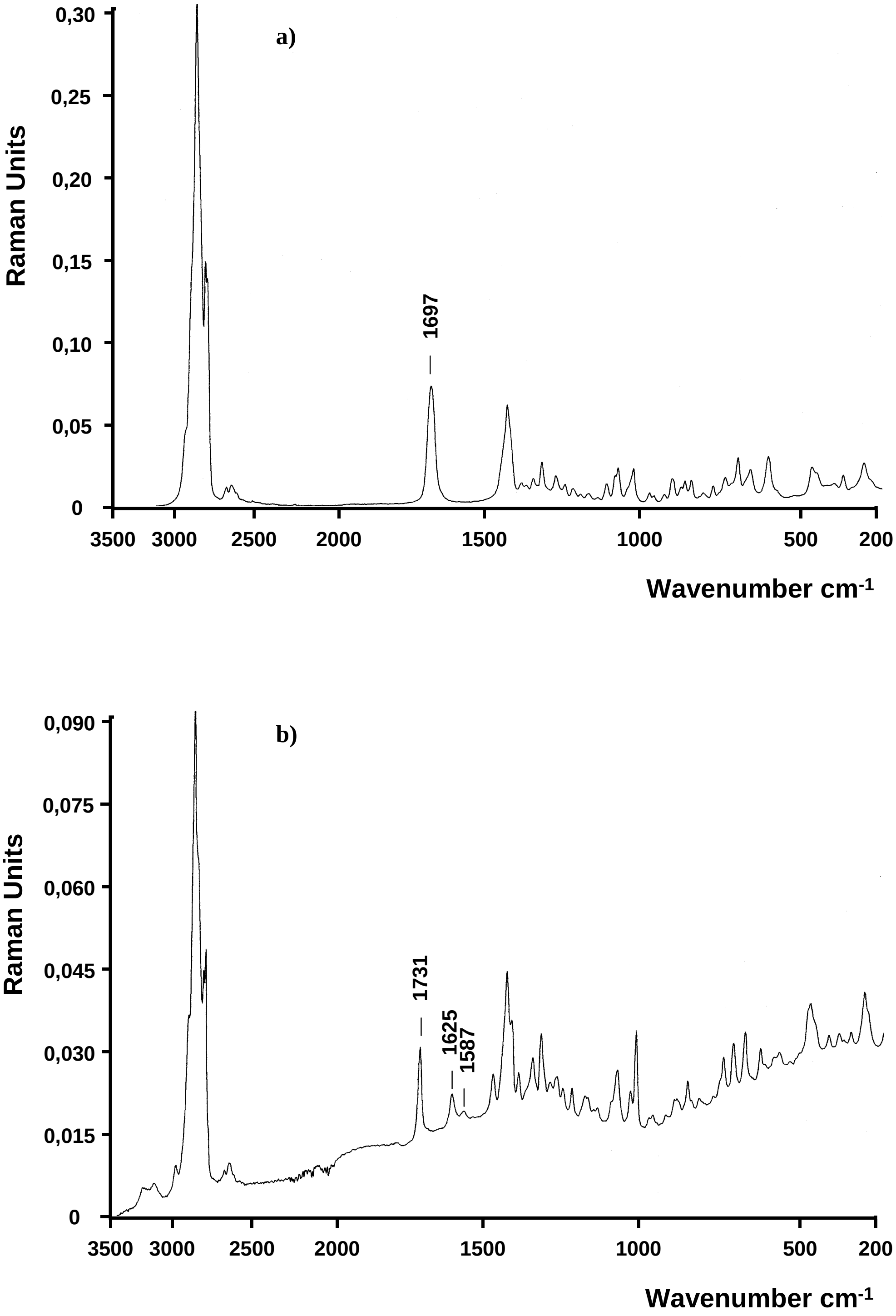


Fig. 4. Raman spectra of N-butyryl-hexano-6-lactam (a) and its complex with $MgBr_2$ (b).

The presence of two asymmetric signals of carboxyl unit indicates differences in the bonding strength of carboxyl groups to Mg atom in the complex and/or the presence of several different conformers. Similar splitting of the signal is also observed in ^{15}N CP/MAS NMR spectrum of amide units (113.5 and 111.5 ppm, Fig. 6). In addition, in ^{13}C CP/MAS NMR spectrum of N-EAA complex we detect four different signals reflecting CH_3- unit at 17.39; 15.13; 14.76 and 14.01 ppm reflecting four slightly different local arrangements of ethyl substituents in the complex.

