Optimization of the Coordination–Insertion Ring-Opening Polymerization of Poly(*p*-dioxanone) by Programmed Decreasing Reaction Temperatures

L. M. Esteves, L. Márquez, A. J. Müller

Grupo de Polímeros USB, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

ABSTRACT: The optimization of the synthesis of poly(*p*-dioxanone), by ring-opening polymerization with tin II bis(2-ethylhexanoic acid) as the catalyst, was conducted by a new method in which programmed decreasing reaction temperatures were employed. The results were compared with those obtained for polymerization reactions performed at constant temperatures in the 80–180°C range. In the novel method, the temperature was gradually reduced, as the reaction proceeded, to maintain a maximum polymerization rate and monomer conversion as the monomer was consumed. The experiments performed at constant temperatures confirmed previous reports that the bulk polymerization of 1,4-dioxan-2-one is an equilibrium polymerization reaction. With increasing polymerization temperature, the initial rate of polymerization increased, but the monomer conversion, reaching equilibrium, decreased. High conversions were obtained at low temperatures and long reaction times. Therefore, reducing the reaction temperature, to ensure working conditions that guaranteed the maximum polymerization rate and monomer conversion, could optimize the polymerization process. These conditions were calculated under the assumption of equilibrium polymerization reaction kinetics. With our proposed method, a 71% conversion was achieved in half the time needed when the polymerization was performed at a constant temperature of 120°C. Similarly, a 78% conversion was obtained with our proposed method in only a third of the time employed when the reaction was carried out at a constant temperature of 80°C. Our method guarantees high conversions in shorter times and a gradual reduction of the polymerization temperature. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 659–665, 2005

Key words: synthesis; kinetics; biodegradable

INTRODUCTION

Aliphatic polyesters such as poly(glycolic acid), poly(lactic acid), poly(ε-caprolactone) (PCL), and poly(*p*-dioxanone) (PPDX) presently constitute the most attractive class of synthetic polymers that can degrade in contact with living tissues or under outdoor conditions. Work performed during the last 2 decades has led to their applications in surgery and pharmacology. These compounds are also interesting for outdoor applications such as packaging and mulch films and in plant therapy for the controlled delivery of pesticides or insecticides in agriculture. Among them, PPDX has shown adequate properties as an osteosynthesis material and has received the approval of the Food and Drug Administration (FDA) to be used as a suture material in gynecology.[1] Previous studies of the properties, structure, and hydrolytic degradation of commercial PPDX and PCL-*b*-PPDX diblock copolymers have been conducted in our laboratory.[2–10]

PPDX can be obtained by the ring-opening polymerization of 1,4-dioxan-2-one (PDX) with organometallic catalysts. Although most of the information on the synthesis is buried in patents because the monomer is not commercially available,[11] recently some publications have reported important aspects of PPDX synthesis and degradation.[12–19] Kricheldorf and Damrau[12] suggested that the polymerization of PDX, with Zn–L-lactate as a catalyst, was an equilibrium reaction; in fact, the polymerization, conducted at 100°C, never exceeded an 80% yield. Lebedev et al.[13] calorimetrically measured the heat capacities and enthalpies of PPDX, and Nishida et al.[14] estimated the thermodynamics parameters for the bulk polymerization of PDX with Sn(II)ethyl hexanoate or triethylaluminum. Therefore, the heat capacities and enthalpies of combustion for both the monomer and polymer have been obtained.[13,14] They found a ceiling temperature of 265°C that explains the thermal instability of PPDX, which was suggested by several authors.[12,17,18] Re-

cently, Raquez et al.,[15] using aluminum trisopropoxide as a catalyst, quantified the thermodynamics of PDX polymerization from the temperature dependence of the monomer concentration at equilibrium. High-molecular-weight PPDX can be obtained within a few minutes at 80°C. A treatment at 80°C for a longer period of time reduces the amount of the unreacted monomer from 20 to 12 wt %; these values correspond to the thermodynamic equilibrium in the melt and crystalline states, respectively. Above 80°C, the polymerization deviates from the reactive scheme, and so the monomer conversion passes through a maximum and then decreases before leveling off at the thermodynamic monomer conversion equilibrium. This means that high conversions can be obtained at low temperatures and times that are long enough to be at thermodynamic equilibrium. In fact, Yoon et al.[16] produced thin films (46–90 nm) of PPDX by heating a mixture of $Sn(Oct)_2$ and PDX over a flat solid surface, such as gold or silicon oxide, at 55 or 70°C for 24 h.

