Journal of

Particle Science and Technology

Synthesis of polyamide 6 by anionic polymerization of ε-caprolactam in an internal mixer: Effect of polymerization reaction time

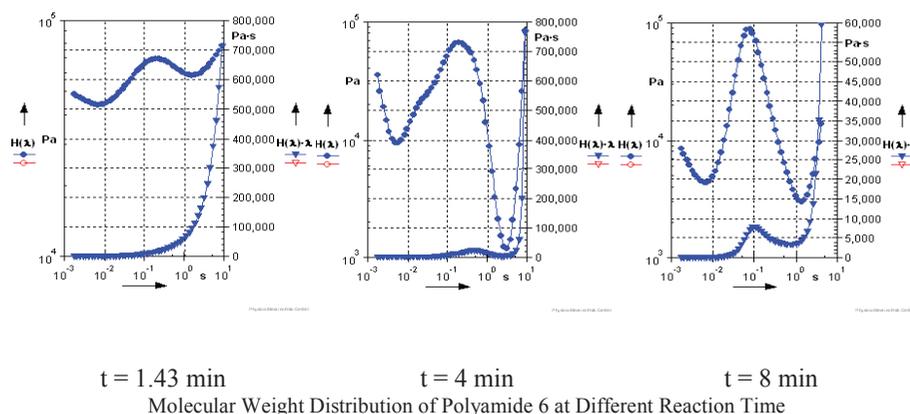**Mohammad Mahdi Salehi[1,*] , Omid Moini[2]**

[1]*Polymer and Science Technology Division, Research Institute of Petroleum Industry, Tehran, Iran*

[2]*Department of Chemical Engineering, College of Engineering, University of Isfahan, Isfahan, Iran*

HIGHLIGHTS

- Polyamide 6 synthesized via an ionic polymerization of ε-caprolactam in an internal mixer.

- The results revealed that the polymerization reaction was very fast.

- The viscoelastic behavior of samples almost remained unchanged during polymerization.

- The viscosity and elasticity of samples decreased with polymerization reaction time.

GRAPHICAL ABSTRACT

t = 1.43 min   t = 4 min   t = 8 min

Molecular Weight Distribution of Polyamide 6 at Different Reaction Time

ARTICLE INFO

ABSTRACT

The main objective of the present work was to synthesis polyamide 6 through anionic polymerization of ε-caprolactam in an internal mixer. The reaction time and the rheological properties of samples during the polymerization were studied. The samples were characterized by thermo-gravimetric analysis (TGA), differential scanning calorimeter (DSC) and FT-IR spectrometer. The melt flow behavior and viscoelastic properties of the samples were studied by using a Rheometric Mechanical Spectrometer (RMS). The polymerization reaction was found to be very fast such that it completed within 6 minutes as could be detected by following the mixing torque which reached to a steady state after passing a maximum. These results suggest that there is a reaction time above which the viscoelastic behavior of the samples almost remained unchanged, while the viscosity and elasticity of the samples continue to decrease with polymerization reaction time as a result of thermochemical degradation.

 * *Corresponding author. Tel.: +98 2148253231; fax: +98 2144739700*
E-mail address: salehimm@ripi.ir (M. M. Salehi).

1. Introduction

Synthesis of polyamide 6 (PA6) by using the anionic ring-opening polymerization of ε-caprolactam has received considerable attention [1], because of the high yield as well as high rate of polymerization. Fundamental features such as propagation mechanism, [2-4], and kinetics of polymerization, [5-6], have been widely investigated. A large number of catalysts and chain initiators are described in the literature to anionically polymerize ε-Caprolactam. The catalyst/initiator combinations used previously published works are: Na/N-acetylcaprolactam [7], Na/hexamethylene-1,6-bis-caprolactam [8], Na/ tetra acetyl hexamethylene diisocyanate [9], Na/ phenylisocyanate [10,11], Na/toluenediisocyanate [12], Na/1,4-diphenylmethanediisocyanate [12], Na/phenylcarbamoyl caprolactam [13], Na/2,4-toluene-bis-carbamoyl caprolactam [13], Na/4,4-diphenylmethane-bis-carbamoyl caprolactam [13], Na/ hexamethylene-bis-carbamoyl caprolactam [13], caprolactam-magnesium-bromide/N-acetylcaprolactam [14,15], caprolactam-magnesium-bromide/N-benzoylcaprolactam [16], caprolactam-magnesium-bromide/N,N'-isophthaloyl-bis-caprolactam [16] and Na/ Cyclohexyl carbamoyl caprolactam [17]. In general, chain initiators are divided to two categories based on functionality. So far scientists have focused on Mono and Bi functional chain initiators. Also chain initiators according to chemical structure are divided to "acylactams" and "isocyanates".

