e-Polymers **2007**, no. 073
http://www.e-polymers.org
ISSN 1618-7229

On heat regimes of anion-activated polymerization of ε-caprolactam

Sevan Davtyan,[1] Hayk Zakaryan,[1] Anahit Tonoyan,[1] Gagik Varderesyan [1]*

[1] State Engineering University of Armenia, 105 Teryan str., 0009 Yerevan, Armenia
Tel: (374-10) 564012, Fax: (374-10) 564012.E-mail: davtyans@seua.am

(Received: 11 May, 2007; published: 27 July, 2007)

Abstract: Quantitatively, the Semenov diagram of heat generation–temperature relationship is analyzed. Critical transitions of heat regimes during anion-activated polymerization of ε-caprolactam are investigated. Various outcomes as compared with classic cases already discussed by Semenov are observed for the polymerization and crystallization processes running sequentially. It was shown that the critical Semenov parameter holds even for the weak-exothermal polymerization reaction when steep transition from quasi-thermal–low temperature to quasi-adiabatic–high temperature heat regime takes place.

Introduction

Formation of polymeric articles is accompanied by heat generation which often leads to reaction media self-heating and shifting of the polymerization heat regimes regardless of the polymerization mechanism (radical, ionic or poly-condensation). Anion-activated polymerization of ε-caprolactam which practically runs in thermo-neutral conditions could serve as a classic example. Adiabatic heating of ε-caprolactam reaches 90–92 ^{0}C although its polymerization heat effect is only ca 13.4 $kJ \cdot mol^{-1}$. Actually, exothermal crystallization of the obtained polymer with ~25 $kJ \cdot mol^{-1}$ adds to reaction heating along with the polymerization.

It has to be stated that for any exothermal chemical process running in quasi-adiabatic high-temperature regime is determined by the ratio of the rates of heat generation and heat removal, i.e. by the Semenov parameter [1]. In this regard, it is interesting to note that the low-temperature–to–high-temperature transition occurs gradually similar to heat explosion propagation case where as at critical Semenov parameter, steep transition is observed.

The aim of the current work is the investigation of the heat regimes as depended on the Semenov parameter for the weakly exothermal polymerization of anion-activated ε-caprolactam for concurrently occurring (at temperatures below 150 ^{o}C processes of polymerization and crystallization proceed together. But at temperatures more than 150 ^{o}C these processes are separated in time – first polymerization go on, then crystallization follow it) and temporally divided process of polymerization and crystallization).

Quantitative analysis of heat generation – temperature diagram

During anion-activated polymerization of ε-caprolactam, temperature elevation rate of the reaction is summed from polymerization and crystallization processes, i.e.;

$$c\rho \frac{dT}{dt} = q_\alpha \frac{d\Pi}{dt} + q_\beta \frac{d\Pi_{cr}}{dt}, \tag{1}$$

where c and ρ are the mean heat capacity and specific density of reaction media; T is the current temperature of the media; q_α and q_β are heat effects of polymerization and crystallization, respectively; Π and Π_{cr} are the quantities of produced polymer and its crystallized part, accordingly; t is the duration.

The conversion (α) and the crystallinity (β) are determined in the following way:

$$\alpha = \frac{M_0 - M}{M_0} = \frac{\Pi}{M_0} = \frac{T_\alpha - T_0}{T_\infty^\alpha - T_0}; \quad \beta = \frac{\Pi_{\kappa p}}{M_0} = \frac{T_\beta - T_0}{\frac{q_\beta}{q_\alpha}\left(T_\infty^\alpha - T_0\right)}, \tag{2}$$

where M_0 and M are the initial and current concentrations of the monomer; T_0 is the initial temperature of the reaction; T_α and T_β are current temperatures of polymerization and crystallization; T_∞^α is the final polymerization temperature calculated for the case of complete conversion of monomer into polymer.

