Kinetics of Microwave-Assisted Polymerization of ϵ-Caprolactone

G. Sivalingam, Nitin Agarwal, Giridhar Madras

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560 012, India

Received 2 December 2002; accepted 27 June 2003

ABSTRACT: The kinetics of polymerization of ϵ-caprolactone (CL) in bulk was studied by irradiating with microwave of 350 W and frequency of 2.45 GHz with different cycle-heating periods (30–50 s). The molecular weight distributions were determined as a function of reaction time by gel permeation chromatography. Because the temperature of the system continuously varied with reaction time, a model based on continuous distribution kinetics with time/temperature-dependent rate coefficients was proposed. To quantify the effect of microwave on polymerization, experiments were conducted under thermal heating. The polymerization was also investigated with thermal and microwave heating in the presence of zinc catalyst. The activation energies determined from temperature-dependent rate coefficients for pure thermal heating, thermally aided catalytic polymerization, and microwave-aided catalytic polymerization were 24.3, 13.4, and 5.7 kcal/mol, respectively. This indicates that microwaves increase the polymerization rate by lowering the activation energy. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1450–1456, 2004

Key words: catalysis; kinetics (polym.); biodegradable; gel permeation chromatography (GPC); ϵ-caprolactone

INTRODUCTION

Microwave radiation may be used as an alternative to thermal polymerization processes.[1] The advantages of microwaves are increased rate of production, improved product characteristics, uniform processing, less floor area, and convenience and controllability of the processes.[2] There are reports[3–6] that show similar kinetics under both microwave and thermal methods, indicating that microwave does not alter the reaction products observed in conventional heating but up to threefold increase in magnitude.

However, some controversy surrounding the mechanism of microwave-aided processes still exists. There are reports that show no enhancement in reaction rate under both microwave and thermal methods at comparable temperatures,[7–9] suggesting simple dielectric heating of materials. Other investigations, however, show enhancement in reaction rates using microwave radiation over thermal method,[10–13] indicating a specific microwave effect rather than dielectric heating. Microwaves are also found to increase the overall diffusion rate of mass transfer limited process and decrease the activation energy for diffusion.[14] The increased reaction rates are attributed to improved transport properties.[14,15] Superior morphological behaviors have been reported for microwave-cured epoxy resins.[16,17] In addition, microwave was also found to increase the selectivity of the product in some Diels–Alder reactions,[18] cracking of solvents,[19] and dry organic dry reactions.[20] Microwave heating has been proven to enhance the rate of polymerization, especially in the case of polar materials.[21] Whitaker and Mingos[22] reported a review on the influence of microwave energy on organic reactions.

Poly(ϵ-caprolactone) (PCL) continues to be the focus of increasing attention for applications in the biomedical field such as biodegradable sutures, artificial skins, and implantable carriers for drug delivery systems.[23] It also serves as an alternative for packing materials because of its interesting properties such as nontoxicity, biodegradability, biocompatibility, and miscibility with other polymers.[24,25]

PCL can be synthesized by various methods such as enzymatic synthesis,[26] step condensation polymerization,[27] monomer insertion mechanisms,[28] activated monomer mechanism,[29] and by use of alkoxides.[30–32] The various catalysts used for catalytic polymerization of ϵ-caprolactone are zinc,[23] tin,[33] aluminum,[34] alkali metals,[35] early transition metals and rare earth halides,[34,36] and organo-lanthanide series.[37] However, high molecular weights are obtained by using coordinate catalysts.[34,36]

From the biomedical viewpoint, extremely high purity of PCL is required especially without any toxic compounds. Ring-opening polymerization (ROP) of ϵ-caprolactone in supercritical CO_2 is reported to be pollution-free mode of PCL preparation.[38] Recently, microwave-assisted ROP of ϵ-caprolactone has been

Correspondence to: G. Madras (giridhar@chemeng.iisc.ernet.in).

Journal of Applied Polymer Science, Vol. 91, 1450–1456 (2004)

reported.[39] Zinc is an oligoelement, which can be present in the human body at a level of 1.36–2.32 g.[40] In this aspect, even if zinc residue is left in the polymeric material, it can be conveniently applied for biomedical applications.[23]

The zinc-aided polymerization is purely catalytic and heterogeneous and thus the downstream processing for the separation of zinc from polymer is relatively easy. This also does not impose any limitation on the upper limit on the usage of the catalyst loading because it can be separated. However, the method of synthesizing PCL by ROP using zinc is fairly new (apart from a recent study demonstrating the use of zinc as a catalyst for PCL synthesis[39]) and results of kinetic investigations with continuous distribution kinetics are presented here.