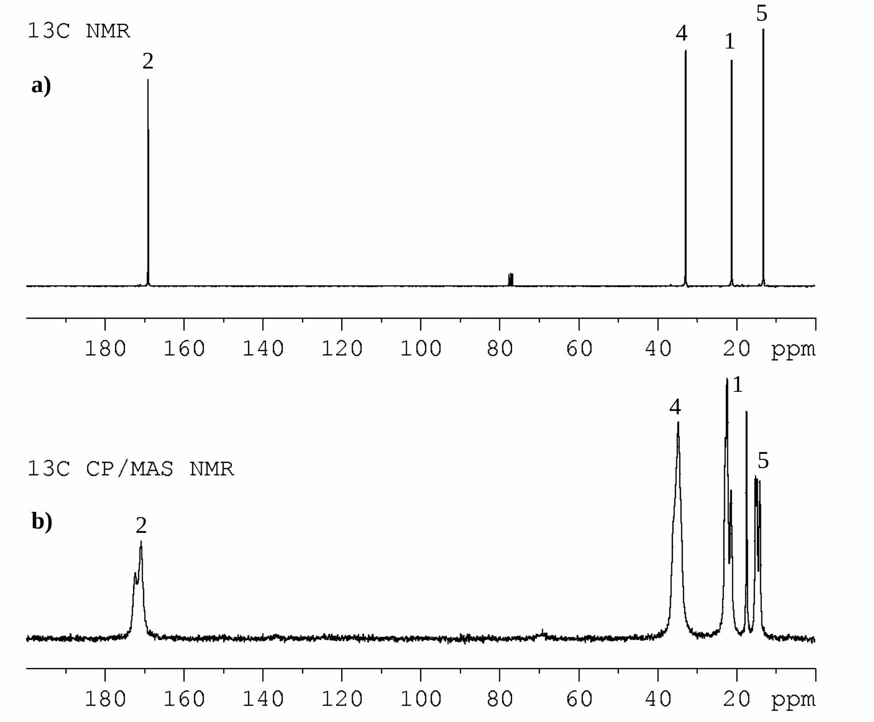


Fig. 5. ^{13}C NMR spectra of N-ethylacetamide in solution of $CDCl_3$ (a) and its complex with $MgBr_2$ in solid state (b) at 300 K.

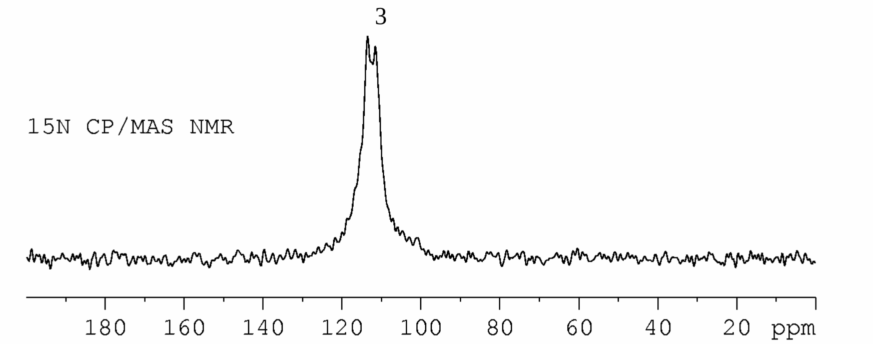


Fig. 6. ^{15}N NMR spectrum of the complex $MgBr_2(N\text{-}EAA)_4$ in solid state at 300 K.

Solution ^{13}C NMR and solid-state ^{13}C CP/MAS NMR spectra of N-BtHL and its complex with $MgBr_2$ are shown in Fig. 7. As the molecules of N-BtHL involved in the complex formation are substantially larger as compared with previously introduced N-EAA, corresponding ^{13}C NMR spectra are rather complicated and individual signals became to overlap. Nevertheless signal assignment is possible and resulted NMR spectra can be qualitatively analyzed. Clearly, formation of the complex with $MgBr_2$ causes low field shift of both carbonyl units of N-BtHL ligands as compared with free N-acyllactam. In addition signal corresponding to CO group of hexano-6-lactam unit (176.9 ppm in solution) splits into two nonequivalent signals in complex (181.6 and 182.7 ppm). The change of chemical shift of this signal (ca. 4-6 ppm) is significantly larger compared with weaker low-field shift of the signal reflecting carbonyl group of acyl unit which is approximately 1 ppm. That is why we suppose that coordination of N-BtHL molecule occurs predominantly through carbonyl unit of the lactam ring.