If anion-activated polymerization of ε-caprolactam is carried out in periodic reactor while temperature gradients in the bulk of the reaction mixture is absent and are focused in the reactor wall, then the balance equation could be written in the following manner if the heat removal obeys Newton's law:

$$c\rho \frac{dT}{dt} = q_\alpha \cdot M_0 \frac{d\alpha}{dt} + q_\beta \cdot M_0 \frac{d\beta}{dt} - \frac{hs}{V}\left(T - T_0\right), \tag{3}$$

where h is the coefficient of heat removal; s and V are the surface area and capacity of the reactor, respectively. The rates of polymerization and crystallization in (3) are specified by the following equations [4-7]:

$$\frac{d\alpha}{dt} = (1-\alpha)K_{10}\, exp\left(-\frac{E_1}{RT}\right) + \alpha(1-\alpha)K_{20}\, exp\left(-\frac{E_2}{RT}\right), \tag{4}$$

and

$$\frac{d\beta}{dt} = K(T)(1 + a_0\beta)\left[\alpha\beta_p(T) - \beta\right], \tag{5}$$

correspondingly. In expression (4), beginning from the small depths of conversion,

$$\alpha(1-\alpha)K_{20}\, exp\left(-\frac{E_2}{RT}\right) >> (1-\alpha)K_{10}\, exp\left(-\frac{E_1}{RT}\right).$$

Consequently, henceforth, in equation (4) we would consider only the second term, while in (5) $\beta_p(T)$ is determined in the following manner [8]:

$$\beta_p(T) = 0{,}54\left[1 - \left(\frac{T}{T_{\pi\lambda}}\right)^4\right]^{\frac{1}{2}}. \tag{6}$$

For constructing Q vs. T diagram it should be taken into account that $T = T_\alpha + T_\beta$, then:

$$c\rho\frac{dT}{dt}=c\rho\frac{d\left(T_{\alpha}+T_{\beta}\right)}{dt}=c\rho\frac{dT_{\alpha}}{dt}+c\rho\frac{dT_{\beta}}{dt}\,. \tag{7}$$

In relationship (7):

$$c\rho\frac{dT_{\alpha}}{dt}=q_{\alpha}\frac{d\alpha}{dt}=\frac{d\left(\alpha\cdot q_{\alpha}\right)}{dt}=\frac{dQ_{\alpha}}{dt}\,. \tag{8}$$

In a similar manner:

$$c\rho\frac{dT_{\beta}}{dt}=\frac{dQ_{\beta}}{dt}\,, \tag{9}$$

where Q_{α} and Q_{β} are polymerization and crystallization heat generations. Taking into account that the general heat generation is the sum of polymerization and crystallization heats, i.e. $Q=Q_{\alpha}+Q_{\beta}$, then equation (3) could be rewritten as:

$$\frac{dQ}{dt}=q_{\alpha}\frac{d\alpha}{dt}+q_{\beta}\frac{d\beta}{dt}-h\frac{s}{v}\left(T-T_{0}\right). \tag{3′}$$

The initial conditions of the system of equations (4), (5) and (3)′ are:

$$t=0;\quad Q=0;\quad \alpha=0;\quad \beta=0;\quad T=T_{0} \tag{10}$$

Q vs. *T* diagram analysis could be done for two cases:

- heat is generated only via polymerization;
- heat is generated via sequential processes of polymerization and crystallization.

