6982 *Macromolecules* **2000,** *33,* 6982−6986

Equilibrium Polymerization Behavior of 1,4-Dioxan-2-one in Bulk

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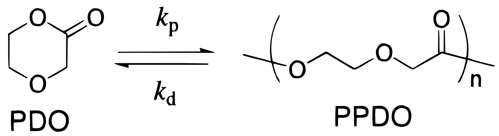
Received March 13, 2000; Revised Manuscript Received July 13, 2000

ABSTRACT: To clarify the equilibrium polymerization behavior of 1,4-dioxan-2-one, PDO, bulk polymerization was investigated with Sn(II) ethylhexanoate or triethylaluminum over a range of 60−180 °C. The thermodynamic parameters ΔH_{ls}, ΔS_{ls}, and ceiling temperature for the polymerization were −14.1 kJ mol^{-1}, −26.1 J mol^{-1} K^{-1}, and 265 °C, respectively. The parameters support the thermal instability of PPDO. The calculated thermal parameters of activation were $E_a = 71.8$ kJ mol^{-1}, $\Delta G_p^{\ddagger} = 106.2$ kJ mol^{-1}, $\Delta H_p^{\ddagger} = 68.5$ kJ mol^{-1}, and $\Delta S_p^{\ddagger} = -95.7$ J mol^{-1} K^{-1} at 120 °C. These parameters of activation are nearly equal to those of L-lactide. PDO and PPDO are easily polymerizable and depolymerizable materials, respectively.

Introduction

Poly(1,4-dioxan-2-one) {poly(*p*-dioxanone), PPDO} is an easily hydrolyzable material used to make monofilament sutures with good tenacity and knotting.[1] Recently, we reported that PPDO is decomposed to CO_2 and H_2O by microorganisms isolated from natural environments.[2] Because of its good physical properties, biocompatibility, and simple synthesis from diethylene glycol, an inexpensive raw material, PPDO is a candidate not only for medical use but also for general uses such as films, molded products, laminates, foams, nonwoven materials, adhesives, and coatings.[3] However, there are only a few reports[4,5] about the polymerization of 1,4-dioxan-2-one (*p*-dioxanone, PDO), and the polymerization behavior has not been described in detail. The polymerization of PDO may be an equilibrium reaction. Hollo and Carothers et al. recovered PDO from PPDO by distillation.[6] Kricheldorf et al.[4] suggested a polymerization equilibrium with Zn L-lactate {Zn(Lac)$_2$} as catalyst. Lebedev et al.[7] calorimetrically measured heat capacities and enthalpies of PPDO combustion. The resulting enthalpy and entropy of polymerization were $-\Delta H^0_{ll} = 15-17$ kJ mol^{-1} and $-\Delta S^0_{ll} = 10-13$ J mol^{-1} K^{-1} at 400−450 K.



The purpose of this paper is to clarify the equilibrium polymerization behavior of PDO. The thermodynamic parameters and the propagation rate constant for the bulk polymerization of PDO with Sn(II) ethylhexanoate {Sn(Oct)$_2$} or triethylaluminum {Al(Et)$_3$} as catalyst were determined and are compared to the well-known equilibrium polymerization of L-lactide.

Experimental Section

Materials. The monomer PDO was prepared by oxidative dehydrogenation of diethylene glycol over Cu(0) catalyst supported on silica particles at 275 °C as reported previously.[8] Proton (^{1}H) NMR spectra of the purified PDO were recorded on a 500 MHz JEOL JNM-LA500 FT-NMR system at 30 °C using tetramethylsilane as the internal standard at 0.00 ppm. Characterization of PDO was previously reported.[8,9] The water content of PDO was measured using a Mitsubishi Chemical Corporation Moisturemeter model CA-20 Karl Fischer titrator. The purified PDO contained 56 ppm of H_2O (i.e., 3.2×10^{-2} mol %).

Sn(II) ethylhexanoate {Sn(Oct)$_2$} was purchased from Wako Pure Chemicals Industries, Ltd. Its purity calculated from Sn content was 95%. Sn(Oct)$_2$ was dissolved in anhydrous toluene in a concentration of 1 M. Triethylaluminum {Al(Et)$_3$} in toluene (1.0 M) was purchased from Kanto Chemical Co. Inc. and used as received. Other chemicals—1-octanol (purity >99.5%), anhydrous toluene, chloroform, and methanol—were purchased from Tokyo Kasei Kogyo and Wako Pure Chemicals, and these were used as received.