In the present investigation, the kinetics of zinc-catalyzed polymerization of ϵ-caprolactone under microwave heating was studied. To quantify the effect of microwave on polymerization, catalytic experiments were conducted under thermal heating. Pure condensation polymerizations under both thermal and microwave heating were carried out to quantify the catalytic effect. The activation energies were determined from temperature-dependent rate coefficients for pure thermal heating, thermally aided catalytic polymerization, and microwave-aided catalytic polymerization.

EXPERIMENTAL

Catalyst characterization

Analytical-grade zinc (S. D. Fine Chemicals, Mumbai, India) was used for the present investigation. Before use, zinc was heated at 250°C for 3–4 h in air for activation. X-ray diffraction (XRD) pattern of Zn was recorded using a Seimens (D-5005, Bruker-AXS, Madison, WI) diffractometer using Cu–K_α radiation with a scan rate of 2°/min and is given in Figure 1. There was no change in the zinc structure during reaction and thus the XRD pattern was unaltered because of the reaction.

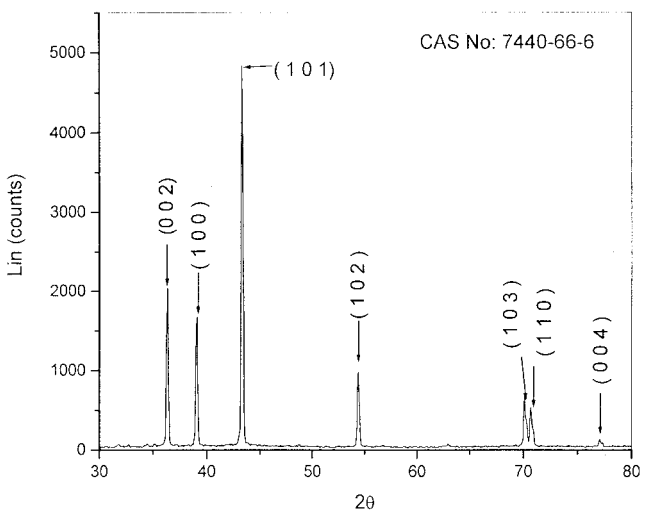

Figure 1 XRD pattern of the catalyst zinc used for the polymerization reaction.

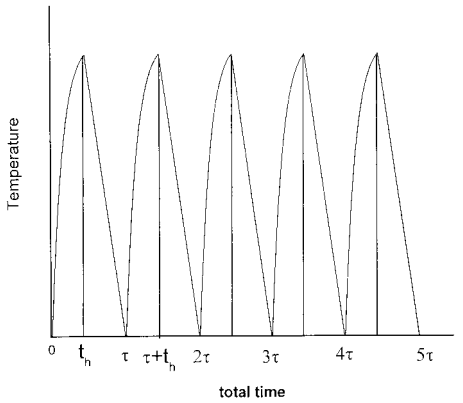

Figure 2 Temperature variation during the heating and falling periods of the microwave cycle.

Polymerization experiments

CL (Aldrich Chemical, Milwaukee, WI) was dried over calcium hydride (CaH_2) for 2 days at room temperature and vacuum distilled just before use. A monomer of 50 mL volume was placed exactly below the magnetron in a top-heated microwave oven (350 W, 2.45 GHz; Essentia, India). The heating cycle times (t_h) were varied from 30 to 50 s. The cyclic operation with period of τ s consisted of heating the reactants for a set cycle time of t_h and cooling in an ice-cooled water bath maintained at 20°C for 60 s (t_c). Each sample was irradiated for 50 cycles ($\tau = t_h + t_c$). For example, the total reaction time for 40-s heating cycle is 5000 s with 2000 s of microwave heating time. The temperature gradient in the solution is negligibly small at low heating cycle times (~ 100 s) because of natural convection of fluid in top-heated microwave ovens.[41] During heating, viscosity of the polymer increases because of polymerization. Thus the exponential rising and linear falling ramps constitute the temperature profile as shown in Figure 2. The time evolution of molecular weight distribution was obtained by gel permeation chromatography (GPC) with THF as eluent at the rate of 1 mL/min. The details of the GPC are presented elsewhere.[42] All experiments were conducted in triplicate sets and the rate coefficients determined had less than 2% SD. Thermal experiments were carried out in a two-neck 100-mL flask by a heating mantle controlled with a PID controller (±2°C) with constant stirring to the required temperature; the calculated amount of zinc was then added to the reaction mixture. The range of temperatures inves-

tigated was 150 to 230°C. Samples of 0.5 mL were collected at regular intervals for GPC analysis.

