

Ring Opening Polymerization of ϵ -Caprolactone Initiated by Decamolybdate Anion: Determination of Kinetic and Thermodynamic Parameters by DSC and $^1\text{H-NMR}$

Aurelio Ramírez-Hernández,¹ Antonio Martínez-Richa²

¹Campus Tuxtepec, Circuito Central #200, Colonia Parque Industrial, Universidad del Papaloapán, Tuxtepec 68301, Oaxaca, México

²Departamento de Química, Universidad de Guanajuato, Noria Alta S/N, Guanajuato, Gto. 36050, México

Received 8 February 2009; accepted 23 August 2009

DOI 10.1002/app.31337

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of this work is the kinetic and thermodynamic study (by differential scanning calorimetry (DSC) and proton nuclear magnetic resonance ($^1\text{H-NMR}$)) of the polymerization of ϵ -caprolactone initiated by ammonium decamolybdate. By means of isothermal kinetics, enthalpies of reaction in the range 150–160°C, as well as constant rates of polymerization (using an n th-order kinetics function model), were determined. From an Arrhenius plot, activation energy ($E_a = 85.3$ kJ/mol) and preexponential factor ($A = 1.78 \times 10^8$ min⁻¹) were estimated. Using dynamic methods, crystallization and melting temperatures for the polymer obtained *in situ*

were derived. Kinetic data for polymerization (obtained by $^1\text{H-NMR}$) were fitted to 13 different model reaction functions. It was found that power law equations represent better the conversion versus time plots for this system. On the basis of experimental facts, a coordination-insertion mechanism involving molybdenum(V) species is proposed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2288–2295, 2010

Key words: ϵ -caprolactone; ammonium decamolybdate; isothermal and nonisothermal kinetics; activation energy; ring-opening polymerization

INTRODUCTION

The synthesis of aliphatic polyesters derived from lactones is carried out by ring-opening polymerization (ROP) of cyclic esters, both in solution and in bulk. Various initiators such as aluminum, zinc, tin, and rare earth derivatives are commonly used to obtain these materials.^{1–3} Synthesis of well-defined functional polymers is an important challenge to researchers working in the polymer area. In the case of ring-opening polymerization, suitable initiators and coinitiators need to be used to produce the desired polymer with specific end-groups, and polymerization must proceed with the minimum amount of backbiting and transesterification reactions.

We have reported the use of decamolybdate anion to quantitatively synthesize well-defined functional polyesters and copolyesters derived from lactones.^{4–7} Decamolybdate anion is obtained in the solid state as the ammonium salt $(\text{NH}_3)_8[\text{Mo}_{10}\text{O}_{34}]$ by thermal decomposition of ammonium heptamolybdate

$(\text{NH}_3)_4[\text{Mo}_7\text{O}_{24}]$. Catalyst recovered after a polymerization batch maintain most of its initial properties, and can be reused to obtain more polyester in an efficient manner. Our results indicate that polymerization occurs in two hours by heterogeneous catalysis at 150°C. Occurrence of transesterification and backbiting reactions is not detected in the range 150–160°C. However, above 160°C polymerization reaction is very fast, control of molecular weight is not possible and transesterification becomes an important side reaction.

Kinetic studies are very important to determine the nature of chemical and polymerization reactions. Understanding the effect of variables such as pH, temperature, pressure, solvent, etc. on reaction rates provide the better way to optimize a chemical and polymerization reactions carried out at the laboratory or at the industrial scale. Reaction rate can be parameterized as a function of state variables such as temperature, pressure, and concentration.

Solid-state reactions (and in particular bulk polymerization) are in general thermally activated. The most common experimental techniques used to study kinetics of thermally activated reactions are thermogravimetry (TG), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). As these techniques measure changes in enthalpy, a kinetic analysis can be performed to data derived

Correspondence to: A. Martínez-Richa (richa@quijote.ugto.mx).

Contract grant sponsor: Universidad de Guanajuato.

TABLE I
Reaction Models Used to Describe Changes Induced by Thermal Activation

Number	Reaction model	$F(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$(2/3)\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2 (\alpha^{-1})$	α^2
6	Mampel (first-order)	$1 - \alpha$	$-\ln(1 - \alpha)$
7	Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1 - \alpha)^{2/3}(1 - (1 - \alpha)^{1/3})^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
11	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
13	Second-order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$

from different experiments. However, as application of classical kinetic concepts in general is limited to homogeneous reactions, one has to keep in mind that in order to get an overall kinetics scheme, chemically specific techniques are necessary to carry out. Other important issue to be considered is the fact that solid-state reactions do not occur by a single step mechanism; rather, they are composed of complex multi-step processes that can become mathematically untreatable.⁸ This means that a kinetics analysis for solid-state reactions must be considered more as a practical tool for data interpretation. Information can be derived from a series of measurements in the form of one or some models with few parameters. These models in turn can help in the prediction of parameters under other experimental conditions.⁹⁻¹³

For thermoanalytical measurements, kinetics is normally studied under the conditions of isothermal and/or nonisothermal (usually linear) heating. Data set are analyzed using one or more kinetic models. The model parameters must be defined in order to describe the different variables that affect the experiment.

