Zinc and Tin Xanthates in the Coordination Polymerization of Propylene Oxide

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ABSTRACT: The polymerization of propylene oxide with zinc and tin xanthates was studied. Polymerization with both systems was found to be a zeroth-order, nonterminating process, where the molecular weight was controlled by transfer reactions. It is discussed that these observations were consistent with a mechanism in which the rate-determining step was the addition of monomer on the growing chain rather than the coordination of the monomer to active sites. These catalysts turned out to be quite stable, even under semiclosed conditions. With zinc isopropyl xanthate, high conversions in short polymerization times could be obtained. The product had a very broad molecular weight distribution and could be split into crystallizable and amorphous fractions. The crystallizable fractions consisted of stereoregular segments separated from each other by stereoirregularities or regioirregularities. The degrees of polymerization of stereoregular segments (S_1's) were estimated from melting point measurements. It was found that the melting points and, hence, average S_1 values changed in different fractions. It was concluded that there was only one type of active center; however, the rates of wrong additions (e.g., head-to-head addition) of incoming monomer controlled the average S_1 value of the chain. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2639–2645, 2011

Key words: catalysts; fractionation of polymers; growth

INTRODUCTION

Cyclic ethers can be polymerized by anionic, cationic, and coordination catalysts; but only the coordination catalysts yield high polymers. Furthermore, polyethers obtained from racemic monomers with coordination catalysts are shown to be partially stereoregular.[1–4] This class of catalysts are usually obtained from organometallic compounds by reactions in molar ratios (r's) with some modifiers (H_2O, H_2O_2, alcohols, H_2S, S, etc.), and their performances are extremely sensitive to the value of r and the presence of atmospheric impurities. Lal and Devlin[5,6] showed that zinc and cadmium xanthates and dithiocarbamates are active catalysts and soluble catalysts for the high polymerization of propylene oxide (PO) and that they did not require any modifier for activation. At first look, these systems sounded more attractive than that of organometallic originated initiators because of their stability in semi-open systems and higher yields of high polymer. Although Lal and Devlin[5] studied the initiation step with zinc xanthates in detail by isolating and identifying intermediates (olefins, ionic sulfur, cyclic dithiocarbonates, carbonates, and plausibly ZnSZn bonds) formed in this stage, but they did not focus on the high polymer formation reactions. They observed high polymer formation but did not characterize (even with an acetone solubility test[6]) whether the products were crystalline or not. Zinc xanthates are also remarkable catalysts from the point that they are the only reported system to copolymerize carbon disulfide to a high-molecular-weight copolymer.[7] Although catalytic activities of tin xanthates are much weaker than that of the zinc xanthates; with the purpose of comparison, we studied the polymerization of PO with both of these catalysts.

EXPERIMENTAL

Materials

All solvents and reagents were purified by standard methods before fractionation by distillation on a 1-m column packed with Fenske helices, with approximately 20 theoretical plates. PO was kept over CaH_2 *in vacuo*.

D-(+)-2-Octanol

An optically active enantiomer was obtained from racemic 2-octanol with the L-brucine method.[8]

Metal xanthates

Zinc xanthates were prepared by the mixture of degassed aqueous solutions of zinc sulfate solutions

Experiment number	H$_2$O/Zn	Conversion (%)	K conversion (%)	$M_v \times 10^{-4}$
1	0.00	72.5	65.6	117
2	0.50	75.8	66.0	81.5
3	0.67	76.8	68.5	84.6
4	0.80	79.9	64.2	78.4
5	1.00	74.2	64.9	60.5
6	2.00	77.2	69.3	41.3
7	Excess H$_2$O	46.9	35.0	36.1
8	Excess H$_2$O+air	58.2	47.8	—

Reaction conditions: t = 18 h, temperature = 355 K, PO = 7.41×10^{-2} mol, Zn = 3.35×10^{-5} mol, Zn/PO = 4.50×10^{-4} mol/mol. K conversion (%), percentage conversion of K polymers.