THEORETICAL MODELS

Model for thermal heating

Continuous distribution kinetics provides a straightforward technique to determine the molecular weight dynamics (MWD). The polymer $P(x)$ of molecular weight x has the distribution $p(x, t)$ by assuming that x is a continuous variable. The MWD is defined in such a way that $p(x, t)\,dx$ is the amount of polymer present at any time between the size interval of $(x, x + dx)$. Because the range of polymerization was limited below a ceiling temperature of above 250°C, the degradation rates were not significant. The general polymerization reaction to form a polymer of molecular weight x is given as follows:

$$P(x') + P(x - x') \xrightarrow{k_a'(x', x-x')} P(x) \qquad \text{(A)}$$

The polymer of molecular weight x can disappear by the reaction with any species such as monomer or any polymeric species. The generalized reaction can be written for the disappearance step of the polymer as follows:

$$P(x') + P(x) \xrightarrow{k_a'(x, x')} P(x + x') \qquad \text{(B)}$$

the population balance for $P(x)$ based on reactions (A) and (B) is

$$\frac{\partial p(x, t)}{\partial t} = -2p(x, t)\int_0^\infty k_a'(x, x')p(x', t)\,dx' + \int_0^x k_a'(x', x - x')p(x', t)p(x - x', t)\,dx' \qquad (1)$$

The factor 2 in the disappearance term of eq. (1) is to satisfy the conservation of mass during the reaction. The polymerization rate coefficients are shown to be dependent on the molecular weight of the reaction constituent.

In practice, however, all the active species are equally active by the equal reactivity condition

$$k_a'(x, x') = k_a'(x', x - x') = k_a \qquad (2)$$

Applying the moment operation $p^{(j)}(t) = \int_0^\infty x^j p(x, t)\,dx$ to eq. (1) results in

$$\frac{dp^{(j)}}{dt} = -2k_a p^{(j)}p^{(0)} + k_a \sum_{i=0}^{j} j_C p^{(j-i)}p^{(i)} \qquad (3)$$

The molar ($p^{(0)}$)and mass ($p^{(1)}$) concentrations are represented by zeroth and first moment and are obtained by setting $j = 0$ and 1, respectively, in eq. (3).

$$\frac{dp^{(0)}}{dt} = -k_a[p^{(0)}]^2 \qquad (4)$$

$$\frac{dp^{(1)}}{dt} = 0 \qquad (5)$$

Using the invariant mass concentration as implied from eq. (5), eq. (4) can be integrated using the initial condition of $p^{(0)}\ (t = 0) = p_0^{(0)}$ to

$$\frac{1}{p_0^{(0)}} - \frac{1}{p^{(0)}} = -k_a t \qquad (6)$$

Rearranging the above equation in terms of molecular weight results in

$$\frac{M_n}{M_{n0}} - 1 = \frac{k_a p_0^{(1)}}{M_{n0}}\,t = kt \qquad (7)$$

Equation (7) suggests that the plot of M_n/M_{n0} against t will result in a straight line with slope being the overall rate coefficient.

Model for microwave heating

The temperature during the reaction continuously varies with time; thus the direct moment solution cannot be used as can be done for thermal heating. The rising temperature profile measured experimentally showed an exponential increase and the falling period was assumed to be linear. The temperature profile used was

$$T = \begin{cases} T_w + T_{\text{peak}}[1 - \exp(-k_h t)] & \forall t \in (0, t_h) \\ T_{\text{peak}} - \dfrac{T_{\text{peak}} - T_w}{\tau - t_h}(t - t_h) & \forall t \in (t_h, \tau) \end{cases} \qquad (8)$$

where T_{peak} is the maximum temperature reached during the heating cycle, T_w is the ice-cooled water bath temperature, t_h is time of microwave heating, τ is the total cycle time, and k_h is the growth coefficient (=0.06213 s^{-1}). The MWD was obtained by simultaneously solving eqs. (1) and (8) numerically. The maximum temperatures obtained were measured experimentally and are depicted in Figure 3. The actual temperature dynamics during the microwave heating and cooling for 40- and 50-s cycles are represented in

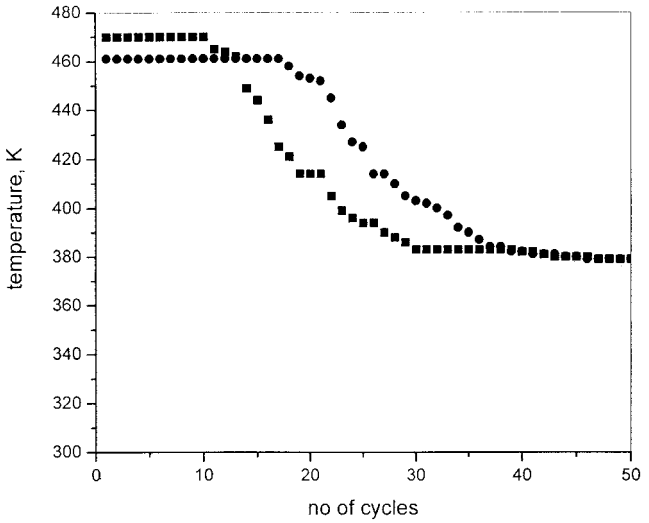

Figure 3 Maximum temperature profile for microwave heating along the number of cycles for ■ 40-s cycle, ● 50-s cycle.