An important parameter to be determined in a kinetic study is the activation energy. By means of thermal analysis, kinetic parameters for several thermal processes like decomposition, oxidation, reduction, crystallization, and polymerization can be derived. If α represents the extent of a reaction (or the degree of conversion), reaction rates of these processes are commonly described by the following rate equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right)f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the reaction rate, t is the time, T is the temperature, E_a is the activation energy, A is the pre-exponential factor, R is the universal gas constant and $k(T)$ is the temperature-dependent rate constant. In the case of polymers, α represents the

degree of monomer conversion, being $f(\alpha)$ a function of the degree of monomer conversion α . $f(\alpha)$ is called the reaction model, and represents the dependence of the reaction rate on α . Several functions have been proposed for the reaction model $f(\alpha)$ (see Table I). Although all of them are concentration dependent functions, interpretation in terms of concentration should be made with caution.^{14,15}

In eq. (1), it is considered that Arrhenius equation provides a good description of the temperature dependence of rate constant. This is almost always true for single-step homogeneous reactions. However, physical interpretation of activation energy E_a and preexponential factor A is limited for solid-state reactions, due mainly to the multiple step nature of these reactions. In most cases, Arrhenius parameters derived for solid-state reactions must be considered as only useful empirical parameters.¹¹⁻¹³

The integrated form of eq. (1) for isothermal conditions is given by

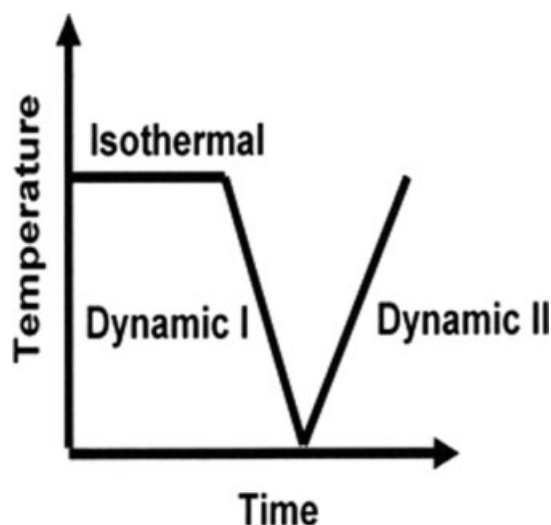
$$g(\alpha) = \int [f(\alpha)^{-1}] d\alpha = k(T)t \quad (2)$$

A basic equation used for isothermal n th order kinetics involves a power-law function of $1 - \alpha$

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3)$$

where $d\alpha/dt$ is the reaction rate, k is the rate constant, α is the degree of conversion, and n is the reaction order. Equation (3) resembles to those equations proposed by reaction models 6, 11, 12 and 13 in Table I.

Values of k and n for different temperatures can be derived from the isothermal curves. With more than two data collected at different temperatures,



Scheme 1 General method used in the study of polymerization of ϵ -CL.

the kinetic parameters $\ln A$ and E_a can be derived from the Arrhenius equation. Equations (1) and (3) can be rewritten as

$$\ln k(T) = \ln A - E_a/RT \quad (4)$$

$$\ln d\alpha/dt = \ln k(T) + n \ln(1 - \alpha) \quad (5)$$

Reaction rate is related with enthalpy by the eq. (6)^{16,17}

$$\frac{dH(t)}{dt} = \Delta H_{rxn} \frac{d\alpha}{dt} \quad (6)$$

As polymerization of ϵ -caprolactone by decamolybdate anion occurs by heterogeneous catalysis, it is anticipated that the use of a power-law function of $1 - \alpha$ [eq. (3)] can be the best choice, as this equation can be fitted to many different processes that involves chemical conversions with relative success.

EXPERIMENTAL AND METHODS

Materials

ϵ -CL (Aldrich Chemicals Co.) was dried over calcium hydride and distilled under reduced pressure before use. Methanol, Chloroform and Acetone

(Fermont) were distilled before use. Ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 0.4 \text{H}_2\text{O}$ (Fluka) was grounded in a mortar and passed through a 100 mesh sieve. The grounded catalyst was dried in an oven at 80°C overnight before use.

Measurements

Solution ^1H NMR spectra were recorded at room temperature on a Varian Gemini 200. Chloroform-*d* (CDCl_3) was used as solvent. Spectra were referenced to the residual solvent signals at δ 7.26 in the ^1H -NMR spectra.