with corresponding potassium xanthate solutions under a nitrogen atmosphere. The collected precipitate was dissolved in hot benzene in a dry box, filtered, and then crystallized at room temperature. After two recrystallizations, the crystals were dissolved in benzene and stored *in vacuo* as a stock solution ($\approx 5 \times 10^{-3}$ mol of Zn/L). However, xanthates from (D,L)-octan-2-ol and D-(+)-octan-2-ol were sticky yellow glasses and were not crystallizable; hence, they were washed with degassed water to remove any free ions before preparation of the stock solution. Tin isopropyl xanthate (Sn^{iso}PXt) was prepared with SnCl$_2$·2H$_2$O, but we could not recrystallize (without decomposing) it from a proper organic solvent. Therefore, the stock solution in benzene was prepared after it was washed with water. Sn^{iso}PXt was found to have 28.8% Sn by atomic absorption spectroscopy (AAS) (theoretical value = 30.5). Zinc isopropyl xanthate (Zn^{iso}PXt; 20.6% Zn by AAS, theoretical value = 19.5) solutions in benzene and diethyl ether were transparent and colorless and remained in that state for prolonged times (years). The catalytic activity of the zinc catalysts did not decrease upon prolonged storage. To test the catalytic stability, some polymerizations with fresh stock solutions were repeated after 3–4 months of storage, and almost the same percentage conversion was observed (Table IX, shown later, experiments 33 and 34, 37 and 38, and 39 and 40). The catalytic activity of such solutions were not markedly affected, even with the addition of water in molar quantities. However, by treatment with excess water and air, the catalytic activity markedly deteriorated (Table I). Sn^{iso}PXt solution in benzene was orange in color, but upon prolonged storage, the initially clear solutions became turbid, possibly because of some leakage in the storage system. The catalytic activity

of the turbid solutions were markedly faded; hence, such solutions were rejected.

Polymerizations

Volumetrically measured stock solution was transferred into a polymerization tube, metal xanthate was freeze-dried, and PO was distilled through a vacuum line to chill the tube with liquid N$_2$. The tube was separated from the vacuum line cutting with a hot flame. The polymerizations were carried out in a temperature-controlled bath. The reaction mixture was dissolved in benzene and shaken with 1 mL of 2M HCl. Excess HCl and water-soluble components were extracted with water, and 1% diphenylamine, as an antioxidant, was added. Finally, the benzene solutions were freeze-dried.

Characterization of the polymers

Like in other coordination polymerizations of PO,[9,10] the product could be split into a high-polymer fraction (K polymer), precipitating from a 273-K isooctane solution (1 g/dL) [viscosity-average molecular weight (M_v) $> 5 \times 10^4$], and an oily polymer fraction [D polymer; that is, a 273-K soluble fraction; number-average molecular weight (M_n) $< 10^3$]. The M_v values of the K polymers were measured by an Ubbelohde viscometer (home made) in toluene at 25°C with Mark–Houwink coefficients as $K = 1.29 \times 10^{-4}$ and $a = 0.75$.[11] The M_n values of the D polymers were measured by cryoscopy in benzene by extrapolation to zero molality and also from end-group analysis for hydroxyl functionality [f_{OH}; phthalic anhydride method[12(a)]] and double-bond functionality (f_{db}) by brominating.[12(b)] ^{1}H-NMR and ^{13}C-NMR measurements were done in deuteriochloroform by a Bruker Spectroscopic Avance DPX 400 instrument (Karlsruhe, Germany). Samples for melting point (T_m) determinations with polarized microscopy were prepared by deposition of a thin film by evaporation of a dilute solution of poly(propylene oxide) (PPO) on a lam. The lam was heated to 363–373 K in an oven and allowed to cool down to room temperature for 15–20 h. The formed spherulites (in the shape of a Maltese cross) were observed under a hot-stage polarized microscope. The temperature of the hot stage was gradually increased (2 K/min), and the temperature at which the last trace of birefringence disappeared was recorded.