Obviously, if only polymerization takes place in the reaction media, then $\frac{d\beta}{dt}=0$, and from (3)′ we could obtain:

$$\frac{dQ_{\alpha}}{dt}=q_{\alpha}K_{10}\,exp\left(-\frac{E_{1}}{RT_{\alpha}}\right)-h\frac{s}{v}\left(T_{\alpha}-T_{0}\right). \tag{11}$$

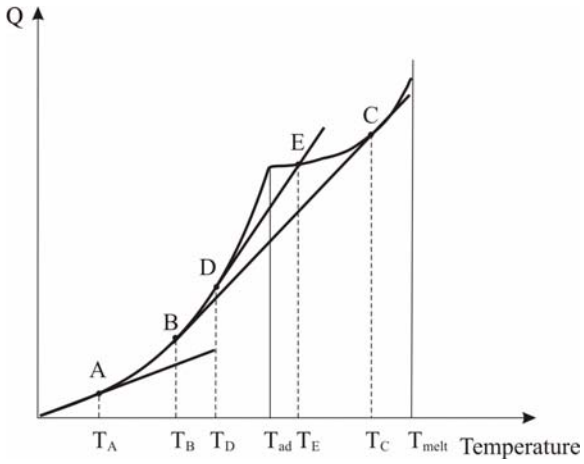

Fig. 1. Heat generation vs. temperature diagram for the sequential polymerization and crystallization processes.

This case is reduced to classical problem being considered already by Semenov [1] and is beyond consideration in this paper.

Analysis for sequential processes of polymerization and crystallization could be conducted under the following restrictions: heat generation coming from polymerization should be limited by the adiabatic heating temperature of reaction media (T_{ad}) in the polymerization region, while the crystallization heat should limited by the melting temperature of the crystalline polymer, i.e. $T_{melt.}$

Actually, up to T_{ad} the rate of crystallization is equal to zero $d\beta/dt$=0, while $d\alpha/dt$=0 for temperatures exceeding T_{ad}.

Solution of the system with indicated limitations is presented in Fig. 1.

Here, the branch of curve of Q vs. T relationship corresponds to polymerization temperature interval ranging from initial up to T_{ad}, while for the crystallization the interval lays from T_{ad} to T_{melt}.

Process develops in three different ways if polymerization and crystallization proceed sequentially:

1. The heat losses line touches the heat generation curve at point *A* due to polymerization (Fig. 1). This is the case described by Semenov [1].

2. The heat losses line touches the heat generation curves at points *B* and *C* due to polymerization and crystallization (Fig. 1). In this case, new conditions are added to the conditions of *BC* losses' line as per the polymerization in point *B* (Fig. 1); i.e. the new conditions of the heat losses line touching the curve of heat generation due to crystallization in point *C* (Fig. 1), that is:

$$\begin{aligned}
&q_{\alpha} K_{10}\, exp\left(-\frac{E_1}{RT_{\alpha B}}\right) = \frac{hs}{v}\left(T_{\alpha B} - T_0\right), \\
&q_{\alpha} K_{10}\, \frac{E_1}{RT_{\alpha B}^2}\, exp\left(-\frac{E_1}{RT_{\alpha B}}\right) = h\frac{s}{v},
\end{aligned} \qquad (12)$$

$$\begin{aligned}
&q_{\beta} K_0\, exp\left[-\frac{E}{RT_{\beta c}} - \frac{\psi T_{пл}}{R\left(T_{пл} - T_{\beta c}\right)}\right] = \frac{hs}{v}\left(T_{\beta c} - T_0\right), \\
&\frac{d}{dT}\left\{q_{\beta} K_0\, exp\left[-\frac{E}{RT_{\beta c}} - \frac{\psi T_{пл}}{T_{\beta c}\left(T_{пл} - T_{\beta c}\right)}\right]\right\} = h\frac{s}{v}\ .
\end{aligned} \qquad (13)$$

Joint solution of the equations (12) and (13) allows finding the relationship between $T_{\alpha B}$, $T_{\beta C}$ and T_0. However, in this case, as different with [1], algebraic equation of the sixth order is obtained, and hence no analysis is provided here.

3. The heat losses line touching the heat generation curve in point *D* due to polymerization, crosses with heat generation curve due to crystallization in point *E* (Fig. 1).

Polymerization proceeds in adiabatic regime and the reaction temperature increases up to T_E as per the condition (12) for point *D*. As it could be seen from Fig. 1, change of heat regime takes place at T_E resulting in adiabatically obtained polymer's crystallization under the isothermal regime.