According to the aforementioned studies, there must be a temperature at which the polymerization rate is maximum for a given monomer concentration. Thus, if the reaction temperature is reduced as the monomer concentration in the medium decreases, the rate of polymerization can reach a maximum. On the basis of these characteristics, this article proposes a method for the synthesis of PPDX in which it is possible to get a high conversion in shorter times. The bulk polymerization of PDX was conducted with tin II bis(2-ethylhexanoic acid) [$Sn(Oct)_2$], which has been accepted as a food additive by the FDA, as the catalyst.[11,20] The reaction was initially performed at a high temperature, which was gradually reduced to a final temperature (T_f) to get the maximum rate of polymerization as the monomer concentration decreased. The reaction conditions were calculated under the assumption of equilibrium polymerization reaction kinetics.

EXPERIMENTAL

Materials

The monomer PDX was prepared by the catalytic dehydrogenation of diethylene glycol with $Cu_2Cr_2O_5$ at 235–250°C and the continuous extraction of the monomer as it was obtained.[11] The monomer was purified by vacuum-fractionated distillation. A Fourier transform infrared (FTIR) spectrum of the purified PDX, recorded on a Nicolet Magna 750 FTIR instrument (San Jose, CA), showed the principal absorption bands as C=O stretching at 1740 cm^{-1} and CO stretching at 1200, 1130, and 1053 cm^{-1} and showed the presence of some traces of alcohol and acidic impurities. The melting point of PDX was 27.25°C.

$Sn(Oct)_2$ (95.5% pure), supplied by Sigma, was used as received and dissolved in toluene.

Polymerization of PDX

The bulk polymerization of PDX was carried out by two methods: the constant-temperature method and the programmed decreasing temperature method. In the first method, a constant temperature was used, ranging from 80 to 120°C. The reaction was conducted in a round-bottom flask with a magnetic stirrer or in capped ampules under a nitrogen atmosphere. The monomer (M) was initially added to the reactor at the desired temperature (80–180°C), and then the initiator diethylene glycol (OH) and the catalyst $SnOct_2$ (C) were added as $1M$ solutions in toluene. The reaction conditions were [M]/[C] = 400, [OH]/[C] = 2, [M]/[C] = 10,000, and [M]/[OH] = 1000. After a predetermined polymerization time, the reactor was cooled to room temperature, and its contents were dissolved in hot 1,1,2,2-tetrachloroethane to eliminate the monomer. The polymer was recovered by selective precipitation into an ether/heptane mixture (1:1 v/v). The monomer conversion was determined by the weighing of the dried polymer.

In the second method, the reaction was conducted at an initial temperature (T_0) at which the maximum rate of polymerization for a specific monomer content was previously calculated. Because the monomer was consumed during the reaction, the temperature was lowered after a certain previously calculated time; therefore, at this new temperature ($T_0 - \Delta T$), the polymerization rate was also maximum. The process was repeated for intervals of decreasing temperature (i.e., every 10°C) until T_f was reached. The reaction times for each temperature were calculated from the kinetic equations for a reaction in equilibrium (as discussed later). The reaction conditions were [M]/[C] = 10,000, [M]/[OH] = 1000, T_0 = 180°C, T_f = 75°C, ΔT = 10°C from 180 to 120°C, and ΔT = 5°C down to 75°C.

Capillary viscometry

The reduced viscosities of the synthesized polymers were measured in 1,1,2,2-tetrachloroethane with a Schott Gerate AVS automated Ubbelohde viscometer (Mainz, Germany) at 20°C.