Fractionation of the polymers

Crystalline PPO samples were fractionated from isooctane solutions (2%) by cooling from initial temperature (T_i) down to the precipitation temperature (T_p).[9,13,14] The highest and lowest values of T_i were

TABLE II
Additive Effects of Water on the Activity of $Sn^{iso}PXt$

Experiment number	H_2O/Sn	Conversion (%)	K conversion (%)	$M_v \times 10^{-4}$
9	0.00	8.4	3.8	101
10	0.20	9.1	4.2	108
11	0.50	8.6	4.4	102
12	0.67	8.8	4.8	93
13	1.00	8.4	4.6	102
14	2.00	8.2	4.3	120

Reaction conditions: $t = 17$ h, temperature = 355 K, PO = 1.43×10^{-1} mol, Sn = 3.56×10^{-4} mol, Sn/PO = 2.50×10^{-3} mol/mol.

TABLE III
Growth of $Zn^{iso}PXt$-Catalyzed PPO with t

Experiment number	t (h)	Conversion (%)	K conversion (%)	$M_v \times 10^{-4}$
15	1.5	8.70	7.50	124
16	5	24.1	20.9	138
17	10	39.0	35.1	117
1	18	72.5	65.6	117

Reaction conditions: temperature = 355 K, PO = 7.41×10^{-2} mol, Zn = 3.35×10^{-5} mol, Zn/PO = 4.50×10^{-4} mol/mol.

340 and 280 K. The difference between T_i and T_p was about 12 K. No crystal structures could be observed by polarized microscopy for samples that were soluble in isooctane at 273 K.

RESULTS AND DISCUSSION

Stability of zinc xanthates

$Zn^{iso}PXt$ solution in benzene was colorless and remained clear unless exposed to atmosphere for a prolonged time. The ultraviolet–visible spectra had two absorption peaks at 224 and 294 nm in diethyl ether (for zinc butyl xanthate, 222 and 294 nm per Lal and Devlin[5]). However, potassium isopropyl xanthate in same solvent absorbed at 208 and 302 nm. Hence, xanthate ion apparently functioned as a ligand in a tetrahedral zinc complex.

A number of metal alkyls and alkoxides were used in the stereoregular polymerization of PO. However, these were only active when they were modified by reaction with water in the molar ratios of r (H_2O/metal $- r$): $0 < r > 1$. The activities increased with increasing molar ratio of water and passed through a maximum (usually at $r = 2/3$), and it faded down above $r > 1$. To detect the role of water as a modifier in polymerization, several polymerization experiments were performed by the treatment of $Zn^{iso}PXt$ with water and air before the addition of monomer (Table I). However, added water did not enhance K polymer production but appa-

rently decreased the molecular weight plausibly by acting a transfer reagent.

A similar set of experiments were also carried out with $Sn^{iso}PXt$, and the results are given in Table II. In these experiments, a measured amount of water vapor was condensed on the catalyst solution by chilling with liquid nitrogen and a mixture in a closed volume and allowed to react at room temperature overnight. The final mixtures became cloudy. After the removal of volatile components with freeze drying, monomer was added. The water-treated residue was soon dissolved in monomer and finally gave a clear gel as a product (PPO swelled in PO). However, in excess water and an air-treated system, the residue did not dissolve, and finally, a turbid gel was formed.

$Sn^{iso}PXt$ was almost insensitive against the added water. $Zn^{iso}PXt$ was also quite resistant to the added water provided in that it was not added in excessive amounts. However, water acted as a transfer agent rather than a promoter in the last case. It appeared that metal xanthates, in contrast to metal alkyls and alkoxides, did not require water as a modifier for the synthesis stereoregular PPO.

It should be noted that when these stock solutions of catalysts were not kept in closed systems under an inert atmosphere, they became turbid and yellowish on prolonged storage.