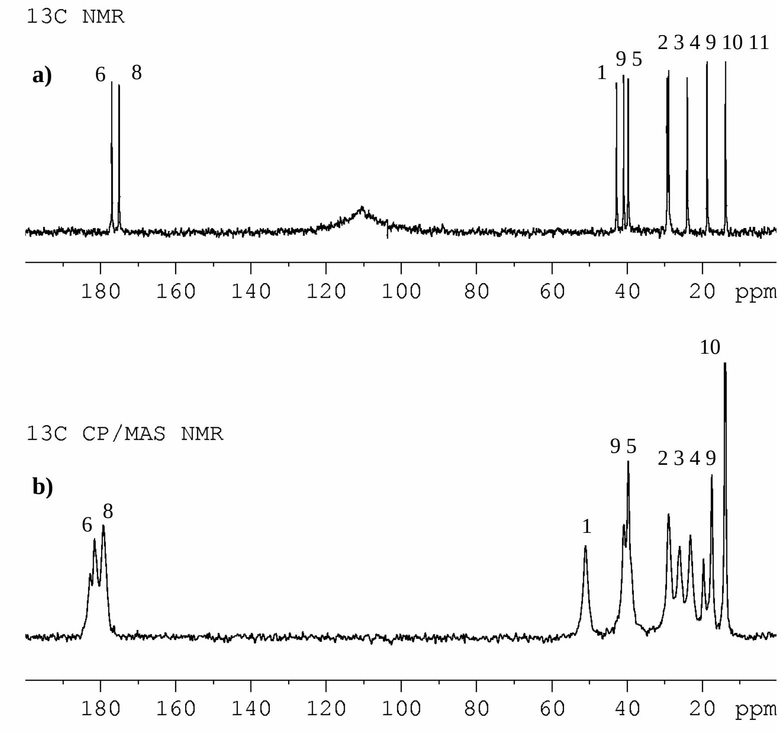


Fig. 7. ^{13}C NMR spectra of N-butyryl-hexano-6-lactam in solution of $CDCl_3$ (a) and its complex with $MgBr_2$ in solid state (b) at 300 K.

Subsequently this molecule can adopt two significantly different conformations; the population of one of them is significantly preferred. The most dramatic change in position of ^{13}C NMR signal is observed for $-CH_2-$ unit neighboring with nitrogen. In contrast to free N-BtHL (42.7 ppm) the corresponding signal in complex is shifted to 51.0 ppm. This reflects significant decrease in electron density around this unit. Although some type of interaction of nitrogen with $MgBr_2$ can not be excluded, we rather suppose significant conformation changes around this unit which involve CO group of acyl moiety. Furthermore, single ^{15}N CP/MAS NMR signal (Fig. 8) confirm rather uniform conformation involving -CO-N-CO- group in the complex.

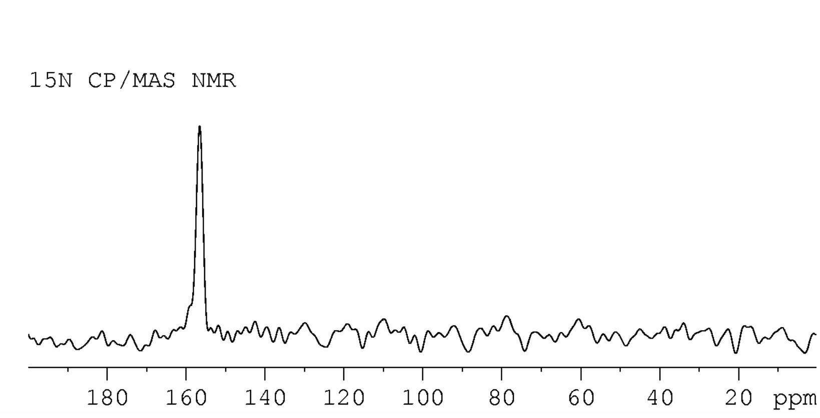


Fig. 8. ^{15}N NMR spectrum of the complex $MgBr_2$(N-BtHL)$_{1-2}$ in solid state at 300 K.