Figure 4(a) and (b), respectively. The kinetic parameters for polymerization can be found by the nonlinear regression of the experimental data.

RESULTS AND DISCUSSION

Proton NMR analysis of the PCL obtained by the zinc-aided polymerization of ϵ-CL was recorded on a Bruker AC-F 200 MHz spectrometer (Bruker Instruments, Billerica, MA) in $CDCl_3$ and chemical shifts were measured in ppm with reference to tetramethyl silane. The proton NMR spectrum of PCL showed resonance signals at 1.4, 1.7, 2.3, and 4.1 ppm, which were assigned to different methylene groups in the PCL chain. This can also be exactly indexed to the PCL synthesized by pure thermal route and standard polymer (80,000 g/mol; Sigma Aldrich, St. Louis, MO) and is consistent with the NMR analysis reported elsewhere.[39]

The microwave-assisted catalytic polymerization of ϵ-caprolactone was investigated at different microwave heating times ranging from 30 to 50 s. The experiments were conducted with zinc concentrations ranging from 0.5 to 5 kg/m^3 by irradiating the reactants for prescribed heating cycle time t_h, and then cooling the reaction mixture in the ice-cooled water bath for 60 s for 50 cycles. Figure 5 shows the effect of amount of catalyst loading on the molecular weight of the polymer formed when exposed to microwave for 20 cycles of the 50-s heating cycle. It can be seen from the figure that the increase in the molecular weight beyond 5 kg/m^3 is small and thus in the present study the zinc concentration of 5 kg/m^3 was used as the optimal concentration. The maximum conversion achieved in the present study was 42% and the polydispersity increased from a monodisperse distribution of monomers (with polydispersity of 1.0) to the polydisperse polymer with saturation polydispersity ranging from 1.5 to 1.9 depending on the heating cycles.

To study the self-polymerization behavior of ϵ-caprolactone, only monomer was heated in the microwave for different heating cycles of 30 to 50 s with 20 cycles each (Fig. 6). It further implies that the rate of polymerization in the absence of initiator or catalyst is considerably less. The molecular weight dynamics during the microwave heating of zinc-catalyzed polymerization for 40- and 50-s cycles for the nonlinearly regressed experimental parameters is shown in Figure 7(a) and (b), respectively. The curves were obtained as theoretical values obtained from the parameters deter-

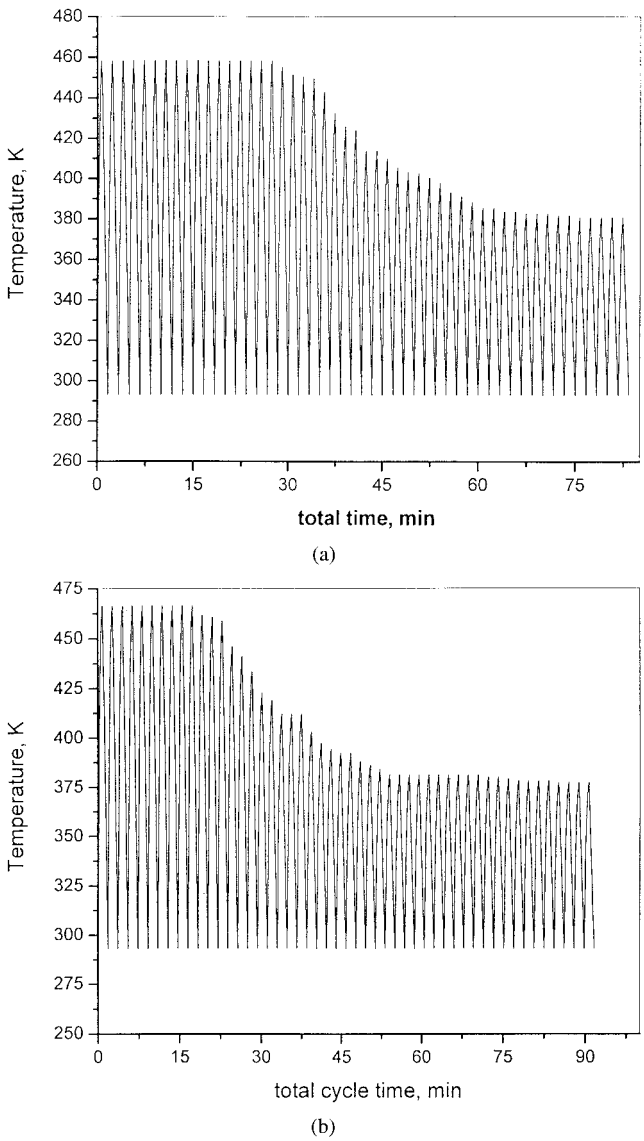

Figure 4 (a) Temperature variation during the microwave heating along the number of cycles for 40-s heating cycle. (b) Temperature variation during the microwave heating along the number of cycles for 50-s heating cycle.