Polymerization Procedure. Ring-opening polymerization of PDO was performed in the bulk with magnetic stirring in oven-dried and silanized 20 mL vials. PDO (5.0 g, 49 mmol) was charged into each vial. The vial was sealed with a butyl rubber stopper. The catalyst, Sn(Oct)$_2$ solution (10 μL, 10 μmol, 2.0×10^{-2} mol %) or Al(Et)$_3$ solution (25 μL, 25 μmol, 5.1×10^{-2} mol %), was injected into the vial through the butyl rubber stopper with a syringe. The vials were then transferred to a temperature-adjusted silicone oil bath and immersed up to their caps. The temperature was controlled to within ±1 °C. The vials were pulled from the reaction bath at predetermined intervals, and a small portion of each vial was separated and then dissolved in cooled $CDCl_3$ for reaction quenching and ^{1}H NMR measurement. The remaining portion of each vial was dissolved in cooled $CHCl_3$. The resulting PPDO was purified by precipitation from the $CHCl_3$ solution with methanol and dried in vacuo.

Analyses of Polymers. ^{1}H NMR spectra were recorded on the FT-NMR system, the purified PPDO (δ, $CDCl_3$): 4.16 ($-OCH_2COO-$, s, 2H), 3.79 ($-OCH_2CH_2OCO-$, t, 2H, $J = 4.8$ Hz), 4.34 ppm ($-OCH_2CH_2OCO-$, t, 2H, $J = 4.7$ Hz). Conversion of the polymerization was determined by comparison between areas of the characteristic peaks for PDO and PPDO, i.e., the peak at $\delta = 3.88$ ppm ($-OCH_2CH_2OCO-$, t, 2H, $J = 4.8$ Hz) of PDO[8] and the peak at $\delta = 3.79$ ppm of PPDO.

Molecular weight of the purified PPDO was measured at 40 °C on a TOSOH HLC-8120 gel permeation chromatograph

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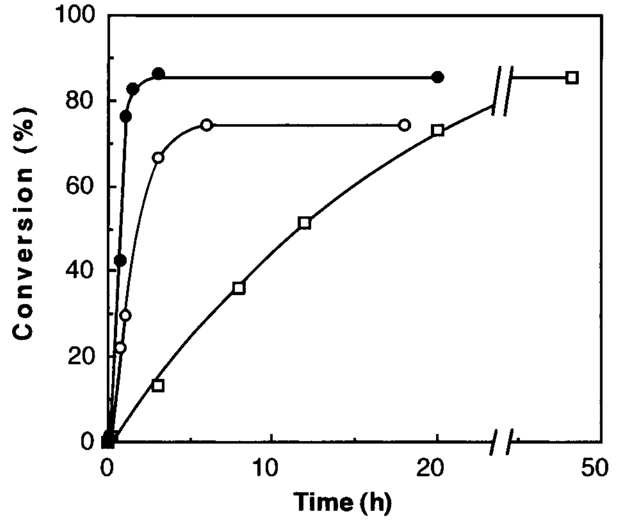

Figure 1. Time−conversion curves of polymerization of PDO in bulk with Al(Et)$_3$ at 80 °C (●) and with Sn(Oct)$_3$ at 80 (□) and 120 °C (○).

(GPC) system with a refractive index (RI) detector under the following conditions: double TSKgel Super HM-H linear columns (linearity range, 10^3−8 × 10^6; molecular weight exclusion limit, 4 × 10^8) and chloroform (HPLC grade) eluent containing 0.3 wt % tri-*n*-octylmethylammonium chloride (TOAC) at a flow rate of 0.6 mL min^{-1}. The calibration curves for GPC analysis were obtained using polystyrene standards with a low polydispersity (2.8 × 10^3, 6.2 × 10^3, 1.03 × 10^4, 4.39 × 10^4, 1.02 × 10^5, 3.55 × 10^5, 1.26 × 10^6, TOSOH Corporation).

Glass transition point (T_g), melting point (T_m), and heat of fusion of the purified PPDO were measured with a Seiko Instruments Inc. DSC 220C in an aluminum pan under nitrogen at a 10 °C/min heating rate.