Growth of the polymer

The percentage conversion with polymerization time (t) increased linearly with time for both systems; this

TABLE IV
Growth of $Sn^{iso}PXt$-Catalyzed PPO with t and Temperature Effects on Growth

Experiment number	t (h)	Temperature (K)	Conversion (%)	K conversion (%)	$M_v \times 10^{-4}$
18	6	355	5.60	1.7	81.2
19	17	355	9.10	3.2	80.4
20	36	355	12.6	4.6	93.2
21	72	355	15.8	6.8	67.8
22	120	355	23.9	8.9	69.4
23	240	355	36.3	12.5	77.4
24	72	369	21.6	5.6	46.1

Reaction conditions: PO = 1.43×10^{-1} mol, Sn = 7.20×10^{-4} mol, Sn/PO = 5.03×10^{-3} mol/mol.

TABLE V
Values of Coefficients a and b in Eq. (1) for $Zn^{iso}PXt$- and $Sn^{iso}PXt$-Catalyzed Polymerizations

Catalyst	[Catalyst] (mol/L)	$[PO]_o$ (mol/L)	a (mol/L)	b (mol L^{-1} s^{-1})	r^2
$Zn^{iso}PXt$	6.46×10^{-3}	14.3	14.1	-1.56×10^{-4}	0.996
$Sn^{iso}PXt$	7.20×10^{-2}	14.3	13.7	-6.11×10^{-6}	0.944

r^2, linear regression coefficient.

indicated a nonterminating, kinetically zeroth-order process for both of the systems. In a related work,[15] we observed that the copolymerization of PO with CS_2 with these catalyst systems was also nonterminating and a kinetically zeroth-order process. The experimental results are given in Tables III and IV.

The plotting of the instantaneous monomer concentration ([PO]) versus t yielded straight lines [Eq. (1)]:

$$[PO] = a - bt \qquad (1)$$

The values of a and b constants under the reaction conditions are given in Table V.

Although the absolute values of these constants showed some variation from one batch of catalyst to another or with aging of the stock solution (the activity of the catalysts increased somewhat with aging), the linear relation always held. However, at the initial stages, there was a noticeable deviation from zeroth-order rate law (e.g., if the point at $t = 0$, initial concentration of PO ($[PO]_o$) $= 14.291$ was omitted, then the r^2 values in Table V increased to 0.998 for Zn and 0.969 for Sn). These deviations were expected because Lal and Devlin[5] already showed that the initiation step involves enormous changes in the chemical nature of zinc xanthates, possibly by formation of Zn—S—Zn bonds after a number of successive steps.

The rate of consumption of PO at a constant $[PO]_o$ as a function of the catalyst concentrations was found, as shown in Tables VI and VII.

The values were obtained with Eq. (2):

$$-d[PO]/dt = c + f[Catalyst] \qquad (2)$$

where c and f are constants.
The values of c and f are given in Table VIII.

Finally, eqs. (1) and (2) could be combined as Eq. (3):

$$[PO] = a - (c + f[Catalyst])t \qquad (3)$$

The rate of polymerization dropped in a low-dielectric solvent, benzene (Table VI). In acetonitrile, together with the rate of process, the molecular weight of the product was markedly decreased. However, the effect of acetonitrile was attributable to its Lewis base character rather than a high dielectric constant. In fact when experiment 16 (Table III) was repeated by the addition of only 3.6 mmol of triethylamine ($Et_3N/Zn = 53$ and $Et_3N/PO = 0.026$ mol/mol), no polymer was formed, even in 18 h. The molecular weight of the polymer formed almost stayed constant with the reaction time for the Zn and Sn systems (Tables III and IV); this showed chain growth character rather than step growth. The molecular weight decreased with increasing catalyst concentration (Tables VI and VII). In general, the overall process for both of systems could be summarized as nonterminating, zeroth-order, chainwise growth where the molecular size was controlled by chain-transfer reactions, possibly second order with respect to growing species.