FTIR spectroscopy

FTIR spectra of the obtained polymers were recorded with a Nicolet Magna 750 FTIR spectrometer on films cast from 1,1,2,2-tetrachloroethane. Each spectrum was recorded from 400 to 4000 cm^{-1} with a total of 32 scans and a resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC)

The thermal properties were measured with a PerkinElmer DSC7 (Boston, MA). The samples were
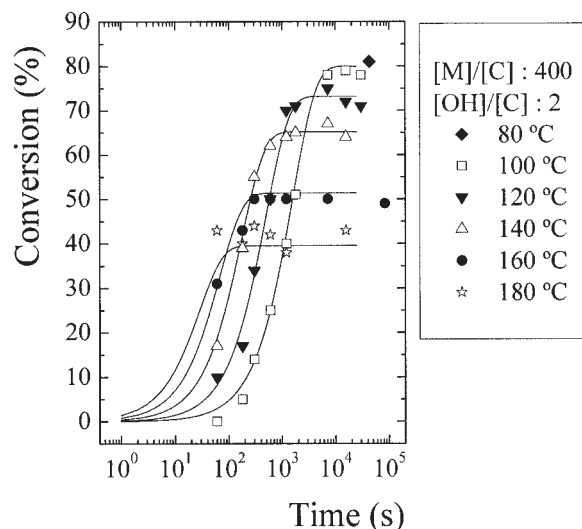
Figure 1 Time–conversion curves for the bulk polymerization of PDX at different temperatures.

encapsulated in aluminum pans, and high-purity dry nitrogen was used as an inert atmosphere. DSC cooling and heating curves were determined at 10°C/min after the samples were held in the melt at 130°C for 5 min to erase all previous thermal history.

RESULTS AND DISCUSSION

The results obtained with the constant-temperature polymerization method are shown in Figure 1: the solid lines represent values calculated with the thermodynamic data reported by Nishida et al.[14] As expected, the initial rate of polymerization increases when the temperature of the reaction is increased, whereas the equilibrium monomer conversion decreases when the polymerization temperature is increased. Several authors[13–15] have demonstrated that the polymerization of PDX is an equilibrium reaction, and as a result, it can be described with a microreversibility model in which the growing chains are able to depolymerize until a constant monomer concentration is reached. Thus, the propagation step should be written as an equilibrium reaction:

$$P_n + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} P_{n+1}$$
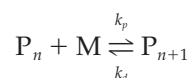
where P_n and P_{n+1} are propagating polymer chains; M is the monomer PDX; and k_p and k_d are the rate constants for polymerization and depolymerization, respectively. For an equilibrium situation, ΔG is 0, and the equilibrium constant is defined by $K = 1/[M]_e$, where $[M]_e$ is the equilibrium monomer concentration. As reported elsewhere,[21] $[M]_e$ can be expressed by the following equation:

$$\ln[M]_e = \ln\left(\frac{k_d}{k_p}\right) = \left(\frac{\Delta H^0}{RT}\right) - \left(\frac{\Delta S^0}{R}\right) \quad (1)$$

where R is the universal constant, T is the absolute temperature, and ΔH^0 and ΔS^0 are the enthalpy change for polymerization under the employed experimental conditions and the entropy change in the standard state, respectively.

A plot of $\ln [M]_e$ versus $1/T$, shown in Figure 2, allows the calculation of ΔH^0 from the slope and ΔS^0 from the intercept. The obtained values are -16.2 kJ/mol for ΔH^0 and -49.8 J/mol K for ΔS^0. These values are in good agreement with those reported by Nishida et al.[14] and by Raquez et al.[15]

From a kinetic point of view, if the catalyst is quantitatively converted into the growing species, the kinetics of chain propagation for an equilibrium polymerization can be defined by the following equation:

$$-k_p[I]_0 t = \ln\left(\frac{[M] - [M]_e}{[M]_0 - [M]_e}\right) \quad (2)$$

where $[I]_0$ is the concentration of the initiator (in this case, the initiator results from the substitution reaction of the acidic group of the catalyst by the alcohol), $[M]_0$ is the initial monomer concentration, $[M]$ is the actual monomer concentration at time t, and k_p is the rate constant. Thus, from a plot of $\ln[([M] - [M]_e)/([M]_0 - [M]_e)]$ versus the reaction time, the values of k_p for different temperatures can be obtained, as shown in Figure 3. The results, obtained from our experimental data, show values of k_p of 0.0173, 0.0774, and 0.1240 at 100, 120, and 140°C, respectively. These values are very similar to those reported by Nishida et al.[14]