Differential scanning calorimetry (DSC) was carried out using a Mettler Toledo DSC822e instrument. Temperature calibration was done with the melting transition of Indium (429.75°K). To obtain the thermograms for monomer and polymer, the methodology was the following: sample was heated from -100 to 100°C , at a speed of $10^\circ\text{C}/\text{min}$. Temperature was maintained at 100°C during two minutes, and then sample was cooled down up to -100°C at a speed of $10^\circ\text{C}/\text{min}$. For kinetic studies, 1 mg of initiator and 20 mg of monomer ($M/I = 25.22$) were mixed thoroughly and placed in 40 μL aluminum pans. A closed empty pan was used as reference. Samples were sealed before acquisition. A general method was created using the software of the equipment, and involves three regimes of analysis: an isothermal regime and two dynamic regimes, as shown in Scheme 1 and Table II. Two runs were made for each sample.

Crystallization and melting temperatures, kinetic values as well as enthalpies (including ΔH_{rxn}) were evaluated using the STAR^e software of the instrument. For kinetics analysis, the *Model Free Kinetics* software was used.

Bulk polymerization of ϵ -CL

Polymerizations were carried out in 10 mL vials previously dried and purged with dry nitrogen (Fig. 1). In a typical run, monomer (CL, 47.5 mmols) and ammonium heptamolybdate $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$ (Hep) (molar ratio CL/Hep = 1000) were added under

TABLE II
Methodology Used to Study the Polymerization of CL

Polymerization Run	Method					
	Isothermal		Dynamic I		Dynamic II	
	Temperature (°C)	Time (min)	Temperature range (°C)	Cooling rate (°C/min)	Temperature range (°C)	Heating rate (°C/min)
1	150	55	150 to -100	20	-100 a 100	20
2	152	55	152 to -100	20	-100 a 100	20
3	155	55	155 to -100	20	-100 a 100	20
4	157	55	157 to -100	20	-100 a 100	20
5	160	55	160 to -100	20	-100 a 100	20

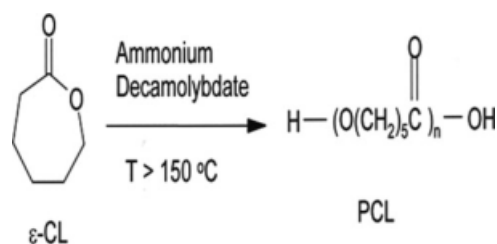


Figure 1 Polymerization reaction studied in this work.

nitrogen atmosphere. Vials were stoppered with a rubber septum and placed in a thermostated bath at constant temperature. Ammonium decamolybdate ($(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ (Dec) catalyst is formed *in situ* above 150°C by thermal decomposition of ammonium heptamolybdate ($(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$ (Hep).⁴ The reaction was stopped at different times, a sample was analyzed and the rest discarded. Reactions were quenched by cooling down in an aqueous bath down to 10°C . Samples were analyzed to determine the degree of conversion (α) at different reaction times by $^1\text{H-NMR}$, using the following equation

$$\alpha = 1 - \frac{I_{\text{mon}}}{I_{\text{mon}} + I_{\text{pol}}} \quad (7)$$

where I_{mon} is the area of the monomer signal at 4.05 ppm and I_{pol} is the area of the polymer signal at 4.25 ppm.

Final polymer was crystallized from chloroform/methanol and dried under vacuum.

RESULTS AND DISCUSSION

To identify phase transitions, DSC thermograms for the initiator, monomer, and polymer were separately obtained.

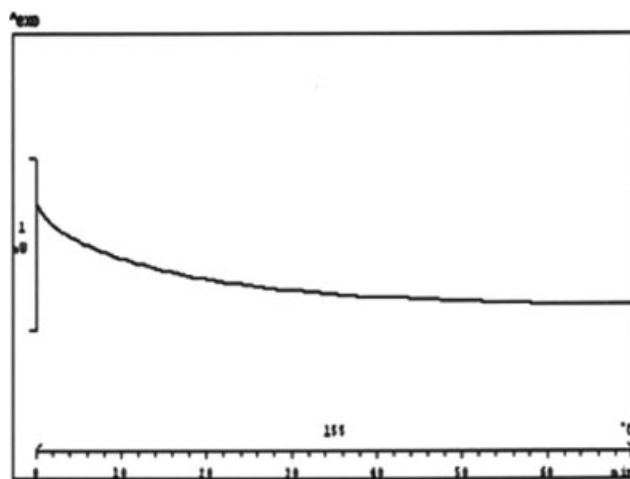


Figure 2 DSC thermogram for ammonium heptamolybdate tetrahydrate obtained at 155°C (isothermal) during 70 min.