Effect of the alkyl group of xanthate on the growth of the polymers

Lal[6] showed that alkyl groups were rapidly transformed into other byproducts at the very beginning of polymerization; hence, one would not expect any important effect of alkyl groups on the growth of the polymer. However, our results indicate that under similar conditions; both the percentage conversion and percentage conversion to K polymers increased in the order of zinc ethyl xanthate

TABLE VI
Change of the Rate of Consumption of PO with $Zn^{iso}PXt$ Concentration in Bulk and in Solvents

Experiment number	$[Zn] \times 10^3$ (mol/L)	Conversion (%)	$-\Delta[PO]$ (mol/L)	$-\Delta[PO]/t \times 10^4$ (mol L^{-1} s^{-1})	$M_v \times 10^{-5}$
25	3.24	13.1	1.87	1.04	19.8
16	6.46	24.1	3.44	1.91	13.8
26	3.02	6.37	0.46	0.23	—
27	3.20	1.80	0.13	0.07	D polymer

Reaction conditions: temperature $= 355$ K, $[PO]_o = 14.3$ mol/L, reaction time $= 5$ h but in experiment 26 (solvent benzene) and experiment 27 (solvent acetonitrile) $[PO]_o = 7.15$ mol/L.

Experiment number	$[Sn] \times 10^2$ (mol/L)	Conversion (%)	$-\Delta[PO]$ (mol/L)	$-\Delta[PO]/t \times 10^6$ (mol L^{-1} s^{-1})	$M_v \times 10^{-5}$
28	1.80	3.18	0.45	7.43	2.36
29	3.60	4.86	0.69	11.3	2.31
30	7.20	9.16	1.31	21.4	1.98
31	18.0	18.6	2.66	43.5	1.40

Reaction conditions: temperature = 355 K, $[PO]_o$ = 14.3 mol/L, reaction time = 17 h.

(ZnEtXt) < zinc 2-octyl xanthate (ZnOctXt) < Zn$^{i\text{-}so}$PXt (Table IX).

We also searched the possibility of performing stereoelective polymerizations (i.e., polymerizing only D or L enantiomer of racemic PO) by using an optically active catalyst, zinc(+)-2-octyl xanthate [Zn(+)OctXt] at different temperatures. No optical activity in the K polymers was detected. To detect any optical activity in the recovered monomer from the polymerization mixture, a large-scale polymerization was performed at lower temperature with a chiral catalyst (experiments 40–43, Table IX). However, the leftover monomer was also optically inactive. However, the effect of chiral alkyl groups was interesting; they decreased the overall conversion, but the percentage conversion into K polymers was almost unaffected.

Characterization of the D polymers

Both f_{OH} (number of moles of OH groups in 1 g of D polymer) and f_{db} were measured, and the M_n value was calculated [$M_n = 2/(f_{OH} + f_{db})$]. The M_n values from end-group analysis and cryoscopic measurements are compared in Table X.

Fractionation of the K polymers

A sample for fractionation was prepared with the ZnOctXt catalyst in similar reaction conditions to those of experiment 37 (Table IX). The K polymers ($M_v > 5 \times 10^4$) were separated from the D polymers ($M_n < 10^3$) by precipitation in an isooctane solution at 273 K (75% of K polymers). Finally, the K polymers were fractionated, as described in the Experimental section. Among several fractions, only three of them were characterized in some detail (Table XI).

Consistent with previous results, precipitation from solution was controlled by T_m but not molecular weight.[9,14]

Assuming that stereoregular PPO was a random copolymer of part of PO that polymerize in isotactic diads (PO$_I$), giving isotactic diads with part of PO that polymerize in irregular diads (PO$_{II}$) but giving irregular diads (syndiotactic or head to head, etc.), we calculated the molar fraction of isotactic repeat units (x_s) from the T_m depressions[16] [Eq. (4)] for fractions F$_2$, F$_3$, and F$_4$ (Table XI):

$$1/T_m - 1/T_m^o = -(R/\Delta, H_u) \ln x_s \qquad (4)$$

where R is the gas constant (8.314 J/molK), T_m^o is the melting temperature of isotactic PPO in the standard state (355 K) and ΔH_u is the enthalpy change of fusion per repeat unit (8360 J/mol).[17]