In recent years, increasing activities have been directed towards using reactive extrusion for polymerization, in particular, the anionic polymerization of ε-caprolactam [18]. The direct ring-opening polymerization of ε-caprolactam using reactive extrusion process compared to conventional condensation polymerization, have three obvious advantages: (1) a short reaction time, generally several minutes for reactive extrusion rather than 10h or more for the conventional condensation polymerization, (2) no by-products coming out when the monomers are polymerized, (3) the molecular weight of the products is several times greater than that produced by conventional condensation polymerization [16].

The aim of the present work was to study effects of the reaction time and the rheological properties of samples during the polymerization of ε-caprolactam in an internal mixer in order to provide information for optimizing the reactive extrusion process condition for producing PA6.

2. Experimental

2.1. Materials

ε-caprolactam was supplied by SHCHEKINOAZOT (Russia), sodium (Merck Chemical Co.) was used as catalyst. A pure (99.9%) Diphenylmethan 4,4′-diisosyanate (MDI) used as chain initiator was supplied from Merck Chemical Co.

2.1. Preparation of the premix reactants

A glass container containing was two moles (226 g) of ε-caprolactam heated under nitrogen blanket, until ε-caprolactam is completely melted. Then, 0.02 moles (0.46 g) of sodium catalyst were added to the container under vigorous stirring. A pale yellow solution (premix catalyst) was formed, which was allowed to cool to ambient temperature. Another container containing two moles (226 g) of ε-caprolactam was heated up to reaching the ε-caprolactam melting point, then, 0.018 moles (4.5 g) of MDI chain initiator were added into the container under vigorous stirring. A clear brown solution was formed, which was allowed to cool to ambient temperature. The premix catalyst was added into this container. This separately premix catalyst and chain initiator was dried and milled to obtain the premix reactants in the form of fine powder.

2.3. Polymerization process

The polymerization of ε-caprolactam was carried out in a 60 mls laboratory internal mixer (Brabender plasticorder W50) equipped with banbury type rotor and a nitrogen gas purging device. All the polymerization processes were performed at rotor speed of 100 rpm and fill factor of 75%. Variations of the torque as well as temperature of the internal mixer were recorded during the polymerization process as two important information sources. For all samples the polymerization were carried out for 8 minutes. The list of the samples recipes and polymerization reaction temperatures are given in Table 1.

2.4. Sample characterization

The degree of conversion of samples was evaluated by Thermo-Gravimetric Analysis (TGA) in N_2 atmosphere. Crystalline melting temperatures (Tm) of polyamide 6 samples were determined by a Mettler

Differential Scanning Calorimeter (DSC). The melt rheological behavior and viscoelastic properties of the samples were studied by using a Rheometric Mechanical Spectrometer (RMS).

Fig. 3 shows complex viscosity (η^*) and storage modulus (G') as functions of angular frequency for samples S2, S3 and S4.

Table 1.
Samples recipes and polymerization reaction temperatures.

Sample No.	Catalyst (mol %)	Chain initiator (mol %)	Temperature (°C)	Rotor speed (rpm)	Reaction time (min)
S1	0.5	0.45	210	100	10
S2	0.5	0.45	210	100	8
S3	0.5	0.45	210	100	4[1]
S4	0.5	0.45	210	100	1.43[2]

3. Results and discussion

Fig. 1 shows a typical torque vs. time obtained for the ε-caprolactam polymerization process in the internal mixer.

Rapid increase in the torque indicates that the polymerization reaction is very fast. The decrease in the torque after passing through a maximum can be attributed to decreasing viscosity as a result of thermomechanical chain breaking down type degradation. The points of S1, S2, S3 and S4 denote the time of sample collection for determination degree of conversion and final reaction time.