Measurement of Density. Densities of PDO and PPDO were measured by a conventional dilatometric technique in the range 30−180 °C. Calibration of the dilatometer was verified with distilled and deionized water and 1-octanol having a well-known density (d_4^{20} = 0.8256)[10] and expansion coefficient (α_1 = 0.78097 × 10^{-3} K^{-1}, α_2 = 1.3506 × 10^{-6} K^{-2}, and α_3 = 0.35018 × 10^{-8} K^{-3}).[11] A Toray Daw Corning silicone oil was used as an immiscible medium for the density measurements of PPDO.

Results and Discussion

Equilibrium Polymerization. Bulk polymerization of PDO proceeded homogeneously in the range 100−180 °C, but not at 60 and 80 °C. At 60 and 80 °C, PPDO gradually condensed or crystallized with increasing conversion. Figure 1 shows typical time−conversion curves of the polymerization of PDO at 80 and 120 °C with Sn(Oct)$_2$ and at 80 °C with Al(Et)$_3$ in bulk. The conversion of PDO was determined by ^{1}H NMR analysis of the reaction mixture. The polymerization of PDO stopped at about 85% conversion at 80 °C and 74% conversion at 120 °C. Table 1 summarizes the results of the bulk polymerization carried out at temperatures in the range 60−180 °C. Each polymerization in Table 1 attained an equilibrium. Similarly, Kricheldorf et al.[4] found that bulk polymerizations of PDO at 100 °C with Zn(Lac)$_2$ never exceeded 80% yield. The Sn(Oct)$_2$-catalyzed polymerization of PDO is relatively fast compared with the Zn(Lac)$_2$-initiated polymerization, and AlEt$_3$ is a more effective initiator. Although the polymerization rates using Zn(Lac)$_2$, Sn(Oct)$_2$, and Al(Et)$_3$ were distinctly different, the equilibrium conversions were almost the same at each temperature. The equilibrium conversions decreased in a similar manner with increasing polymerization temperature. These results indicate that whichever initiator is used for the polymerization of PDO, the conversion of the polymerization converges to a thermodynamic equilibrium. The equilibrium conversions for PDO are lower than those reported for L-lactide (for example, 98.68 and 97.85% at 130 and 160 °C, respectively[12]). This indicates that the free energy change of polymerization for PDO is less negative than that for L-lactide.

Table 1. Bulk Polymerization of PDO

entry	initiator	[M]/[I] (mol/mol)	temp (°C)	time (h)	conv^b (%)	M_n^{c} (×10^4)	PDI^d
1	AlEt$_3$	1960	60	6	93.5	29.9	2.1
2	AlEt$_3$	1960	80	3	85.5	23.3	2.2
3	AlEt$_3$	1960	100	1.5	79.4	24.0	2.0
4	AlEt$_3$	1960	120	1.5	73.5	12.3	2.0
5	AlEt$_3$	1960	140	1.5	66.2	7.7	1.7
6	AlEt$_3$	1960	160	1.5	58.5	4.3	1.8
7	AlEt$_3$	1960	180	1.5	50.3	2.5	1.6
8	Sn(Oct)$_2$^{a}	4900	80	20	85.5	8.0	4.8
9	Sn(Oct)$_2$	4900	100	20	79.4	14.2	2.5
10	Sn(Oct)$_2$	4900	120	6	74.1	8.3	3.9
11	Sn(Oct)$_2$	4900	140	1.5	67.1	7.2	2.2
12	Sn(Oct)$_2$	4900	160	1.5	58.1	3.2	1.8
13	Sn(Oct)$_2$	4900	180	1.5	50.5	1.6	1.7

[a] Sn(II) 2-ethylhexanoate. [b] Estimated by ^{1}H NMR (solvent CDCl$_3$). [c] Estimated by GPC (solvent, CHCl$_3$ containing 0.3 wt % TOAC, PSt standards). [d] Polydispersity.

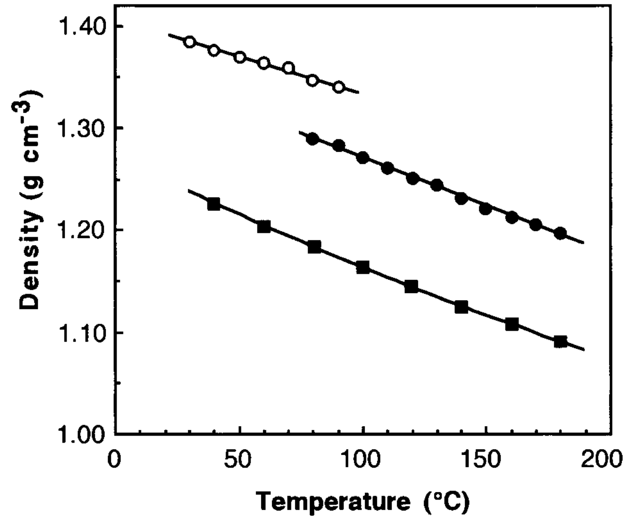

Figure 2. Density versus temperature for PDO (■), crystallized PPDO (○), and melt PPDO (●). The solid curve and straight lines are the density models defined by eqs 1, 2, and 3.