Knowledge of the thermodynamic and kinetic behavior of PDX polymerization makes possible the optimization of the synthesis to get higher levels of conversion at shorter polymerization times. If increasing
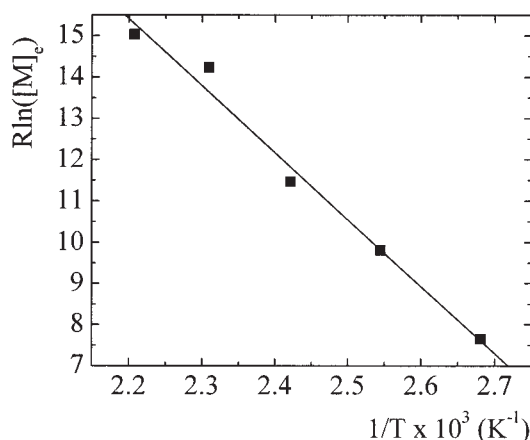
Figure 2 Relationship between $R \ln [M]_e$ and $1/T$ for the bulk polymerization of PDX with $Sn(Oct)_2$ as the catalyst.
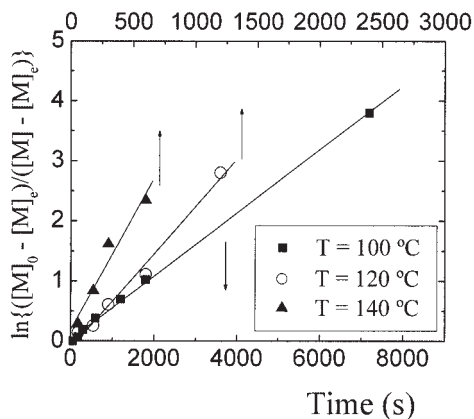
Figure 3 Kinetic behavior of the bulk polymerization of PDX at three different temperatures.

the reaction temperature to enhance the polymerization rate produces a decrease in the maximum conversion achieved, how can the conversion be increased without the catalyst content increasing? Until now, the best answer to this question has been to conduct the reaction at an intermediate temperature, such as 120°C, at which the conversion is acceptable and the polymerization time is short enough. An alternative method is proposed here; the idea is to reduce the polymerization time by the rate of polymerization always being kept at a maximum. This is made possible by a detailed knowledge of the reaction conditions.

The rate of polymerization (V) at a given value of T is given by

$$-\frac{d[M]}{dt} = k_p[I]_0([M] - [M]_e) = V \qquad (3)$$

Figure 4(a) shows the theoretical expectation for the variation of the rate of the monomer disappearance, which is equal to the polymerization rate, as a function of the monomer concentration and reaction temperature calculated according to eqs. (1) and (3), the Arrhenius expression $k_p = Ae^{-E_a}/RT$ (where A is a constant and Ea is the activation energy), and the thermodynamic data reported by Nishida et al.[14]
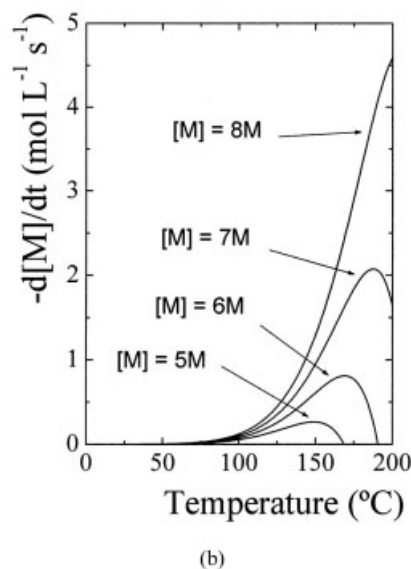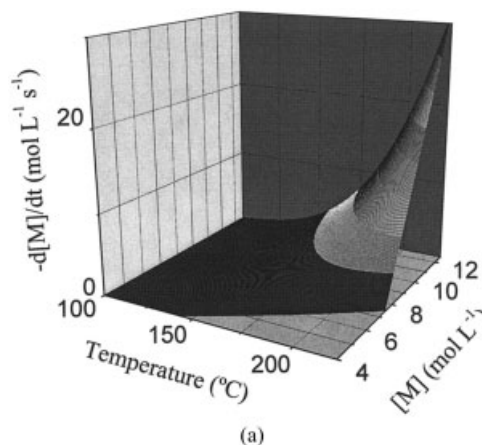
The polymerization rate increases with the reaction temperature and with the monomer concentration; however, as the monomer is consumed, the rate of polymerization decreases and can achieve values lower than those obtained at lower temperatures. The variation of the polymerization rate, as a function of the reaction temperature for different monomer concentrations, is plotted in Figure 4(b). These curves show that a maximum in the rate of polymerization exists for each monomer concentration at a specific temperature. Therefore, if we want to keep the maximum rate of reaction, we have to decrease the reaction