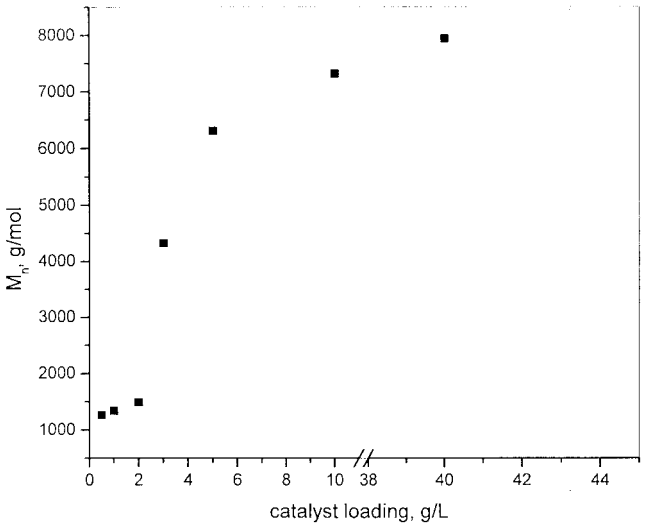

Figure 5 Effect of different catalytic loading on the polymerization for caprolactone for 50-s cycle with 20 cycles each.

mined from the experimental data by nonlinear regression. This curve essentially represents the solution of eq. (1) with a temperature constraint imposed by eq. (8). It can be seen from the figure that molecular weight increases in steps. The steep rise in the molecular weight corresponds to the heating period where the rates are higher as the temperature increases. The saturating or horizontal portion is attributed to the cooling period where the rates descend as the temperature is decreasing. These two steps constitute a complete heating and cooling cycle.

Figure 8 shows the experimental molecular weight variation for the microwave-catalyzed reaction. The solid lines are the model prediction obtained by using

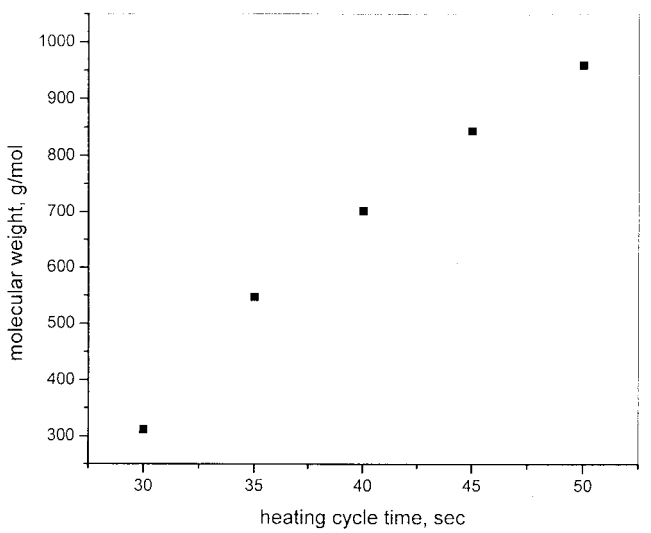

Figure 6 Effect of cycle times for uncatalyzed microwave-aided polymerization of 20 cycles each.