For sequential regimes of polymerization and crystallization, crossing of their heat removal line with curves of heat generation again produces some variations as compared with classic case [1]. Actually, if the heat removal line crosses only the heat generation curve due to polymerization (Fig. 2, point 1, 2) then the heat regimes are similar with [1]. In this case point 2 (Fig. 2) supports unstable state of reaction mixture. On the other hand, if the heat removal line crosses the heat generation curve due to polymerization and crystallization in points 1, 2′, 3 (Fig. 2), then three different regimes are produced.

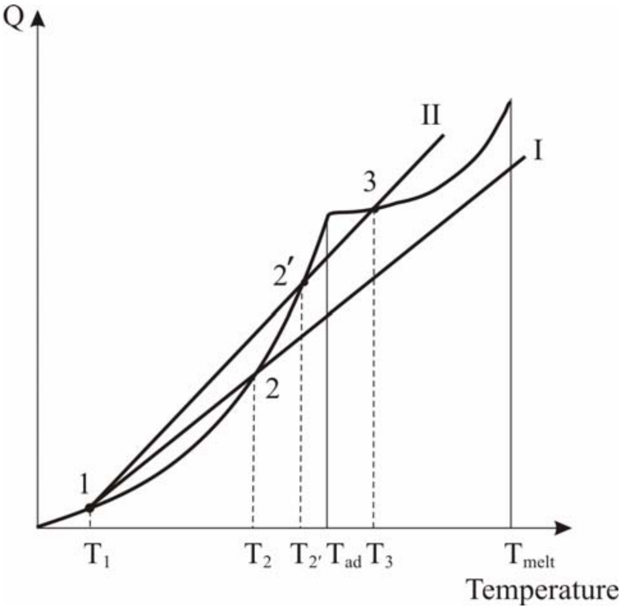

Fig. 2. Heat generation vs. temperature diagram for the sequential polymerization and crystallization processes.

T_1 temperature supports stable isothermal polymerization regime, while thermal explosion occurs at T_2 temperature. Again, heat regimes change and further crystallization held under isothermal regime at T_3.

On Heat Regime Critical Transitions during anion-activated polymerization of ε-caprolactam

Numerical calculation of (3), (4) and (5) equation system for the determination of heat regimes of anion-activated polymerization of ε-caprolactam is conducted in non-dimensional variables according to Frank-Kamenecki [9] with the use of following designations:

$$\theta=\frac{E}{R_gT_0^2}(T-T_0),\ \gamma_1=\frac{c\rho R_gT_0^2}{q_\alpha E_1},\ \gamma_2=\frac{c\rho R_gT_0^2}{q_\beta E},\ \mathrm{c}_1=\frac{h}{c\rho}\frac{s}{vk_1(T_0)},\ \mathrm{c}_2=\frac{k_2(T_0)}{k_1(T_0)},$$

$$\mathrm{c}_3=\frac{k_3(T_0)}{k_1(T_0)},\ \sigma_1=\frac{E_2}{E_1},\ \sigma_2=\frac{E_3}{E_1},\ \varepsilon=\frac{R_gT_0}{E_1},\ \varphi=\frac{\psi}{T_0},\ \delta=\frac{T_0}{T_{melt}},\ \tau=k_1(T_0)t$$