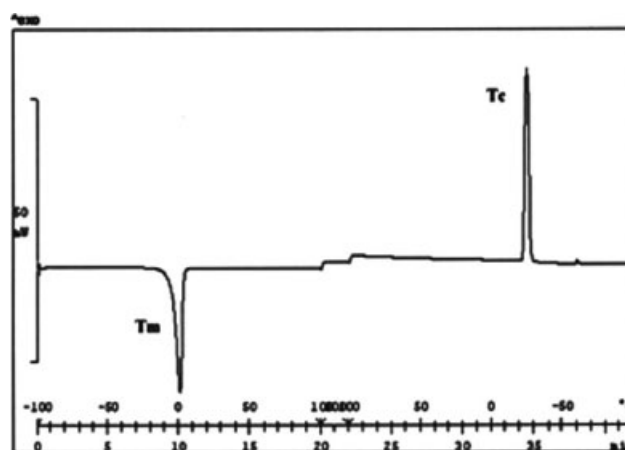


Figure 3 DSC thermogram for monomer ϵ -CL.

In DSC thermogram of ammonium heptamolybdate tetrahydrate (Fig. 2), no phase transition was observed in the range of temperature studied. Formation of decamolybdate anion is not observed in this period. For ϵ -caprolactone (monomer), two phase transitions are observed: one corresponding to the melting temperature (T_m) at -1.0°C and the other (upon cooling) to crystallization temperature (T_c) at -23°C (see Fig. 3). In the DSC thermogram for polymer (Fig. 4), phase transitions for T_m and T_c at 60.0 and 29.0°C respectively were observed.

DSC study of PCL polymerization

Using the isothermal method, it is observed that thermograms for reaction mixtures show different peaks, as a function of the initial temperature. In Figure 5, representative thermograms obtained for reaction mixtures treated at 150 , 155 , and 160°C are shown. A phase transition corresponding to the reaction

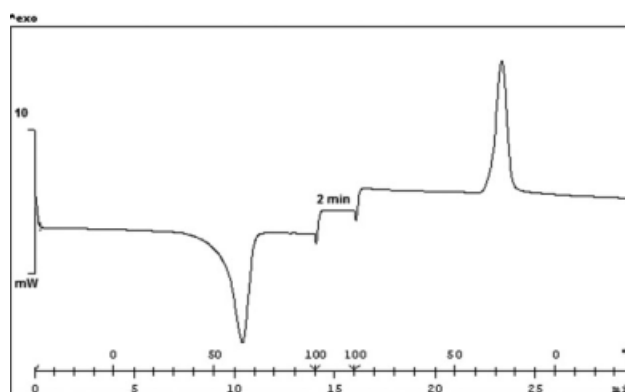


Figure 4 DSC thermogram for PCL.

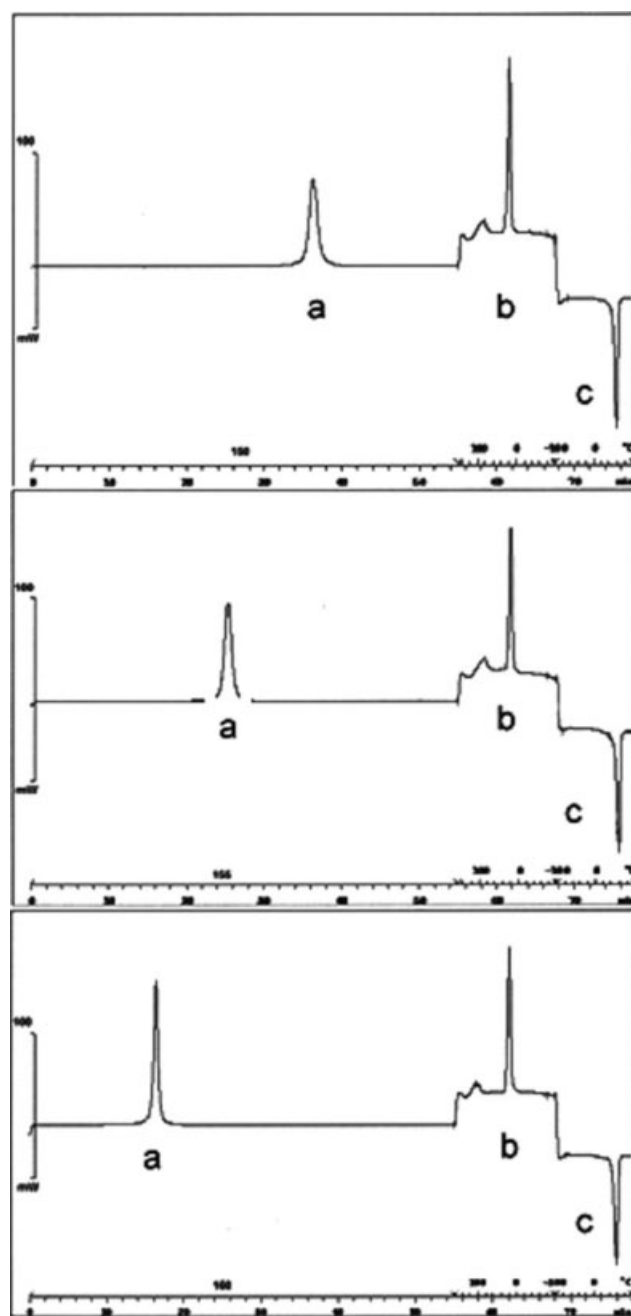


Figure 5 DSC thermograms of CL polymerization at different temperatures (isothermal method): (a) top 150°C, (b) middle 155°C, and (c) bottom 160°C.