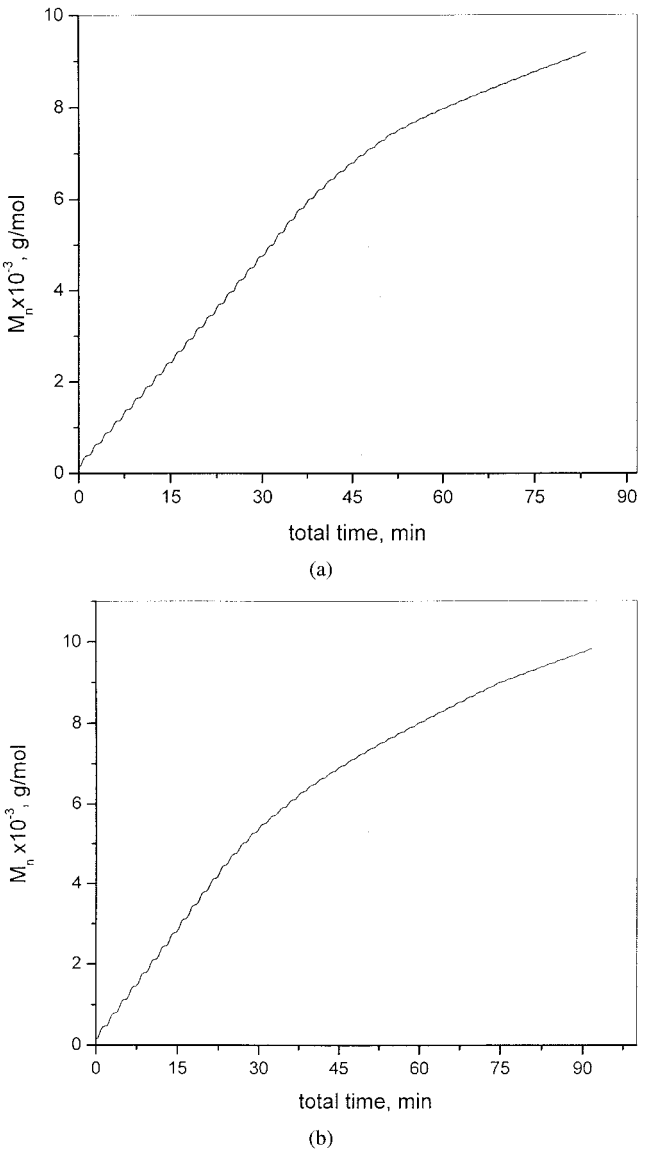

Figure 7 (a) Molecular weight dynamics during the microwave heating for 40-s heating cycle. (b) Molecular weight dynamics during the microwave heating for 50-s heating cycle.

the kinetic parameters obtained by using the nonlinear regression as explained earlier. The agreement between the experimental and model predictions is satisfactory. The activation energy obtained from the experimental data is 5.7 kcal/mol.

Thermally aided polymerizations were conducted under both catalytic and noncatalytic conditions. These reactions were carried out at constant temperatures using heating mantles under constant stirring controlled by the PID controllers with temperature variation of ± 1°C. The molecular weight variation was determined by analyzing the samples at different reaction times. Figure 9 shows the variation of molecular weight distribution with time of heating for the catalyzed reactions at various temperatures (150–230°C). The rate coefficients were

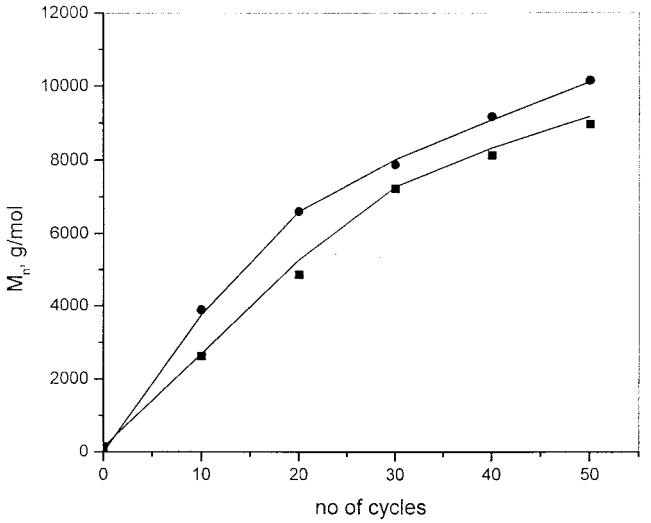

Figure 8 Molecular weight variation of microwave-aided catalyzed polymerization of caprolactone: ■, 40-s heating; ●, 50-s heating.

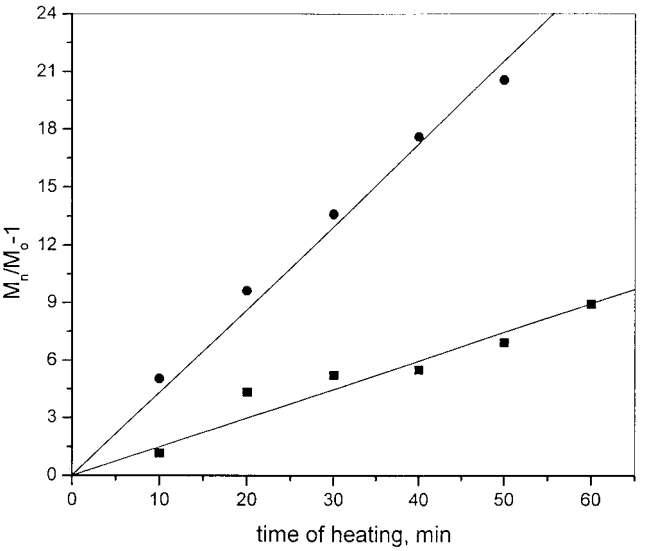

Figure 10 Variation of number-average molecular weight for pure condensation reaction with thermal aid: ■, 210°C; ●, 230°C.

determined from the slope of the plots. This plot shows the validity of eq. (7) derived for isothermal reaction cases. Figure 10 shows the variation of number-average molecular weight with time for noncatalyzed reaction at 210 and 230°C. The rate coefficients were determined from the slopes of lines. The monomer conversions were determined at various times and followed a first-order kinetics. This is also true in accordance with our assumption made in eq. (1). The activation energies were determined from the Arrhenius plot of rate coefficients, as shown in Figure 11. The activation energies for the catalyzed and noncatalyzed reactions are 13.4 and 24.3 kcal/mol, respectively, which suggests that microwave-assisted catalytic polymerization followed a low activation energy path compared to thermally aided processes.