Thermodynamic Parameters of Equilibrium Polymerization. To determine the equilibrium monomer concentration, $[M]_e$, the densities of PDO and PPDO were measured by conventional dilatometry at 30−180 °C (Figure 2). Number- and weight-average molecular weights, T_g, T_m, and heat of fusion of the PPDO sample for the density measurements were 78 800, 150 700, −5.9 °C, 107.9 °C, and 65.5 J g^{-1}, respectively. The density of PDO was fit to a quadratic curve parameter model, while the density of PPDO was fit to two linear parameter models for crystallized and melt polymers. Densities of PDO and PPDO were calculated using the following expressions.

$$\rho_{\mathrm{PDO}}\ (\mathrm{g\ cm^{-3}}) = 1.273 - 1.197 \times 10^{-3}T\ (°\mathrm{C}) + 1.027 \times 10^{-6}T\ (°\mathrm{C})^2 \quad (1)$$

$$\rho_{\mathrm{crystallized\ PPDO}}\ (\mathrm{g\ cm^{-3}}) = 1.406 - 7.071 \times 10^{-4}T\ (°\mathrm{C}) \quad (2)$$

$$\rho_{\mathrm{melt\ PPDO}}\ (\mathrm{g\ cm^{-3}}) = 1.368 - 9.664 \times 10^{-4}T\ (°\mathrm{C}) \quad (3)$$

The data of $\rho_{\mathrm{melt\ PPDO}}$ at 80−100 °C in Figure 2 indicate it is in a supercooled state.

The equilibrium monomer concentration is related to the temperature by Dainton's equation:[13]

$$\ln[\mathrm{M}]_\mathrm{e} = (1/T)(\Delta H_\mathrm{p}/R) - \Delta S_\mathrm{p}{}^0/R \quad (4)$$

where ΔH_p is the enthalpy of polymerization under the prevailing experimental conditions and $\Delta S_\mathrm{p}{}^0$ is the entropy change at the standard state ($[\mathrm{M}]_\mathrm{e} = 1$ mol L^{-1}). The plot of $\ln[\mathrm{M}]_\mathrm{e}$ vs $1/T$ in the bulk polymerization of PDO in Figure 3 is a line at temperatures above 80 °C. The deviation at 60 and 80 °C is attributable to condensation or crystallization of PPDO during the polymerization,[14] since PPDO is only slightly soluble in PDO at these temperatures. However, PPDO did not crystallize during the polymerization at 100 °C. The slope of the line is $\Delta H_\mathrm{ls}/R$ and the intercept is $-\Delta S_\mathrm{ls}{}^0/R$, which corresponds to ΔH_ls and $\Delta S_\mathrm{ls}{}^0$ of −14.1 kJ mol^{-1} and −45.3 J mol^{-1} K^{-1}, respectively. The value of ΔH_ls is close to that reported by Lebedev et al. ($-\Delta H_\mathrm{ll}$ = 17−15 kJ mol^{-1} at 400−450 K).[7] However, the value is less negative than that reported for L-lactide ($-\Delta H_\mathrm{p}$ = 22−29 kJ mol^{-1}).[12,15] This may be attributed to less ring strain for the nonsubstituted ether−ester PDO ring than for the substituted diester L-lactide ring. Using eqs 1 and 4, the ceiling temperature, T_c, for the polymerization was determined as 265 °C, at which temperature $[\mathrm{M}]_\mathrm{e} = [\mathrm{M}]_0$. The $[\mathrm{M}]_0$ means the initial monomer concentration at the corresponding temperature. The T_c is significantly lower than that for bulk polymerization of L-lactide, 640−786 °C.[12,15] Moreover, the entropy of bulk polymerization, ΔS_ls, was calculated to be −26.1 J mol^{-1} K^{-1}, which is more negative than that of L-lactide (ΔS_ls = −22.0 J mol^{-1} K^{-1}).[12] This may be attributed to an unfavorable synergistic influence on the segmental mobility of PPDO as reported by Kricheldorf et al.[4]

