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Stereochemical Factors in Epoxide Polymerization by Base and Coordination Catalysts*

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ABSTRACT

The amorphous fraction accompanying isotactic poly(propylene oxide) or poly(*tert*-butylethylene oxide) formed by coordination catalysts was shown by degradation to the dimer glycols to involve inversion of configuration at every ring opening at the secondary carbon atom for (*R*) - [or (*S*) -] PO and to involve no stereoselection in the coordination step for *tert*-BuEO. The crystalline poly(*tert*-BuEO) formed by polymerization with *tert*-BuOK was similarly shown to give equal amounts of erythro and threo dimer glycol. It is proposed that these dimer units arise from regular alternate isotactic and syndiotactic placements (*iso,syn*). Aryl glycidyl

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[†]From the doctoral dissertations of M. K. Akkapeddi (Stereochemistry and Kinetics of Base-Catalyzed Polymerization of Epoxides, 1971), B. T. DeBona [The Stereochemistry of Abnormal Diads in Amorphous Poly(propylene Oxide), 1971], and B. C. Furie [The Structures of Poly(*tert*-butylethylene Oxides), 1970].

ethers polymerized by *tert*-BuOK gave crystalline fractions shown to be isotactic (by comparison with crystalline polymer formed by coordination catalysts). The amount of the crystalline fractions decreased in the order $p\text{-CH}_3\text{O} > p\text{-CH}_3 > \text{H} > \text{Cl} \approx 2,6\text{-(CH}_3)_2$. Crystallinity for both *tert*-BuEO and aryl glycidyl ethers was markedly diminished in the presence of DMSO, HMPT, or dicyclohexyl-18-crown-6 macrocyclic ether. All of these observations are in accord with a model for the transition state involving coordination of the potassium ion at the active chain end with at least the next two adjacent ether groups.

I. AMORPHOUS POLYMER FROM COORDINATION CATALYSTS

By ozone degradation to dimeric glycol, it has been previously shown that the principle irregularity in the structure of the amorphous poly(propylene oxide) accompanying the isotactic polymer prepared by coordination catalysts does not arise from random configurations (atactic sequences), but from head-to-head sequences [1]. Price and Tumolo [1] advanced the hypothesis, based only on the optical rotation of such amorphous polymer fractions from the (*R*) [or (*S*)] monomer, that each insertion of a head-to-head unit involved an inversion of configuration in the structurally inverted monomer. In other words, the S_N2 ring opening which must occur at the asymmetric secondary carbon atom of the epoxide must, as expected, proceed with inversion of configuration at that atom.

The earlier degradation studies [1] were carried out on a polymer prepared from racemic monomer. We here report studies on the diad sequences in amorphous polymer fractions from (*R*) [or (*S*)] monomer. Examination of the sequences in such a polymer chain, III, reveals that if inversion of configuration accompanies structural inversion, the abnormal head-to-head (or tail-to-tail) diads will produce the two symmetrical dimer glycols V and VI in the meso configuration only.

By GLC, the diglycols from butyllithium degradation [2] of III can be resolved into four fractions. In order of increasing retention times, these are VI (meso and racemic), IV (erythro and threo), V (racemic), and V (meso).

Samples of meso and active dimer glycols V and VI were synthesized and characterized both to confirm the identity for the glc-separable isomers of V and to work out an assay procedure for the glc-inseparable

polymer was developed from the observation of significant difference in the ir spectra of the bis-p-nitrobenzoate esters in the 8.5-9- and 9.5-11.5- μ regions. The bands actually used were those at 8.69 (meso- and rac-VI) and 8.51 μ (meso-VI only).

The properties of the polymer samples studied and their degradation to dimer are summarized in Table 1. Note that the fractions prepared from acetone at -30° have a higher molecular weight and higher optical rotation than those from n-hexane at -78° , indicating that the latter procedure is significantly more selective.

One problem of concern to our interpretation of the degradation data is the extent to which an assumption of random cleavage to dimer glycols is justified. We have no experimental evidence for the random cleavage down to dimer, but the equally disturbing possibility of nonrandom further cleavage of dimer we have tested. The results are summarized in Table 2.

The data do indeed indicate some degree of selectivity, the rate of degradation being in the order rac-V > meso-V \approx IV > VI. However, the differences, even for the more severe conditions of the experiments reported in Table 2, suggest that we do not err substantially in interpreting the dimer glycol fractions from polymer degradation (Table 1) as being reasonably accurate reflections of the diad sequences in the original polymer.

The data in Table 1 clearly show that the amorphous polymer from racemic monomer (Samples 1, 2, and 3) gave the diprimary and disecundary glycols in roughly equal amounts of their meso and racemic diastereoisomeric forms. The lower amount for the racemic diprimary is in accord with its more rapid destruction by n-butyllithium (see Table 2).

The amorphous polymer from optically active monomer degraded to give largely meso-V and -VI. The fact that these are not more nearly 100% meso is not due to incomplete inversion of the head-to-head units, but due to the optical impurity of the monomer as shown in the last column of Table 1. Franzus and Surridge [3] have shown that, in the conversion of optically pure propylene glycol to bromohydrin, two isomers are formed. One is optically pure 1-bromo-2-propanol, which gives optically pure propylene oxide, $[\alpha]_D -8.39^\circ$ (CHCl_3). The other is 2-bromo-1-propanol, which gives propylene oxide of $[\alpha]_D -1.50^\circ$. Our intermediate bromohydrins had about 20% of the 2-bromo isomer by GLC. On the basis of the observed rotations of our monomer samples, one can calculate the enantiomer composition as indicated in the last column of Table 1. Considering the sources of error in analysis and in nonrandom degradation, the agreement of the observed results with those calculated in Table 1 based on the assumption of inversion at every ring opening at the secondary oxirane carbon is quite satisfactory. Further support for this hypothesis comes from the correlations of observed amount of