Conclusions

The existence of complexes of low-molecular model compounds containing amide or imide groups with magnesium bromide can support the assumption of the interactions between magnesium compounds and functional groups of (macro)molecules formed in the hexano-6-lactam anionic polymerization initiated by Grignard compounds. The complexes of N-ethylacetamide or N-butyryl-hexano-6-lactam with $MgBr_2$ are stable upto 110 or 150°C respectively. According to the results of thermal analyses, features of coordination are saved in the temperature interval of 160 – 200°C, which is typical for anionic lactam polymerization. In the polymerization system, however, the replacement of linear ligands by lactam molecules cannot be excluded.

Experimental part

Synthesis of complexes

N-ethylacetamide / magnesium bromide complex:

N-ethylacetamide (16.32 mmol) was dosed in drops (30 min) into the suspension of $MgBr_2$ (2.72 mmol) in dried toluene (50 ml) during stirring at ambient temperature. The reaction mixture cleared up during 1 hr refluxing. The sediment was filtered, and after the filtrate cooled, the precipitated crystalline product was three times rinsed with dried toluene. The dried product was extracted with hexane (twice for 4 hr), dried at ambient temperature (2 kPa for 24 hr) and then to the constant weight at 40°C/ 20 Pa. The yield was 54%.

Elemental analysis for $MgBr_2(C_4H_9NO)_4$ (532,1 g/mol):

Calc.	C 36.08	H 6.76	N 10.52	Br 30.03	Mg 4.57
Found	C 35.94	H 6.82	N 10.04	Br 29.94	Mg 4.50

N-butyryl-hexano-6-lactam / magnesium bromide complex:

The reaction mixture, 2.72 mmol $MgBr_2$ and 16.29 mmol of N-butyryl-hexano-6-lactam (N-BtHL) in 50 ml of dried toluene, was prepared as described above. The mixture was then intensively stirred under argon atmosphere at ambient temperature.

The light brown heterogeneous reaction mixture changed into white suspension during 24 hr. After 72 hr stirring the reaction product was filtered under Ar atmosphere, dried and extracted with hexane as described above. The yield was 32%.

Elemental analysis for (N-BtHL)MgBr$_2$ (352.1 g/ mol):

Calc.	C 32.68	H 4.63	N 3.81	Br 45.53	Mg 6.62

Elemental analysis for (N-BtHL)$_2$MgBr$_2$ (520.1 g/ mol):

Calc.	C 43.62	H 6.18	N 5.09	Br 29.05	Mg 4.42
Found	C 38.24	H 6.08	N 4.34	Br 32.02	Mg 5.41

Thermal analysis

The DSC measurements were performed using 910 Differential Scanning Calorimeter (DuPont Instruments) in the temperature range of 20-200°C, with a heating rate of 10°C/ min and nitrogen purge (50 ml/ min). Before sealing, the DSC hermetic sample pans were flushed by argon. Thermogravimetric analysis was performed with Thermogravimetric analyzer TGA 951 (DuPont Instruments) at a heating rate of 20°C/ min at atmospheric pressure and 50 ml/ min nitrogen purge.

NMR spectroscopy

NMR spectra were measured using a Bruker DSX 200 NMR spectrometer at frequencies of 20.26, 50.33 and 200.14 MHz (for ^{15}N, ^{13}C and ^{1}H, respectively). Samples were placed in a 4 mm ZrO_2 rotor. Magic angle spinning (MAS) frequencies were 4 and 10kHz and intensity of B_1 field (^{1}H, ^{13}C and ^{15}N) was 62.5 kHz. ^{13}C RAMP/CP/MAS (Ramped/Cross-polarization/Magic Angle Spinning) NMR experiments were used with repetition delays of 4. The CP contact pulse was 1 ms. The ^{15}N and ^{13}C scales were calibrated by external standard NH_4Cl (0 ppm) and glycine (carbonyl signal at 176.03 ppm), respectively. Temperature of bearing inlet air was set to 30^{o}C. The actual sample temperature due to the frictional heating of rotor was higher by 2 - 14^{o}C at 4 - 10 kHz of MAS frequency.

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