temperature as the monomer is consumed. These temperatures, at which the rate of polymerization is maximum for a given monomer concentration, can be calculated from the first derivative of the equation of the rate of monomer disappearance, with respect to the temperature. Such a derivation is described in detail next.

The partial derivative of V as a function of T at a constant value of $[M]$ can be calculated as follows:

$$\left(\frac{\partial V}{\partial T}\right)_{[M]} = \left(\frac{\partial k_p}{\partial T}\right)_{[M]}[I]_0([M] - [M]_e) + \left(\frac{\partial [I]_0}{\partial T}\right)_{[M]} k_p([M]$$

$$- [M]_e) - \left(\frac{\partial [M]_e}{\partial T}\right)_{[M]} k_p[I]_0 \quad (4)$$

Because $[I]_0$ is constant, eq. (4) can be simplified to

(a)

(b)

Figure 4 (a) Theoretical behavior of the rate of polymerization as a function of the monomer concentration [M] and the temperature T calculated with the thermodynamic data reported by Nishida et al.[14] and (b) variation of the polymerization rate as a function of the reaction temperature for different monomer concentrations.

$$\left(\frac{\partial V}{\partial T}\right)_{[M]} = \left(\frac{\partial k_p}{\partial T}\right)_{[M]}[I]_0([M] - [M]_e) - \left(\frac{\partial [M]_e}{\partial T}\right)_{[M]}k_p[I]_0 \tag{5}$$

If V has a maximum with respect to the temperature, then

$$\left(\frac{\partial V}{\partial T}\right)_{[M]} = 0 = \left(\frac{\partial k_p}{\partial T}\right)_{[M]}[I]_0([M] - [M]_e)$$
$$- \left(\frac{\partial [M]_e}{\partial T}\right)_{[M]}k_p[I]_0 \tag{6}$$

$$\left(\frac{\partial k_p}{\partial T}\right)_{[M]}[I]_0([M] - [M]_e) = \left(\frac{\partial [M]_e}{\partial T}\right)_{[M]}k_p[I]_0 \tag{7}$$

$$\left(\frac{\partial k_p}{\partial T}\right)_{[M]}([M] - [M]_e) = \left(\frac{\partial [M]_e}{\partial T}\right)_{[M]}k_p \tag{8}$$

From previously reported results[14] for the kinetic and thermodynamic behavior in the equilibrium, the concentration of the monomer at the equilibrium and the rate constant can be expressed by the following approximations:

$$[M]_e = e^{-1695.83T^{-1}+5.4483} \tag{9}$$

$$k_p = e^{-8643.2T^{-1}+19.35473} \tag{10}$$

A derivation with respect to T gives

$$\left(\frac{\partial [M]_e}{\partial T}\right)_{[M]} = 1695.83T^{-2}e^{-1695.83T^{-1}+5.4483} \tag{11}$$

If

$$f(T) = -1695.83T^{-1} + 5.4483 \tag{12}$$

and

$$f'(T) = 1695.83T^{-2} \tag{13}$$

then

$$[M]_e = e^{f(T)} \tag{14}$$

$$\left(\frac{\partial [M]_e}{\partial T}\right)_{[M]} = f'(T)e^{f(T)} \tag{15}$$