enthalpy is observed. Transitions were observed between 20 and 30 min, and peak position and shape in the thermograms vary depending on the initial temperature used. This transition is not present in the decamolybdate and monomer thermograms.

In dynamic method I, only one phase transition is observed. This corresponds to PCL crystallization (-25.88°C). In dynamic method II, an endothermic signal at 51.5°C is observed. This phase transition is due to PCL melting point. From the $^1\text{H-NMR}$ spectrum, it is clear that no monomer is present in this sample. The evaluated data of these thermograms are reported in Table III.

As formation of decamolybdate anion is not observed at 155°C after 70 min in the thermogram shown in Figure 2, it is concluded that catalyst is only formed *in situ* in the presence of CL.

Crystallization and melting temperatures reported in Table IV are in agreement with data found in the literature.^{18,19} Crystallization temperatures for PCL oscillate between 25 and 30°C , and the melting temperatures between 50 and 55°C . T_m and T_c values are directly related with the polymer molecular weight. Enthalpy of polymerization (ΔH_{rxn}) is around -180 J/g (which corresponds to -20.9 kJ/mol of CL, see Table III), and do not depend on temperature in the range studied ($150\text{--}160^{\circ}\text{C}$). A value of -28.8 kJ/mol at 298°K has been reported for polymerization of CL using an equilibrium monomer concentration approach.^{20,21} ROP of CL involves an entropy decrease, due mostly to the loss of translational degree of freedom. For polymerization of CL, a value of $-53.9\text{ J}/(\text{mol}^{\circ}\text{K})$ is reported at 298°K .²⁰ As $\Delta G_p = \Delta H_p - T\Delta S_p$, this means that the driving force for polymerization is the enthalpy term.

Values of $\ln k_T$ (logarithm of rate constant) were derived using the *Model Free Kinetics* software. From the plot of $\ln k_T$ against $1/T$ (see Fig. 6), the activation energy and the pre-exponential factor can be derived. Values of the activation energy and the pre-exponential factor for PCL are 85.3 kJ/mol and $\ln A = 19\text{ min}^{-1}$ (being $A = 1.78 \times 10^8\text{ min}^{-1}$), respectively.

TABLE III
Evaluated Data from DSC Thermograms

Polymer ($^{\circ}\text{C}$)	Isothermal method		Dynamic I method		Dynamic II method	
	ΔH_{rxn} (J/g)	$-\ln k_T$	Temperature of crystallization ($^{\circ}\text{C}$)	ΔH_{T_c} (J/g)	Melting temperature ($^{\circ}\text{C}$)	ΔH_{T_m} (J/g)
150	-180.1	5.2	26,9	44,7	54,7	43,7
152	-174.9	5.0	27,8	70,3	54,8	75,3
155	-180.1	4.9	25,9	71,6	51,9	76,2
157	-180.3	4.7	25,4	42,6	54,8	51,5
160	-180.1	4.6	27,0	79,0	51,4	85,5

TABLE IV
Melting Temperatures and their Corresponding Enthalpies

Polymerization time (min)	Monomer		Polymer	
	T_m ($^{\circ}\text{C}$)	ΔH_f (Jg^{-1})	T_m ($^{\circ}\text{C}$)	ΔH_f (Jg^{-1})
30	-1,2	102,0	-	-
50	-1,1	101,1	-	-
60	-1	24,2	41,6	60,3
70	-	-	54,6	75,5
80	-	-	55,0	79,5
90	-	-	50,8	-75,9
120	-	-	50,2	-69,7

DSC thermograms at different stages of polymerization

Thermograms for samples at different reaction times of polymerization are shown in Figure 7. Calculated data are shown in Table IV. A signal at -1.2°C due to the monomer is the only peak detected during the first hour. At 60 min, a peak due to PCL appears. At 70 min, only the peak due to the polyester is observed. Analysis by $^1\text{H-NMR}$ indicates that at 70 min some monomer is still present (around 10%). This result indicates that a direct measure of the degree of conversion α using DSC is not possible, as this technique is not sensitive enough to detect low amounts of some species.

As $^1\text{H-NMR}$ is more sensitive to monomer concentration, conversion curves for this polymerization was obtained using this technique.