The corresponding conversion data is given in Table 2. By comparing these results one may find that increasing the reaction time has small effect on polymerization rate and degree of conversion.

Fig. 2 compares the FT-IR spectrum of the prepared polycaprolactam sample (S2) with that of conventional PA6 (Ultramid B5). As one can clearly see there is very close agreement between a characteristic picks of two samples.

Table 3 presents a thermal analysis results of the final prepared sample (S2) and commercial PA6 (Ultramid B5), obtained from DSC thermograms. Comparing these results indicate that the melting temperature of this sample (210-215°C) is very close to that of PA6 (220°C).

However, as it can be seen the heat of crystallization of this sample (S2) is greater than that of the conventional PA6, indicating that this sample possess greater potential for crystallinity.
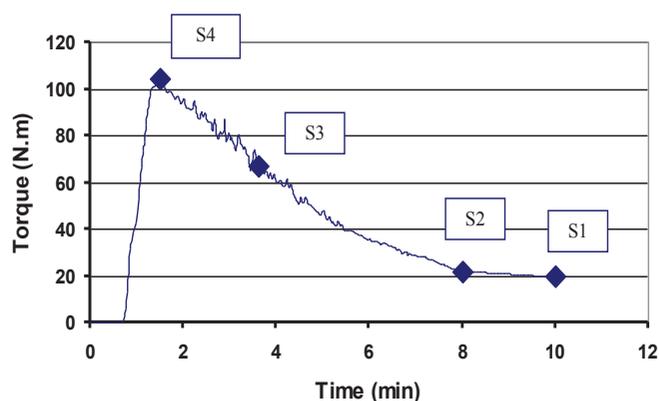
Fig. 1. Torque vs. reaction time of polymerization of ε-caprolactam at 210°C in an internal mixer.

Table 2.
The conversion data for samples prepared at different reaction time.

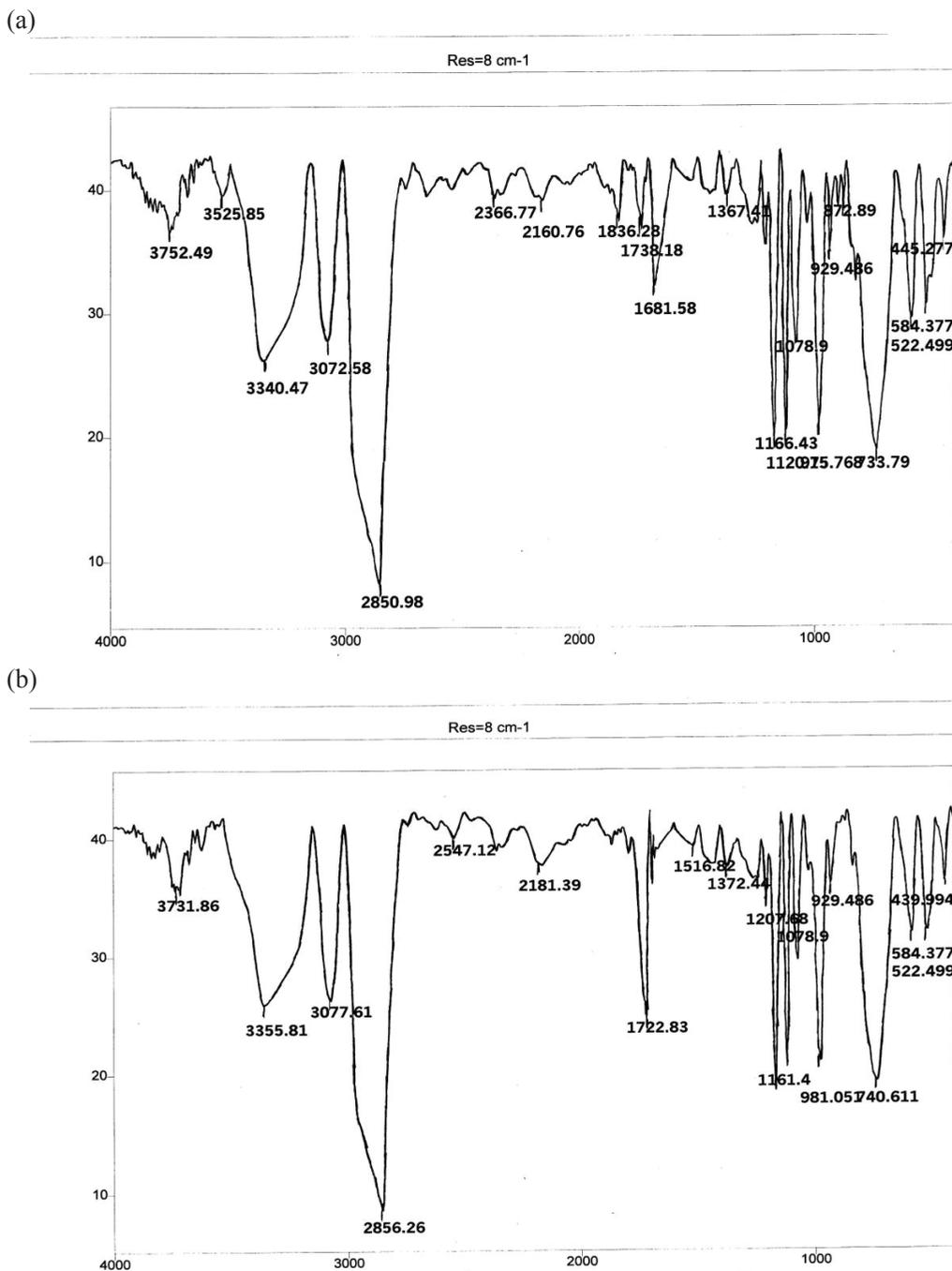| Sample	Reaction time (min)	Conversion (%)
S1	10	95.4
S2	8	95.4
S3	4	96.2
S4	1.43	94.6