Then (3), (4), (5) equation system would take the following form:

$$\frac{d\theta}{d\tau}=\frac{1}{\gamma_1}\frac{d\alpha}{dt}+\frac{1}{\gamma_2}\frac{d\beta}{dt}-c_1\theta,$$

$$\frac{d\alpha}{d\tau}=(1-\alpha)exp\left(\frac{\theta}{1+\varepsilon\theta}\right)+c_2\alpha(1-\alpha)exp\left(\frac{\sigma_1\theta}{1+\varepsilon\theta}\right),$$

$$\frac{d\beta}{d\tau}=c_3\,exp\left[\frac{\sigma_2\theta}{1+\varepsilon\theta}+\frac{\varphi}{(1+\varepsilon\theta)[1-\delta(1+\varepsilon\theta)]}\right](1+c\beta)[\alpha\beta_p(\theta)-\beta],$$

$$\beta_p(\theta)=0{,}54\left[1-\left(\frac{\varepsilon\theta+1}{\varepsilon\theta_{пл}+1}\right)^4\right]^{\frac{1}{2}},$$

with the following initial conditions:

$$\tau=0;\ \alpha=\beta=0;\ \theta=0. \tag{14}$$

Analysis of solution of (12) system is convenient to carry out with the use of Semenov parameters

$Se^{\alpha}=q_{\alpha}K_{10}\frac{E_1}{R_gT_{\alpha}^2}\exp\left(-\frac{E}{R_gT_{\alpha}}\right)\frac{v}{hs}$; $Se^{\beta}=q_{\beta}K_0\frac{E}{R_gT_{\beta}^2}\exp\left(-\frac{E}{R_gT_{\beta}}\right)\frac{v}{hs}$. While in the dimensionless form:

$$Se=Se^{\alpha}+Se^{\beta}=\frac{1}{c_1}\left(\frac{1}{\gamma_1}+\frac{\sigma_2\cdot c_3}{\gamma_2}\right).$$

As a dimensional values of kinetic, thermodynamic and thermophysical parameters have been used data of [4–8, 10].

The relationship of limiting heating temperature of the reaction mixture both for polymerization and concurrently occurring polymerization and crystallization are presented in Fig. 3.

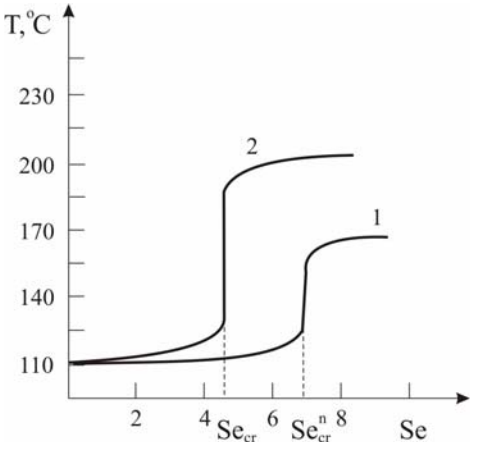

Fig. 3. Dependance of limiting temperatures on the Se parameter for polymerization (1) and polymerization + crystallization (2) processes.

As it follows from curve 1, there is critical Semenov parameter value for which heating is inconsiderable (ca 5-7 ^{0}C) at $Se < Se^{П}_{cr}$ and polymerization proceeds in quasi-isothermal–low-temperature regime during weakly exothermal polymerization of ε-caprolactam. Polymerization develops considerably non-isothermally at

$Se \geq Se_{cr}^{\Pi}$, heating reaches up to 45 ^{0} and over and quasi-adiabatic high-temperature polymerization takes place.

Critical value of *Se* parameter depends on initial temperature of crystallization as well as on the temperature of environs. As these temperatures are equal to T_0 for our case, then here we can analyze the influence of T_0 on *Se*.

Actually, Se_{cr} monotonically diminishes with increasing T_0 if we don't take into account crystallization (Fig. 4a). However, Se_{cr} vs. T_0 relationship takes non-monotonous character in the presence of crystallization (Fig. 4b).

From Fig. 4b it follows that Se_{cr} decreases at first then increases with T_0 augmentation. If the initial temperature of the media is equal 148–150 ^{0}C, then Se_{cr} drops down to values characteristic for polymerization.