CONCLUSIONS

The kinetics of polymerization of CL catalyzed by zinc in bulk was studied under microwave irradiation. To quantify the effect of microwave on polymerization, catalytic experiments were conducted under thermal heating. The effect of catalyst loading on polymerization was also studied. Pure condensation polymerizations under both thermal and microwave heating were

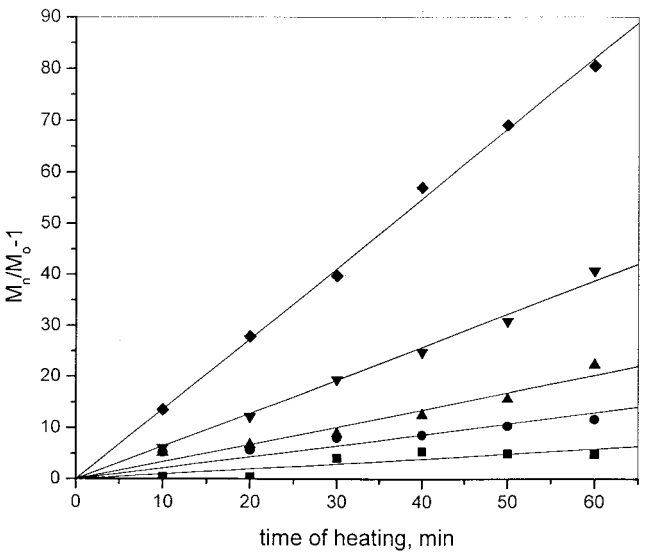

Figure 9 Variation of number-average molecular weight for catalyzed reaction with thermal aid: ■, 150°C; ● 170°C; ▲ 190°C; ▼, 210°C; ◆, 230°C.

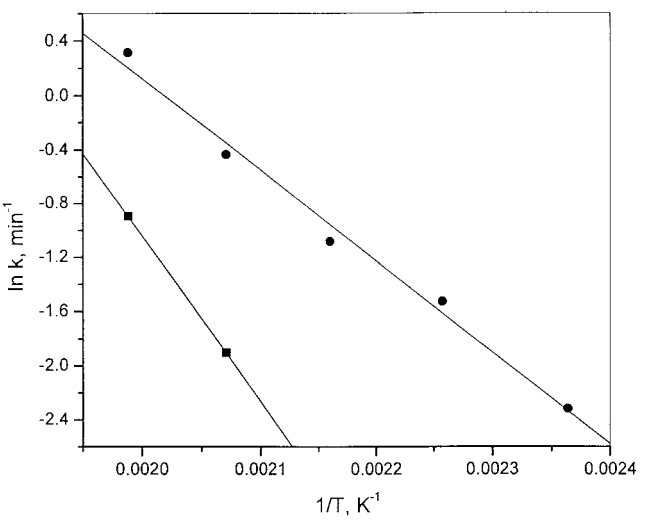

Figure 11 Arrhenius plot of thermally aided polymerization for catalyzed and uncatalyzed reactions: ■, uncatalyzed; ●, catalyzed.

done to quantify the catalytic effect. A model based on continuous distribution kinetics with time/temperature-dependent and -independent rate coefficients were proposed for microwave-aided and thermally aided processes, respectively. The agreement between experimental and model predictions was satisfactory. The activation energies for pure thermal heating, thermally aided catalytic polymerization, and microwave-aided catalytic polymerization were 24.3, 13.4, and 5.7 kcal/mol, respectively.

The authors gratefully acknowledge financial support provided by the Department of Science and Technology.