The thermodynamic parameters mean that PDO polymerization has a less negative free energy than that for L-lactide. The parameters also support the polymerization characteristics of PDO and the thermal instability of PPDO suggested so far.[4−6]

Polymerization Kinetics. The bulk PDO polymerization kinetics were investigated at 80−140 °C using Sn(Oct)$_2$ and at 80 °C using Al(Et)$_3$. All of these reactions were homogeneous during the 5−300 min reaction time. The kinetics of propagation for an equilibrium polymerization system is generally expressed as

$$\ln\{([\mathrm{M}]_0 - [\mathrm{M}]_\mathrm{e})/([\mathrm{M}] - [\mathrm{M}]_\mathrm{e})\} = k_{\mathrm{app}}t \quad (5)$$

where [M] is the monomer concentration at time t, and k_{app} is the apparent rate constant. The value of [M] was calculated from the conversion of PDO and the densities of PDO and PPDO.

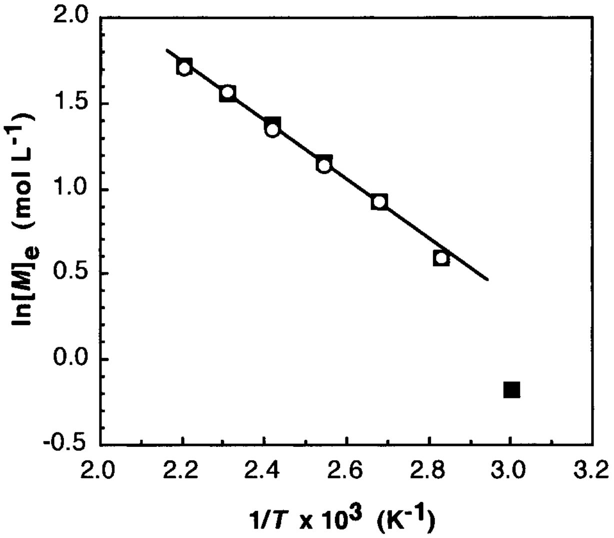

Figure 3. Plot of $\ln[\mathrm{M}]_\mathrm{e}$ vs $1/T$ for the determination of thermodynamic parameters. Initiator: Sn(Oct)$_2$ (○) and Al(Et)$_3$ (■).

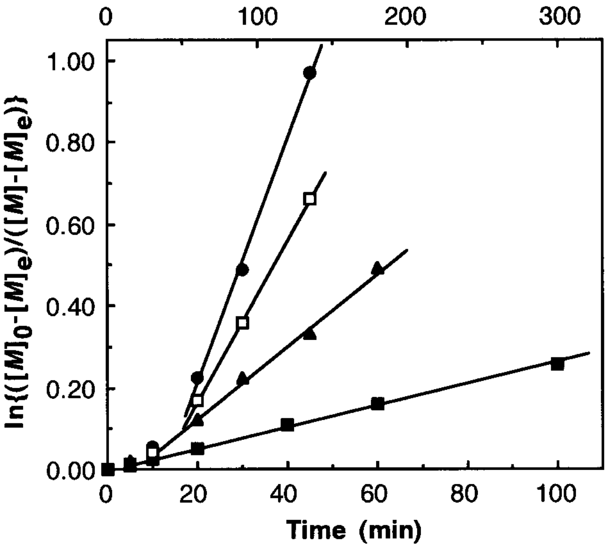

Figure 4. Kinetics results for the bulk polymerization of PDO at several temperatures with Sn(Oct)$_2$ or Al(Et)$_3$. Conditions: at 80 (■), 120 (▲), and 140 °C (●) with Sn(Oct)$_2$ ($[\mathrm{M}]_0/[\mathrm{Cat}]_0$ = 4900) and 80 °C (□) with Al(Et)$_3$ ($[\mathrm{M}]_0/[\mathrm{Cat}]_0$ = 1960). Time scale: ■ (top), ▲, ●, and □ (bottom).

The results obtained are plotted in Figure 4. In all cases, linear relationships between $\ln\{([\mathrm{M}]_0 - [\mathrm{M}]_\mathrm{e})/([\mathrm{M}] - [\mathrm{M}]_\mathrm{e})\}$ and the reaction time were determined after each induction period, about 5−13 min. The induction period could be attributed to the formation of active initiating species.[16] Similar induction periods were reported for the polymerizations of L-lactide[17] and ϵ-caprolactone[18] with aluminum alkoxides.