Again by assuming that irregular repeat units coming from PO$_{II}$ were randomly distributed along the PO$_I$ residues, we calculated the degree of polymerization of isotactic segments between two irregular repeat units from Eq. (5)[16] (S_1; Table XI):

$$1/T_m - 1/T_m^o = (R/\Delta, H_u)(2/S_1) \qquad (5)$$

It should be noted that both of the previous assumptions ignored the possibility of stereoblocks (blocks of PO$_I$ and PO$_{II}$) of the microstructure of PPO. If the stereoblock structure existed, then, because of a diluent effect of atactic blocks, the x_s values would be lower, but the S_1 values would be higher than those calculated from eqs. (4) and (5). Whichever the case, the S_1 (and x_s) values of K polymers decreased gradually from one fraction to another as T_p decreased until the noncrystalline fraction appeared ($S_1 \leq 6$). Even in noncrystalline fractions, this gradual decrease in S_1 was observed in the ^{13}C-NMR data, where splitting in the methyl, methylene, and methane peaks due to stereoirregular and regioirregular dyads and triads increased with decreasing fractionation temperature.[9] Hence, there was no reason to postulate two different types of catalytic species that produced only isotactic chains and that produced only atactic chains.[1,18]

Catalyst	c (mol L^{-1} s^{-1})	f (s^{-1})	r^2
Zn^{iso}PXt	1.62×10^{-5}	2.71×10^{-2}	Only experiments 16 and 25 in Table VI were used
Sn^{iso}PXt	3.92×10^{-6}	2.22×10^{-4}	0.996

r^2, linear regression coefficient.

TABLE IX
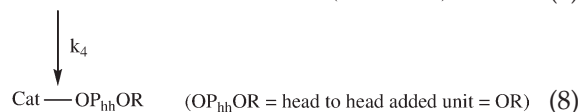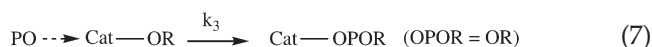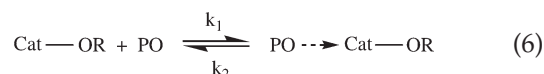**Effect of Alkyl Groups on Zinc Xanthates on the Growth of the Polymers**

Experiment number	Catalyst	Time (h)	Temperature (K)	Conversion (%)	K conversion (%)	$M_v \times 10^{-6}$
1	Zn^{iso}PXt	18	353	72.5	65.6	1.17
32	ZnEtXt	24	355	44.3	35.2	1.20
33	ZnEtXt	39	355	56.3	45.1	1.80
34	ZnEtXt	39	355	55.3	44.7	2.10
35	ZnEtXt	39	333	44.2	41.8	—
36	ZnEtXt	39	298	35.1	28.2	—
37	ZnOctXt	39	355	83.3	66.8	1.20
38	ZnOctXt	39	355	83.3	—	—
39	Zn(+)OctXt	39	357	73.3	67.2	1.10
40	Zn(+)OctXt	39	357	67.2	61.4	—
41	Zn(+)OctXt	39	328	53.8	47.6	0.30
42	Zn(+)OctXt	39	325	52.3	—	—
43	Zn(+)OctXt	39	312	20.1	16.2	0.12

Discussion on the growth mechanism of PPO

Potassium ethyl xanthate and potassium benzyl xanthate as a catalyst only yielded a low-molecular-weight (M_n = 250–350) oily product containing large quantities of cyclic thiocarbonates[7] from PO. However, in contrast, Zn (and Sn) xanthates, which functioned as a coordination catalyst, polymerized PO into a high-molecular-weight, partially crystalline polymer. The zeroth-order rate law could be satisfactorily explained by eqs. (6) and (7). In the reaction in Eq. (6), the hole in the coordination sphere of the catalyst, which was already carrying a growing polymer chain as an anion (RO), was rapidly filled with any enantiomer of the monomer. In other words, this step did not involve any stereoselection between the enantiomers. On the other hand, in the reaction in Eq. (7), RO, which was a ligand on the same metal (or more likely on the next metal of a bimetallic active center[4]), added a coordinated PO onto growing chain. Propagation was a high-activation-energy process because stereoselection occurred in this step[19] ($k_3 \ll k_1$ and k_2, where k_1, k_2, k_3 are the rate constants of corresponding reactions). The hole in the coordination sphere that was formed after the addition of monomer was rapidly refilled with the reaction in Eq. (6). Hence, the instantaneous concentration of monomer coordinated species did not depend on the monomer concentration and yielded a zeroth-order (or near to zeroth order) process.