(a)

(b)

Fig. 2. FT-IR spectra of (a) prepared sample (S2) and (b) commercial PA6 (Ultramid B5).

Table 3.
Thermal analysis results of the final prepared sample (S2) and commercial PA6 (Ultamid B5).

	T_m (°C)	T_c (°C)	ΔH_c (J g^{-1})
S2	215.25	186.72	56.66
Ultamid B5	220.30	169.63	51.04

(a)

(b)

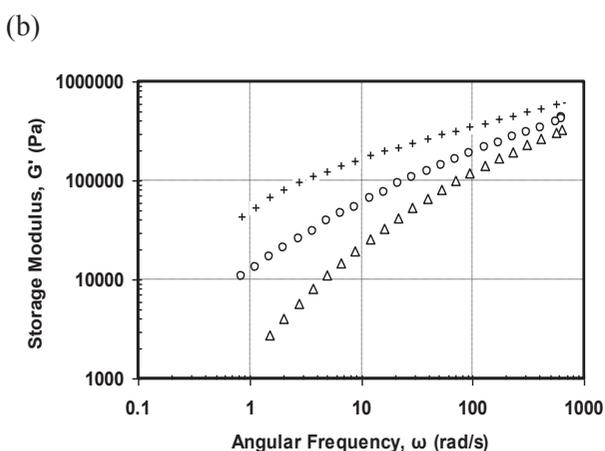**Fig. 3.** (a) Complex viscosity (η^*) and (b) storage modulus (G') vs. angular frequency (ω) for samples S2, S3 and S4 at temperature 260°C.
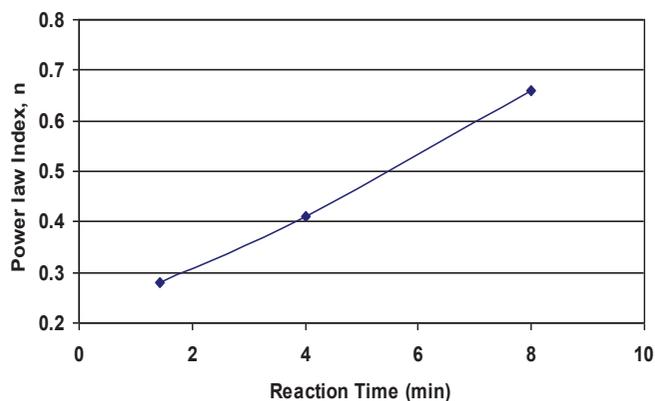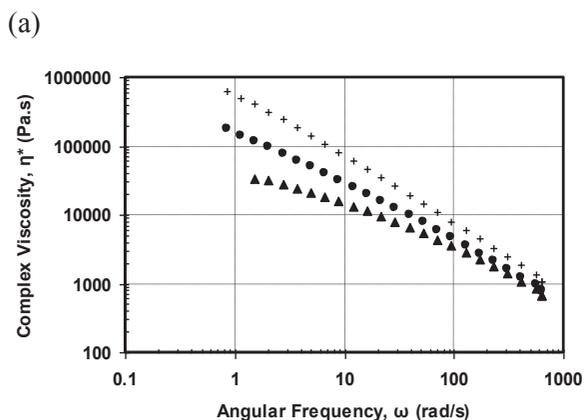
Fig. 4. The power law index of the samples collected at different reaction time.