Figure 5 shows the average molecular weights of PPDO as a function conversion at 80 °C. The number- and weight-average molecular weights increased linearly with conversion. Similar results were determined on the other polymerizations. These results suggest that this process is a living mechanism. However, since the polymerization is an equilibrium polymerization, the polydispersity of the polymers broadened to about 2, i.e., the most probable distribution of molecular weight, with increase in conversion. Equilibration and depropagation probably occur by bimolecular transesterification as in the case of ϵ-caprolactone reported by Kowalski et al.[16] and Schindler et al.[19]

Table 2. Propagation Rate Constants on Bulk Polymerization of PDO with Sn(Oct)$_2$ or Al(Et)$_3$

catalyst	T (°C)	$[\text{Cat}]_0 \times 10^3$ (mol L^{-1})	$[\text{M}]_0/[\text{Cat}]_0$	$[\text{M}]_e$ (mol L^{-1})	$k_{app} \times 10^5$ (s^{-1})	k_p (L mol^{-1} s^{-1})
Sn(Oct)$_2$	80	2.37	4900	1.945	1.45	0.0061
	120	2.29	4900	3.166	14.76	0.0645
	140	2.25	4900	3.899	50.19	0.2229
Al(Et)$_3$	80	5.92	1960	1.945	32.89	0.0555

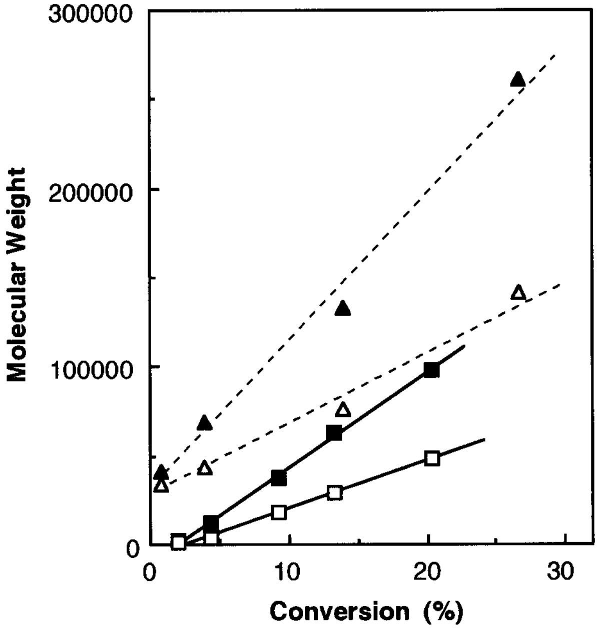

Figure 5. Relationships between number- (M_n) and weight-average molecular weight (M_w) and monomer conversion for the bulk polymerization of PDO. Conditions: at 80 °C {M_n (□), M_w (■)} with Sn(Oct)$_2$ ($[\text{M}]_0/[\text{Cat}]_0 = 4900$), and 80 °C {$M_n$ (△), M_w (▲)} with Al(Et)$_3$ ($[\text{M}]_0/[\text{Cat}]_0 = 1960$).

The two pairs of plots in Figure 5 deviated from the origin. In the case of the polymerization initiated with Sn(Oct)$_2$, many oligomers with lower molecular weight were produced at the beginning, while in the case of Al(Et)$_3$ fewer polymers with higher molecular weight were produced. This may reflect the difference in the initiating mechanism of each catalyst.[16,20] Sn(Oct)$_2$ would catalyze reactions between monomers and the active proton compounds included, and the resulting OH end groups would function as co-initiators, while some Al(Et)$_3$ would change into aluminum alkoxides as a true active species for the polymerization. These initiating processes could be reflected as the induction periods.