If a similar derivative is calculated for k_p

$$\left(\frac{\partial k_p}{\partial T}\right)_{[M]} = 8643.2T^{-2}e^{-8643.2T^{-1}+19.35473} \tag{16}$$

if

$$g(T) = -8643.2T^{-1} + 19.35473 \tag{17}$$

and

$$g'(T) = 8643.2T^{-2} \tag{18}$$

then

$$k_p = e^{g(T)} \tag{19}$$

$$\left(\frac{\partial k_p}{\partial T}\right)_{[M]} = g'(T)e^{g(T)} \tag{20}$$

Upon substitution, we have

$$g'(T)e^{g(T)}([M] - e^{f(T)}) = f'(T)e^{f(T)}e^{g(T)} \tag{21}$$

$$g'(T)([M] - e^{f(T)}) = f'(T)e^{f(T)} \tag{22}$$

$$[M] - e^{f(T)} = \frac{f'(T)}{g'(T)}e^{f(T)} \tag{23}$$

$$\frac{f'(T)}{g'(T)} \cong 0.1962 \tag{24}$$

$$[M] = 0.1962e^{f(T)} + e^{f(T)} \tag{25}$$

$$[M] = 1.1962e^{f(T)} \tag{26}$$

or

$$[M] = 1.1962[M]_e \tag{27}$$

The previous equations can be modified to obtain the temperature at which the rate of polymerization is maximum as a function of [M]:

$$\frac{[M]}{1.1962} = e^{f(T)} \tag{28}$$

$$\ln\left(\frac{[M]}{1.1962}\right) = f(T) = \frac{-1695.83}{T} + 5.4483 \tag{29}$$

$$\ln\left(\frac{[M]}{1.1962}\right) - 5.4483 = \frac{-1695.83}{T} \tag{30}$$

$$T = \frac{1695.83}{5.4483 - \ln\left(\frac{[M]}{1.1962}\right)} \tag{31}$$

Equation (31) shows that the temperatures at which the rate of polymerization is maximum depends ex-

TABLE I
Conversions Achieved for the Polymerization of PDX with the Constant-Temperature Method (80 and 120°C) and the Programmed Decreasing Temperature Method

| Time (min) | Programmed decreasing temperature method | | | Constant-temperature method | | | |
| | | | | $T = 80°C$ | | $T = 120°C$ | |
	T (°C)	C_{exp}	C_e	C_{exp}	C_e	C_{exp}	C_e
24	180	32	38	0	0.8	0	7.9
36	170	40	46	—	1.2	—	11.5
55	160	45	53	0	1.9	8	17.1
89	150	51	58	—	3.0	—	25.5
149	140	58	62	—	4.9	—	37.4
258	130	62	67	7	8.3	35	52.0
335	120	63	69	—	10.6	—	58.6
442	115	65	71	—	13.7	—	64.5
589	110	68	72	14	17.7	58	68.9
793	105	70	74	—	23.0	—	71.6
1,080	100	71	76	—	29.6	—	72.8
1,487	95	73	77	—	37.8	—	73.2
2,069	90	75	79	34	47.4	71	73.2
2,909	85	76	80	—	57.9	—	73.2
4,134	80	79	82	—	67.9	—	73.2
5,922	75	80	83	62	76.5	71	73.2
14,400	—	—	—	78	83.3	—	—

clusively on [M]; because [M] changes as the polymerization proceeds, the only way of keeping the maximum rate of polymerization is reducing the temperature as the polymerization progresses.

In each step, the reaction is allowed to proceed at a given temperature (T_i) until the rate of polymerization corresponds to the maximum rate of reaction at the next temperature $T_{i+1} = T_i - \Delta T$ because of the monomer conversion [see Fig. 4(b)]. That means that the initial monomer concentration must be reduced to a value given by the following equation:

$$[M]_{Ti} = 1.1962[M]_{eTi+1} \quad (32)$$

where $[M]_{eTi+1}$ represents the equilibrium monomer concentration at the next temperature T_{i+1}. At this moment, the temperature of the system is reduced to the next value T_{i+1}, and the reaction is carried out until the maximum rate of polymerization at T_{i+2} is achieved. The time (t_i) for each step of the reaction can be obtained from eq. (2) and is given by the following expression:

$$t_i = -\frac{1}{k_{p(T_i)}[I]_0} \ln\left(\frac{1.1962[M]_{eT_{1+i}} - [M]_{eT_i}}{0.1962[M]_{eT_i}}\right) \quad (33)$$