References

1. Jacob, J.; Chia, L. H. L.; Boey, F. Y. C. J Appl Polym Sci 1997, 63, 787.
2. Stuchly, M. A.; Stuchly S. S. IEEE Proc 1983, 130, 467.
3. Correa, R.; Gonzalez, G.; Dougar, V. Polymer 1998, 39, 1471.
4. Chia, L. H. L.; Jacob, J.; Boey, F. Y. C. J Mater Proc Technol 1995, 48, 445.
5. Jacob, J.; Chia, L. H. L.; Boey, F. Y. C. Polym Test 1995, 14, 343.
6. Mallon, F. K.; Ray, W. H. J Appl Polym Sci 1998, 69, 1203.
7. Mijovic, J.; Wijaya, J. Macromolecules 1990, 23, 3671.
8. Mijovic, J.; Fishbain, A.; Wijaya, J. Macromolecules 1992, 25, 986.
9. Raner, K. D.; Stranus, C. R. J Org Chem 1992, 57, 6231.
10. Marand, E.; Baker, K. R.; Graykeal, J. D. Macromolecules 1992, 25, 2243.
11. Berlan, J. S.; Aiboreau, S.; Lefeuvre, S.; Marchand, C. Tetrahedron Lett 1991, 32, 2363.
12. Bram, G.; Loupy, M.; Majdoub, M.; Autierez, E.; Hitzkey, E. R. Tetrahedron 1990, 46, 5167.
13. Baghurst, D. R.; Mingos, D. M. P. J Chem Soc Chem Commun 1992, 674.
14. Gibson, C.; Matthews, I.; Samuel, A. J Microwave Power Electromagn Energy 1988, 23, 17.
15. Meek, T. T.; Blake, R. D.; Katz, J. D.; Bradbury, J. R.; Brooks, M. H. J Mater Sci Lett 1998, 7, 928.
16. Karmazsin, E.; Satra, P.; Rochas, J. F. Thermochim Acta 1985, 93, 305.
17. Singer, S. M.; Jow, J.; Delong, J. D.; Hawley, M. C. SAMPE Q 1989, 20, 4.
18. Linders, T. M.; Kokje, J. P.; Overhand, M.; Lie, T. S.; Maat, L. Recl Trav Chim Pays-Bas 1988, 107, 449.
19. Roussy, G.; Thiebaut, J. M.; Anzarmou, M.; Richard, C.; Martin, R. J Microwave Power Electromagn Energy Symp 1987, 169.
20. Alloum, A. B.; Labiad, B.; Villemin, D. J Chem Soc Chem Commum 1989, 386.
21. Xu, W.; Bao, J.; Zhang, J.; Shi, M. J Appl Polym Sci 1998, 70, 2343.
22. Whittkaer, A.; Mingos, D. M. P. J Microwave Power Electromagn Energy 1994, 29, 195.
23. Barakat, I.; Dubois, Ph.; Jerome, R.; Teyssie, Ph. Macromolecules 1991, 24, 6542.
24. Fang, X.; Hutcheon, R.; Scola, D. A. J Polym Sci Part A: Polym Chem 2000, 38, 1379.
25. Moila, C.; Hamaide, T.; Spitz, R. Polymer 1997, 38, 5667.
26. Doi, Y. Microbial Polyesters; VCH: New York, 1990.
27. Dubois, Ph.; Jacobs, C.; Jerome, R.; Teyssie, Ph. Macromolecules 1978, 11, 68.
28. Kricheldorf, H. R.; Saunders, I. K.; Boettcher, C. Polymer 1995, 36, 1253.
29. Kowalski, A.; Duda, A.; Penczek, S. Macromolecules Rapid Commun 1998, 19, 567.
30. Sosnowski, S.; Slomkowski, S.; Penczek, S. Reibel, L. Makromol Chem 1983, 84, 2159.
31. Ito, K.; Hashizuka, Y.; Yamashita, Y. Macromolecules 1977, 10, 821.
32. Ito, K.; Yamashita, Y. Macromolecules 1978, 11, 68.
33. Okuda, J.; Rushkin, I. L. Macromolecules 1993, 26, 5530.
34. Ouhadi, T.; Stevens, C.; Teyssie, Ph. Makromol Chem Suppl 1975, 1, 191.
35. Endo, M.; Aida, T.; Inoue, S. Macromolecules 1987, 20, 2982.
36. Shen, Y.; Shen, Z.; Shen, J.; Zhang, Y.; Yao, K. Macromolecules 1996, 29, 3441.
37. Yasuda, H.; Tamai, H. Prog Polym Sci 1993, 18, 1097.
38. Stassin, F.; Halleux, O.; Jerome, R. Macromolecules 2001, 34, 775.
39. Liao, L. Q.; Liu, L. J.; He, F.; Zhuo, R. X.; Wan, K. J Polym Sci Part A: Polym Chem 2002, 40, 1749.
40. Ethel-Browning, M. D. Toxicity of Industrial Metal; Butterworths: London, 1961; Chapter 44, p. 313.
41. Ayappa, K. G.; Brandon, S.; Derbym, J. J.; Davis, H. T.; Davis, E. A. AIChE J 1994, 40,1268.
42. Madras, G.; Chattopadhyay, S. J Appl Polym Sci 1996, 2001, 81.