Fig. 5 shows the viscoelastic properties of a conventional grade of PA6 (Ultramid B5). From comparing these results with those shown in Fig. 4 for sample S2 suggests that although the prepared polycaprolactam sample (S2) exhibit lower viscosity that PA6, it shows match greater elasticity. This can be attributed to broader molecular weight distribution resulted from very longer chain and/or highly branch molecules existing in sample S2 compared with PA6.

These results clearly indicate that, a considerable change in viscoelstic properties of samples occurs when the polymerization reaction passes through its maximum conversion. For example the sample S4 exhibits match greater melt elasticity and viscosity, in particular, at low shear rates compared to sample S2. These results can be attributed to thermomechanical degradation taking place after the reaction passes through its maximum conversion. That is, the thermomechanical degradation selectivity occurs on longer and/or highly branch molecules. This is evidenced by increasing the power law index as a function of reaction time shown in Fig. 4. Similar results have been reported for polymerization of ε-caprolactam using bifunctional initiator [18].
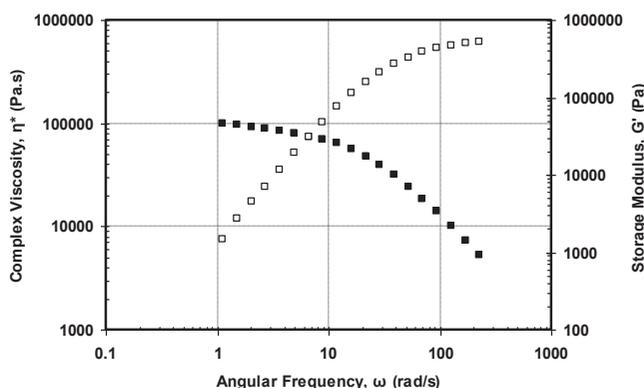

Fig. 5. Complex viscosity (η^*) (■) and storage modulus (G') (□) vs. angular frequency (ω) for conventional grade of PA6 (Ultramid B5).

As in the present work the polycaprolactam samples were prepared by using mixture of two and three functional chain initiator. It is possible that the three functional chain initiator initiates and propagates the polymerization reaction through its all three function resulting in a polymer chain with a very long single side chain. This can, in turn, assist the three dimensional molecular entanglements and, therefore, increases the viscoelasticity of the products.

Fig. 6 compares the viscoelastic properties of two samples (S1 and S2) collected at 10th and 8th minutes of the polymerization, respectively (in the torque steady state region). These results suggest that there is a reaction time above which the viscoelastic behavior of the samples almost remained unchanged, while the viscosity and elasticity of the samples continue to decrease with polymerization reaction time as a result of thermochemical degradation.
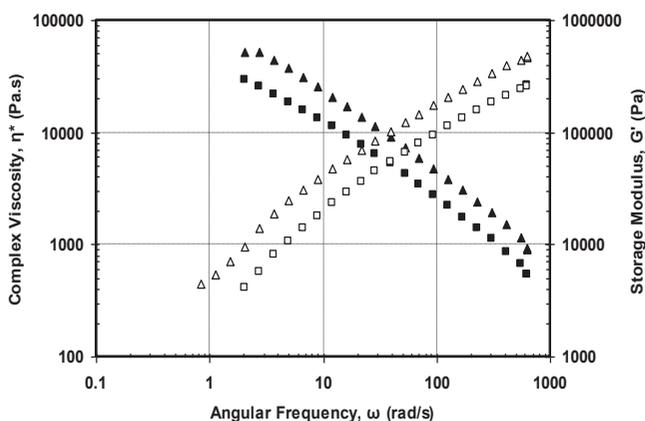