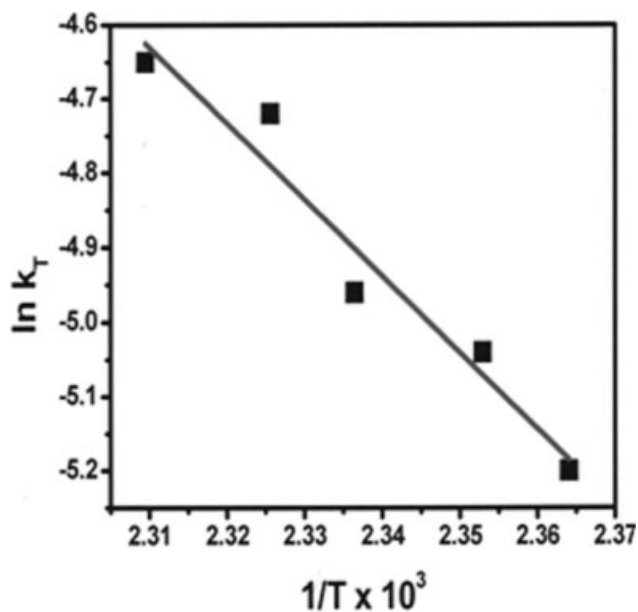


Figure 6 Plot of $\ln k_T$ versus the inverse of the temperature.

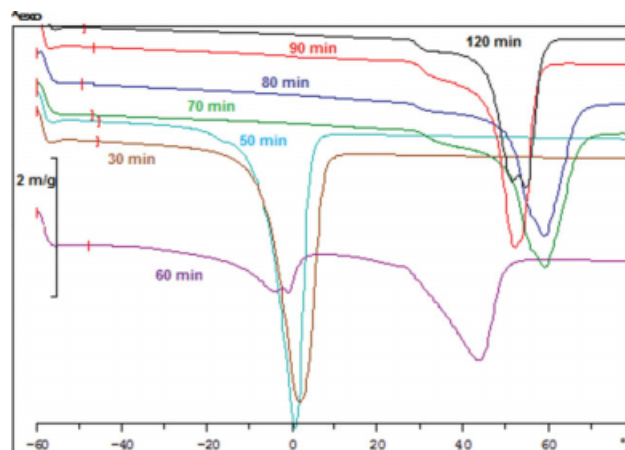


Figure 7 DSC thermograms of the polymerization of CL at different reaction times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Conversion curves

Plots of degree of conversion (α , obtained by $^1\text{H-NMR}$) against reduced time are shown in Figure 7. Reduced time is represented here as the ratio $t/t_{\alpha=0.9}$, where $t_{\alpha=0.9}$ represent the time necessary to obtain 90% of conversion. From these plots, we can verify graphically how the different models shown in Table I fit to the experimental data (see Fig. 8). The reaction model number 11 is the one that better fits to the experimental data curves obtained at 155 and 160°C (Fig. 8). This result is in agreement with eq. (3), with $n = 2/3$.

Mechanistic aspects

In the ring opening polymerization of lactones by decamolybdate anion, a blue color is observed just before a rise in the viscosity of the reaction media occurs. This color change is associated with (a) a redox reaction of decamolybdate anion, that produces Mo(V) from Mo(VI) and (b) chain propagation and growing of polymer chains.²² In the UV-visible spectrum, a wide band centered at 750 cm^{-1} is detected, which is characteristic of what is called *molybdenum blue*.²³ When polymerization is carried out in the presence of hydroxyl compounds (ROH), insertion of RO- as end-group is observed.

Figure 9 show the relationship between conversion and the molecular weight of the polymer produced during the ring opening polymerization of CL in bulk, initiated by decamolybdate anion at 155°C . A similar behavior is observed in the $150\text{--}160^{\circ}\text{C}$ temperature range. A little increase in molecular weight in the initial stages of polymerization is observed. At a percent conversion of 66%, dimeric species are mainly formed (M_n value of around 246 Da is