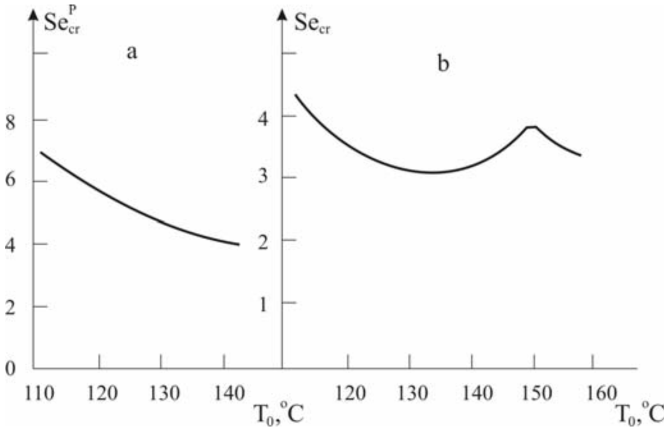

Fig. 4. Dependence of Se parameter on the initial temperature for polymerization (a) and polymerization + crystallization (b) processes.

Non-monotonous $Se_{cr}(T_0)$ relationship for combined polymerization and crystallization could be explained by diverse influence of T_0 on heat generation coming from polymerization and crystallization.

Actually, the rate of polymerization heat generation increases with T_0 elevation as per the conventional Arrhenius relationship. However, crystallization heat generation rate proceeds through maximum which corresponds to 135–140 ^{0}C of initial temperature. Obviously, in this case, decrease of crystallization heat generation rate diminishes the net heat generation. Hence, minimum appears at T_0 = 135–136 ^{0}C on the $Se_{cr} - (T_0)$ curve. Further increase of T_0 somehow increases Se_{cr} up to 148–150 ^{0}C at which the relative rate of crystallization decreases down to point when polymerization is fully completed. Beginning from this point, Se_{cr} is determined by the rate of heat generation coming only from polymerization. Hence, it decreases down to point characteristic for polymerization (Fig. 4).

Thus, analysis of the results show that there is critical Semenov parameter when steep quasi-isothermal–to–quasi-adiabatic high temperature heat regime transition is observed even for weak exothermal polymerization processes with heat effects of the order of magnitudes of 13.5 kJ·mol^{-1}.

Acknowledgements

The work is supported by NFSAT-CRDF, MES RA (Grant BRAU -01-05).

References

[1] Semenov, N.N. *Chain reactions*“Goskhimtekhizdat, Leningrad, **1934**.
[2] Maksimov, E.I. *Dokl AN SSSR* **1970**, 191 (5), 1091.
[3] Jirkov, P.V.; Davtyan, S.P.; Karyan, A.A. *Visokomolek Soed.* **1984**, 26A (7), 1405.
[4] Begishev, V.P.; Keapin, I.A.; Malkin, A.Ya. *Visokomolek Soed.* **1982**, 24B (6), 656.
[5] Malkin, A.Ya.; Frolov, V.G; Ivanov, A.I.; Andrianova, E.S. *Visokomolek Soed.* **1979**, 21A (3), 632.
[6] Tonoyan, A.O.; Pogosyan, M.G.; Gevondyan, R.V.; Varderesyan, A.Z.; Davtyan, S.P. *Izvestiya NAN RA i GIUA* **2006**, 59(1), 44.
[7] Tonoyan, A.O.; Pogosyan, M.G.; Sargsyan, A.G.; Christoph Shik; Davtyan, S.P. *Izvestiya NAN RA i GIUA* **2006**, 59(2), 293.
[8] Belyaeva, N.A.; Klichnikov, L.V.; Davtyan, S.P.; Khudyaev, S.I. *Thezisi III Vsesoyuznoy konferencii po nelineynoy teorii uprodosti, Siktivkar*, **1987**, 51.
[9] Frank-Kamenecki, D.A. *Diffusion and Heat transfer in chemical kinetics*, “Nauka”, Moscow, **1967**.
[10] Kubota, H.; Nowell, J.B. *J. Appl. Polymer Sci*. **1975**, 19 (6), 1521.