(S4)

(S3)

Fig. 6. Complex viscosity (η^*) and storage modulus (G') vs. angular frequency (ω) for two samples S1(▲,△) and S2 (■,□).
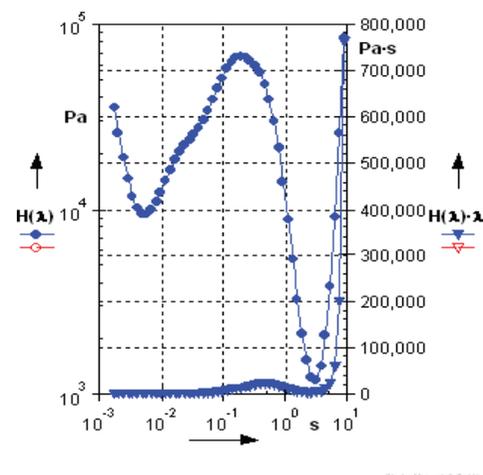
The results of relaxation time distribution, H(λ), of these samples are shown in Fig. 7.

Comparing these results suggest match narrower distribution for sample S2 compared to other three samples. From the above it can be realized that the thermomechanical degradation process predominately occurs on three dimensional molecular entanglements formed by the polymer chains produced by three functional initiators.
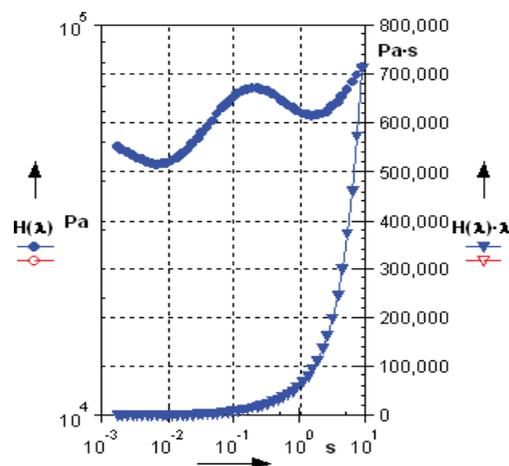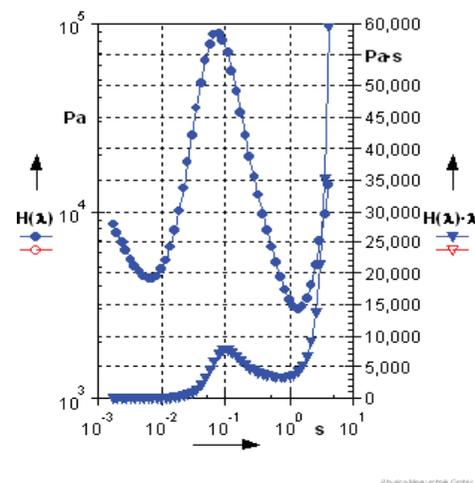

(S2)

Figure. 7. Relaxation time distribution, H(λ) of samples S2, S3 and S4.

4. Conclusions

Polycaprolactam with similar to those of commercial polyamide 6 can be produced via reactive anionic polymerization of ε-caprolactam in an internal mixer. The polymerization rate was found to be very fast such that it reaches to the maximum conversion in two minutes and completed within eight minutes after passing through the maximum conversion; the process which could be followed by recording the torque of the internal mixer. The pronounced decrease in internal torque was mainly attributed to the thermomechanical degradation which was found to occur predominately on three dimensional molecular entanglements resulted from long side chain produced by the three functional chain initiator. The melt linear viscoelastic properties of the prepared samples shown greater extent of elasticity and shear thinning compared which those reported for commercial polyamide 6. As a result of higher extent of chain branching formed by three functional chain initiators. The viscoelastic behavior of the samples almost remained unchanged during polymerization reaction while the viscosity and elasticity of the samples decreased with polymerization reaction time.