The rate of the reaction in Eq. (7) is controlled by the chiralities of enantiomers. If the configuration of the coordinated monomer is not compatible with the active center: it is either removed from the coordination site by the reverse reaction in Eq. (6), or it is added on the growing chain to form a head-to-head

linkage [or syndiotactic dyad, Eq. (8); $k_3 > k_4$, where k_4 is the rate constant of corresponding reaction]:

$$\text{Cat} - \text{OR} + \text{PO} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{PO} \dashrightarrow \text{Cat} - \text{OR} \quad (6)$$

$$\text{PO} \dashrightarrow \text{Cat} - \text{OR} \xrightarrow{k_3} \text{Cat} - \text{OPOR} \quad (\text{OPOR} = \text{OR}) \quad (7)$$

$$\downarrow k_4$$

$$\text{Cat} - \text{OP}_{hh}\text{OR} \quad (\text{OP}_{hh}\text{OR} = \text{head to head added unit} = \text{OR}) \quad (8)$$

Zeroth-order rate law also implicitly indicates the absence of any termination reaction. If this is the case, then a step growth increase of molecular weight of the product with increasing t is expected. However, in Tables III and IV, no such increase was observed; on the contrary, the molecular weights almost stayed constant, like in a chain growth process. This showed the intervention of a transfer process, as observed from the presence of D polymers and the very broad molecular weight distribution of the K polymers.

TABLE XI
Fractionation of K Polymers from ZnOctXt-Polymerized PO

Fraction	T_p (K)[a]	$M_v \times 10^{-6}$[b]	T_m PM (K)[c]	T_m DSC (K)[d]	S_i[e]	x_s[f]
F$_2$	316	0.68	335	334	11.5	0.84
F$_3$	309	2.2	323	325	7.1	0.75
F$_4$	302	0.54	317	—	5.9	0.71

[a] T_p from isooctane solution.
[b] Viscosity-average molecular weight of fractions.
[c] Melting temperatures measured by polarized microscopy.
[d] Melting temperatures measured by differential scanning calorimetry.
[e] Estimated degree of polymerization of isotactic segments between two irregular repeat units with Eq. (5).
[f] Molar fraction of isotactic dyads estimated with Eq. (4).

TABLE X
M_n's of the D Polymers

Sample	M_n (cryoscopy)	f_{OH} (mmol/g)	f_{db} (mmol/g)	M_n (end group)
D polymers	528	0.13	4.16	466

These ideas on the zeroth-order reaction mechanism were strongly supported by the results obtained in the copolymerization of CS_2 with PO.[15]

CONCLUSIONS

A number of modified organometallic compounds were used for the synthesis of partially stereoregular PPO. However, all of these systems were too complicated to elucidate the exact nature of the catalyst and, therefore, the mechanism of stereoregular polymerization. Complications arose mainly from the unstable nature of the organometallic compounds, the fast rate of termination due to deactivation of the catalyst throughout the polymerization, and the formation of large amounts of D polymers throughout the process.

$Zn^{iso}PXt$ turned out to be quite stable, even under semiclosed conditions. Most importantly, the absence of any termination step led to a quite uncommon zeroth-order process, and this was interpreted as follows: not the stereoselection of the proper antipodes of monomer on the coordination site but rather the insertion of a coordinated monomer on the growing chain was the rate-determining step. In a forthcoming article, we will also show that these catalysts are unique in the synthesis of the high-molecular-weight copolymer of CS_2 with PO.[15]

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