where

$$[M]_{0Ti} = 1.1962[M]_{eTi}$$

and

$$[M]_{Ti} = 1.1962[M]_{eTi+1}$$

The results obtained for the proposed programmed decreasing temperature method and two experiments realized at constant temperatures (80 and 120°C) are shown in Table I, which lists the polymerization temperature (T), the time of reaction (t), the expected conversion (C_e), and the experimental conversion (C_{exp}). As previously reported,[12–15] the polymerization of PDX achieved about 78% conversion at 80°C and 73% conversion at 120°C. Kricheldorf and Dannau,[12] Nishida et al.,[14] and Raquez et al.[15] reported the polymerization of PDX with different catalysts such as Zn-bis lactate (Zn(lactate)$_2$, Sn(Oct)$_2$, and aluminum tri-isoproproxide (Al(OiPr)$_3$)); although the polymerization rates were quite different, the conversions were almost the same at each temperature. Table I shows that the conversions achieved with our proposed method at the same reaction time are always higher than those obtained when the polymerizations are conducted at constant temperatures. Moreover, the same conversion can be obtained in shorter times when the reaction is carried out with programmed decreasing temperatures. A 71% conversion can be reached in half the time required for the polymerization at 120°C. Similarly, a conversion of 78% can be obtained in one-third of the time employed for the reaction at 80°C.

Figure 5 shows a plot of the conversion versus the reaction time. The experimental data are compared with the prediction of the following equation:

$$C = C_{eq}(1 - e^{-k_p[I]_0 t}) \quad (34)$$

where C is the monomer conversion and C_{eq} is the equilibrium monomer conversion. This figure con-
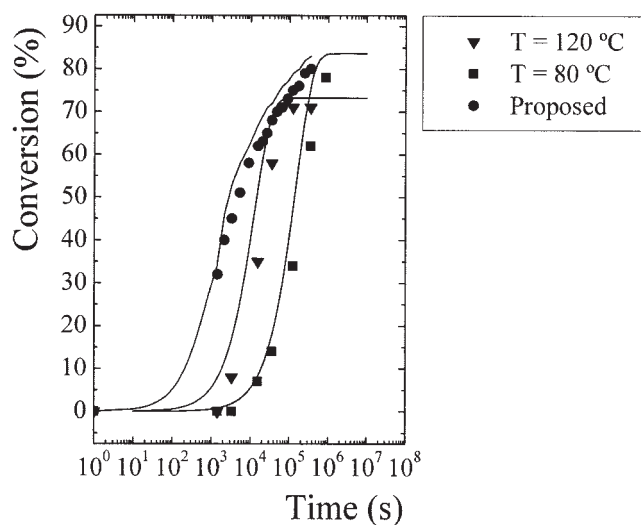
Figure 5 Conversion–time curves for the polymerization reactions conducted isothermally at 80 and 120°C with the programmed decreasing reaction temperature method.

firms that shorter times are required for this method to achieve similar conversions. This method can be applied to optimize the synthesis of monomers for which the polymerization reaction reaches equilibrium. Thus, higher levels of conversion can be achieved in shorter times if the kinetics and thermodynamic behavior of the reaction are known.

The polymers that we obtained were very similar, regardless of the method employed to produce them. All had similar reduced viscosities, ranging from 0.18 to 0.29, and similar melting temperatures, between 71.4 and 84.9°C. Both cooling and melting DSC scans produced results that were typical of low-molecular-weight PPDX, as previously reported.[7] These results reveal that low molecular weights were obtained, and this can be attributed to the presence of hydroxyl impurities in the monomer.[22] To simplify the mathematical model, we have assumed that these impurities do not affect the rate of polymerization or the conversion. However, it has been reported that $Sn(Oct)_2$-based initiators are complex dynamic systems that respond to all changes in the reaction conditions by changes in the structure and concentration of the active species.[23,24]

CONCLUSIONS

The bulk polymerization of PDX by $Sn(Oct)_2$ was conducted with a new programmed decreasing temperature method, in which the reaction temperatures were gradually reduced from 180 to 75°C, and it was compared with the processes at constant temperatures of 80 and 120°C. The polymerizations at constant tem-

peratures confirmed the equilibrium behavior of the polymerization process of PDX: the initial rate of the reaction increased with increasing temperature as the equilibrium conversion decreased. Experiments conducted at variable temperatures showed that the maximum rate of polymerization and monomer conversion could be achieved by a gradual reduction of the temperature as the reaction proceeded. The method proposed here also guarantees higher conversions in shorter times and a reduction in the total consumed energy by a gradual reduction of the temperature of the process.

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