References

[1] M. Xanthos, Reactive Extrusion Principles and Practice, Hanser publishers, Munich, 1992.

[2] J. Sebenda, Lactam Polymerization, J. Macromol. Sci. Chem. A 6 (1972) 1145-1199.

[3] N. Mougin, C. A. Veith, R. E. Cohen, Y. Gnanou, Anionic polymerization of lactams in the presence of metal dialkoxyaluminum hydrides: presentation of a new mechanism, Macromolecules 25 (1992) 2004-2016.

[4] K. Udipi, R. S. Dave, R. L. Kruse, L. R. Stebbins, Polyamides from lactams via Anionic Ring-Openning polymerization: 1. Chemistry and Some Recent Findings, Polymer 38 (1997) 927-938.

[5] J. Stehlicek, J. Sebenda, Anionic polymerization of ε-caprolactam-lix effect of the ratio of reacting components, of the medium and of the ring size on the initial stage of the anionic polymerization of lactams, Eur. Polym. J. 22 (1986) 769-773.

[6] D. Crespy, K. Landfester, Anionic Polymerization of ε-Caprolactam in Miniemulsion: Synthesis and Characterization of Polyamide-6 Nanoparticles, Macromolecules 38 (2005) 6882-6887.

[7] R. Z. Greenley, J. C. Stauffer, J. E. Kurz, The Kinetic Equation for the Initiated, Anionic Polymerization of η-Caprolactam, Macromolecules 2 (1969) 561-567.

[8] P. R. Hornsby, J. F. Tung, K. Tarverdy, Characterization of Polyamide 6 Made by Reactive Extrusion. 1. Synthesis and Characterization of Properties, J. Appl. Polym. Sci. 53 (1994) 891-897.

[9] E. Sittler, J. Sebenda, Alkaline polymerization of 6-caprolactam. XXXII. The kinetics of polymerization activated by N,N,N',N'-tetraacetylhexamethylenediamine, Collect. Czech. Chem. Commun. 33 (1968) 270-277.

[10] P. W. Sibal, R. E. Camargo, C. W. Macosko, Designing nylon-6 polymerization systems for RIM, Polym. Process Eng. 1 (1984) 147-169.

[11] J. D. Lin, J. M. Ottino, E. L. Thomas, A kinetic study of the activated anionic polymerization of ε-caprolactam, Polym. Eng. Sci. 25 (1985) 1155-1163.

[12] S. A. Bolgov, V. P. Begishev, A. Y. Malkin, V. G. Frolov, Role of the functionality of activators during isothermal crystallization accompanying the activated anionic polymerization of ε-caprolactam, Polym. Sci. USSR 23 (1981) 1485-1492.

[13] A. Y. Malkin, S. L. Ivanova, V. G. Frolov, A. N. Ivanova, Z. S. Adarinova, Kinetics of anionic polymerization of lactams. (Solution of non-isothermal kinetic problems by the inverse method), Polymer 23 (1982) 1791-1800.

[14] K. Ueda, M. Nakai, M. Hosoda, K. Tai, Synthesis of high molecular weight nylon 6 by anionic polymerization of ε-caprolactam. mechanism and kinetics, Polym. J. 29 (1997) 568-573.

[15] J. Stehlicek, R. Puffr, Anionic polymerization of 6-hexanelactam. fast catalytic systems in the anionic polymerization of 6-hexanelactam, Makromol. Chem. 193 (1992) 2539-2545.

[16] G. Rusu, K. Ueda, E. Rusu, M. Rusu, Polyamides from lactams by centrifugal molding via anionic ring-openning polymerization, Polymer 42 (2001) 5669-5678.

[17] L. Ricco, S. Russo, G. Orefice, F. Riva, Anionic Poly(ε-caprolactam): relationships among conditions of Synthesis, chain regularity, reticular order, and polymorphism, Macromolecules 32 (1999) 7726-7731.

[18] B. H. Lee, J. L. White, Comparison studies of anionic polymerization of caprolactam in different twin screw extruders, Int. Polym. Process. 16 (2001) 172-182.