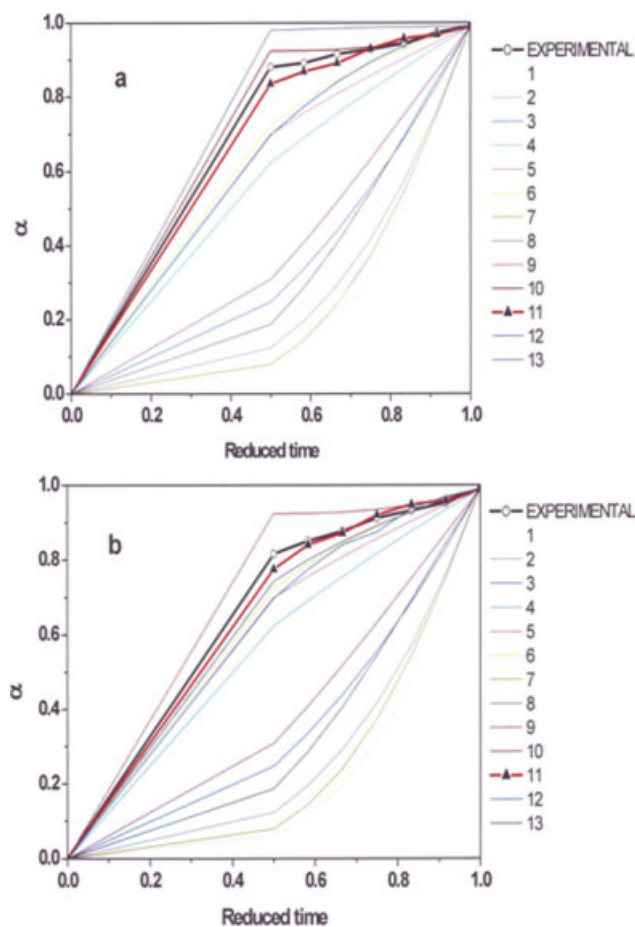


Figure 8 Reduced time plots for the polymerization of ϵ -caprolactone catalyzed by decamolibdate anion. The curves in black (circles) represent the experimental curves obtained at 155°C (a) and 160°C (b). The curves in red (triangles) are the reaction model that fits better to the experimental curve. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

recorded by $^1\text{H-NMR}$). M_n remains almost constant up to at least 90% of conversion. PCL molecular weight increases with conversion only at the final stages of polymerization.

On the basis of these facts, a coordination-insertion mechanism can be proposed, which involves acyl-oxygen bond cleavage of the monomer and insertion into the molybdenum (V)-oxygen bond of the initiator (Scheme 2).²²

In this mechanism, the first step involves coordination between the hydroxyl group of the co-initiator (alcohol or water) and oxygen linked to a molybdenum (V) species. Through coordination, the formation of a more active hydroxyl species, capable of adding new monomer molecules, is achieved; also, it is expected that lactone exocyclic oxygen coordinates to the metal, making the carbonyl carbon of CL more susceptible to nucleophilic attack. Once these coordinated species are formed, nucleophilic

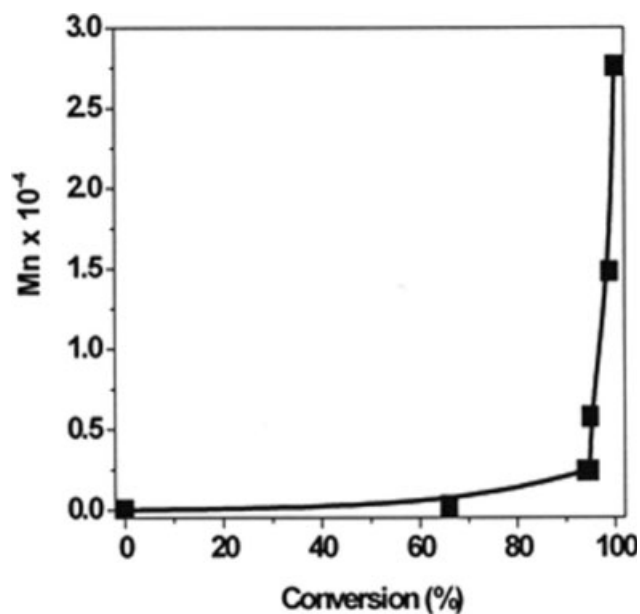
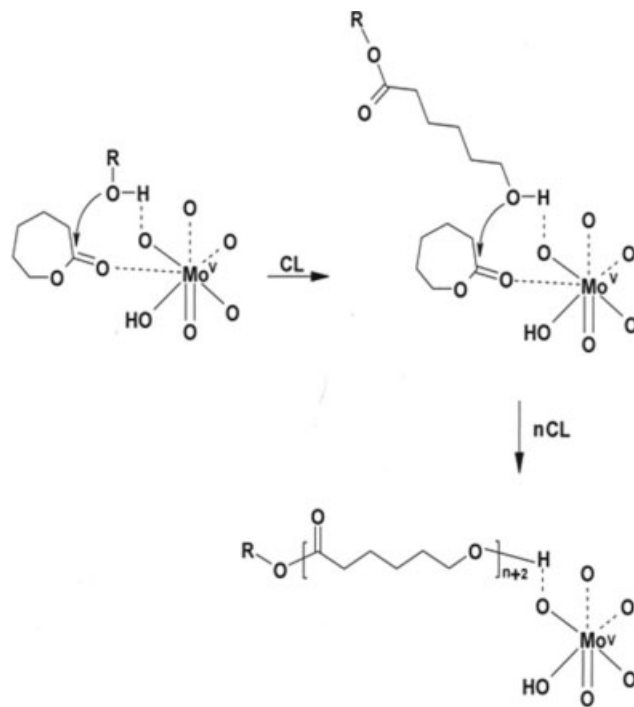