On the basis of the linearity of the relationships in Figure 4, we can calculate the kinetic parameters of PDO bulk polymerization with Sn(Oct)$_2$. Witzke et al.[12] investigated the reversible kinetics of L-lactide bulk polymerization with Sn(Oct)$_2$. They reported that the rate of propagation is first order in Sn(Oct)$_2$, i.e., $k_{app} = k_p[\text{Cat}]_0$, where k_p is the propagation rate constant. In this study, assuming that the catalysts are quantitatively converted to the growing species, k_p values were regressed from the linear part of the polymerization data. The results are summarized in Table 2. Al(Et)$_3$ is obviously the more effective catalyst for the PDO polymerization at 80 °C. Regression of the data at 120 °C and $[\text{M}]_0/[\text{Cat}]_0 = 4900$ gave $k_{p,\text{PDO}} = 0.0645$ L mol^{-1} s^{-1}. Witzke et al. reported that the regression of the L-lactide polymerization under similar conditions, at 130 °C and $[\text{M}]_0/[\text{Cat}]_0 = 2940$, gave $k_{p,\text{L-lactide}} = 0.0488$ L mol^{-1} s^{-1} (13.8 h^{-1} catalyst mol %$^{-1}$). This indicates that $k_{p,\text{PDO}} \geq k_{p,\text{L-lactide}}$ in the bulk polymerization at 120–130 °C with Sn(Oct)$_2$.

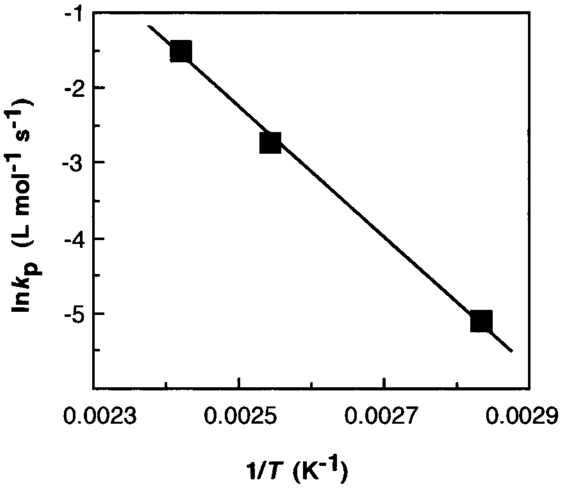

Figure 6. Temperature dependence of the propagation rate constant of PDO with Sn(Oct)$_2$. Solid line is the Arrhenius model.

The temperature dependence of k_p is depicted with an Arrhenius plot in Figure 6. Using the k_p values at 80, 120, and 140 °C, the activation energy was determined: $E_a = 71.8$ kJ mol^{-1}. Witzke et al. calculated $E_a = 70.9$ kJ mol^{-1} for the L-lactide bulk polymerization. Both activation energy values of the PDO and L-lactide polymerizations are nearly equal.

The thermodynamic parameters of activation were also calculated by the theory of the activated complex:

$$k_p = (k'T/h)\exp(-\Delta G_p^{\ddagger}/RT) = (k'T/h) \times \exp(-\Delta H_p^{\ddagger}/RT)\exp(\Delta S_p^{\ddagger}/R) \quad (6)$$

$$\Delta H_p^{\ddagger} = E_a - RT \quad (7)$$

where k', h, $\Delta G_p^{\ddagger}$, $\Delta H_p^{\ddagger}$, and $\Delta S_p^{\ddagger}$ are the Boltzmann constant, Planck constant, activation free energy, enthalpy, and entropy, respectively. The thermodynamic parameters were calculated for the bulk polymerization of PDO at 120 °C, i.e., $\Delta G_p^{\ddagger} = 106.2$ kJ mol^{-1}, $\Delta H_p^{\ddagger} = 68.5$ kJ mol^{-1}, and $\Delta S_p^{\ddagger} = -95.7$ J mol^{-1} K^{-1}. The thermodynamic parameter values were also nearly equal to those of the bulk polymerization of L-lactide, which are calculated from the data of Witzke et al.[12]

Conclusions

Equilibrium polymerization of PDO by Sn(Oct)$_2$ or Al(Et)$_3$ in bulk was investigated over a range of 60–180 °C. The equilibrium monomer concentrations significantly higher than these for L-lactide The determined thermodynamic parameters ΔH_{ls}, ΔS_{ls}, and T_c of the polymerization support the polymerization characteristics of PDO and the thermal instability of PPDO. The thermodynamic parameters of activation were nearly equal to those of the bulk polymerization of L-lactide. This suggests that the bulk polymerizations of PDO and L-lactide by Sn(Oct)$_2$ catalyst proceed via a similar activated complex under these conditions.

Although PPDO depolymerizes at lower temperature, PDO is easily polymerized by conventional initiators and produces a sufficient high molecular weight polymer that may have industrial applications. The easy polymerizability and depolymerizability properties of PDO and PPDO may be favorable for feedstock recycling.

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MA000457T