Figure 9 Dependence of polymer molecular weight on conversion for the bulk polymerization of CL by decamolibdate anion. Reaction conditions: 47.5 mmols of CL, molar ratio CL/Hep = 1000, temperature = 155°C.

philic addition of hydroxyl group to the CL carbonyl carbon occurs. Coordination with other CL molecule leads to the formation of an intermediate species I, which in turn produce dimers, trimers, tetramers,



Scheme 2 Proposed coordination-insertion mechanism for the polymerization of ϵ -caprolactone by decamolibdate anion (Dec). Active species is a Mo(V) derivative. A coordination number of 6 is considered for molybdenum.

and so on. Results indicate that a dimeric species (such as *I*) are accumulated until almost all the CL molecules have been ring-opened. Propagation step involves successive ring-opening of CL in a concerted mechanism. Final polymer contains COOR and CH₂—OH end-groups.

CONCLUSIONS

Enthalpies of reaction (ΔH_{rxn}) for the polymerization of ϵ -CL by decamolybdate anion were derived at different temperatures using an isothermal method. Recorded values are around -180 J/g (-20.9 kJ/mol of CL). The kinetic parameters (activation energy and the pre-exponential constant) were derived fitting the calorimetric data to an Arrhenius equation function. Values of the activation energy and the pre-exponential factor are 85.3 kJ/mol and $\ln A = 19$ min⁻¹. On the basis of experimental evidence, a coordination-insertion mechanism—which involves the formation of an active intermediate with two CL molecules—is operating in this polymerization.

Authors are indebted to Karla A. Barrera-Rivera for her help in the preparation of the figures.

References

1. Okada, M. *Prog Polym Sci* 2002, 27, 87.
2. Coulebiera, O.; Degeé, P.; Hedrickb, J. L.; Dubois, P. *Prog Polym Sci* 2006, 31, 723.
3. Tadeusz, B.; Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromol Symp* 2006, 240, 47.
4. Báez, J. E.; Martínez-Rosales, J. M.; Martínez-Richa, A. *Polymer* 2003, 44, 6767.
5. Báez, J. E.; Marcos-Fernández, A.; Martínez-Richa, A. *Macromolecules* 2005, 38, 1599.
6. Báez, J. E.; Martínez-Richa, A. *Polymer* 2005, 46, 12118.
7. Báez, J. E.; Marcos-Fernández, A.; Lebrón-Aguilar, R.; Martínez-Richa, A. *Polymer* 2006, 47, 8420.
8. Atkinson, A. C.; Bogacka, B. *Chemom Intell Lab Syst* 2002, 61, 17.
9. Opfermann, P. *J Therm Anal* 2000, 60, 641.
10. Vyazovkin, S.; White, C. A. *Annu Rev Phys Chem* 1997, 48, 125.
11. Vyazovkin, S. *J Therm Anal Calorimetry* 2001, 64, 829.
12. Vyazovkin, S. *Int Rev Phys Chem* 2000, 19, 45.
13. Vyazovkin, S. *Anal Chem* 2002, 74, 2749.
14. Brown, M. E.; Dolimore, D.; Galwey, A. K. *Reactions in Solid State, Comprehensive Chemical Kinetics*; Elsevier: Amsterdam, 1980; Vol. 22, p 340.
15. Sestak, J. *Thermophysical Properties of Solids, Comprehensive Analytical Chemistry*; Elsevier: Amsterdam, 1984; Vol. 12, p 440.
16. Vyazovkin, S.; Sbirrazzuoli, N. *J Phys Chem B* 2003, 107, 882.
17. Vyazovkin, S.; Sbirrazzuoli, N. *Int Rev Phys Chem* 2000, 19, 60.
18. Goulet, L.; Prud'homme, R. E. *J Polym Sci, Part B: Polym Phys* 1990, 28, 2329.
19. Deniz, A. K.; Chang, L. *J Micromech Microeng* 2000, 10, 80.
20. Lebedev, B. V.; Evstropov, A. A.; Lebedev, B. V.; Karpova, E. A.; Lyudvig, E. A.; Belenkaya, B. G. *Vysokomolekulyarnye Soedin Ser A* 1978, 20, 1974.
21. Duda, A.; Kowalski, A. In *Handbook of Ring-Opening Polymerization*, Dubois, P., Coulebier, O., Raquez, J.-M., Eds.; Wiley-VCH: Germany, 2009; pp 1–52.
22. Baez, J. E. PhD Tesis, Universidad de Guanajuato, México, 2006.
23. Müller, A.; Serain, C. *Acc Chem Res* 2000, 33, 2.