TABLE 1. Amorphous Poly(propylene Oxide) Samples and Their Degradation to Dimer Glycols

Monomer	Catalyst	% yield ^a	[α]D (deg)	\bar{M}_n^b	Degradation results (dipropylene glycols, % rel)			
					1°, 2°	2°, 2° (% meso) ^c	1°, 1° (% meso) ^c	Calc % meso ^d
RS	Et ₂ Zn-H ₂ O	80 ^c	0.0		81.0	8.9 (40)	10.3 (67)	50
RS	Et ₂ Zn-H ₂ O	50 ^d	0.0	2800	69.7	15.0 (40)	15.3 (69)	50
RS	FeCl ₃ -PO	82 ^c	0.0	5000	70.0	15.2 (42)	14.7 (64)	50
R	Et ₂ Zn-H ₂ O	85 ^d	-9.2	3000	66	16 (87)	18 (94)	90
R	Et ₂ Zn-H ₂ O	60 ^d	-5.9	2500	61.5	18.3 (79)	20.1 (84)	78
S	Et ₂ Zn-H ₂ O	75 ^c	-13.9	6500	80.8	8.8 (76)	10.4 (94)	82
S	FeCl ₃ -PO	87 ^c	+13.0	6000	69.1	13.7 (90)	17.2 (96)	88
S	FeCl ₃ -PO	69 ^d	+ 4.0	3500	60.8	20.2 (76)	19.0 (95)	76
RS	Et ₂ Zn-H ₂ O	e	0.0		98	~1	~1	

^aPercent yield after separation of crystalline fraction.

^bVapor pressure osmometer.

^cSoluble in acetone at -30°.

^dSoluble in n-hexane at -78°.

^eCrystalline polymer, mp 58° (capillary); $\bar{M}_v = 110,000$.

^fAverage of at least two mixtures.

^gEstimated from IR spectra of bis-p-nitrobenzoate esters.

^hCalculated as $100(N_S^2 + N_R^2)$, where N_S [mole fraction of (S)-propylene oxide in monomer] was estimated from the relationship $[\alpha]D = -16.78^\circ N_S + 8.39^\circ$.

TABLE 2. Control Degradations of Dimer Glycol Mixtures

Mixed glycols	Composition		BuLi/glycols
	Before (%)	After (%)	
Sample A			
Dissecondary	37	40	
Primary-secondary	45	47	
Diprimary (active)	8	6	2/1
Diprimary (meso)	9	6	
Sample B			
Dissecondary	37	50	
Primary-secondary	45	39	3/1
Diprimary (active)	8	2	
Diprimary (meso)	9	8	
Sample C			
Dissecondary	50	58	3/1
Primary-secondary	50	42	
Sample D			
Diprimary (active)	72	67	3/1
Diprimary (meso)	28	33	
Sample D	72	52	10/1
	28	48	

diprimary plus dissecondary glycols with that calculated from optical rotations of the amorphous polymer samples, assuming that all such diads would always be formed by inverting the configuration of the monomer unit inserted by attack at the secondary carbon atom (Table 3).

The polymerization of tert-butylethylene oxide (tert-BuEO) by coordination catalysts gives a crystalline polymer, mp 150°, assumed to be isotactic [4-6]. We have found by butyllithium degradation that this polymer gives a single dimer glycol VIIe, mp 48°. There was only about 3-7% of the threo isomer, VIIl, mp 60°, which may arise either from imperfections in the isotactic chains or imperfect separation of the amorphous polymer.

When the amorphous polymer fraction accompanying the isotactic poly(tert-BuEO) was similarly degraded [2], all three isomeric dimer glycols were observed on glc, as indicated in Table 4.

As has been shown to be the case for amorphous poly(propylene oxide)² formed via coordination catalysts, the amorphous fractions of poly(tert-BuEO) from such catalysts have many units incorporated in a

TABLE 3. Comparison of the Observed Amounts of Abnormal Di-propylene Glycols Isomers with Those Calculated from the Optical Rotation Values of the Corresponding Polymers

[α]D of polymer (deg)	Total diprimary and dissecondary glycols (%)	
	Obs ^a	Calc ^b
- 9.2	34	32
- 5.9	38.4	39
+13.9	19.2	23
+13.0	30.9	25
+ 4.3	39.2	42

^aSum of the values from Table 1.

^bAssuming one inversion for each head-to-head unit; [α]D \pm 26.3° for pure isotactic polymer.

TABLE 4. Dimer Glycols from Amorphous Poly(tert-BuEO) (Et₂Zn.H₂O Catalyst)

	IX	VIII	VII	% VIIe ^a
Sample I	20.0	40.8	39.1	42.6
	25.5	39.2	35.4	43.3
	26.5	42.0	31.5	39.3
Sample II	23.2	46.1	30.7	42.7
	24.8	44.6	30.6	42.7

^aBased on VII only.

head-to-head, tail-to-tail sequence. In fact, despite the neopentyl-like hindrance which might have been expected for ring opening at the secondary carbon in tert-BuEO, there is considerably more head-to-head polymer than for propylene oxide (compare Tables 3 and 4). If such sequences degraded purely randomly, there should have been an equal amount of the symmetrical dimer glycols VIII and IX formed. In every case (Table 4), the amount of the 1°,1°-isomer IX is less. This may

well be due to the fact that an ether link flanked by two tert-butyl groups (which would need to be preserved to give IX) is so strained that it degrades preferentially.

Another interesting feature which emerges from the data in Table 4 is that the sites which produce amorphous polymer are not only indiscriminate in the mode of ring opening, but must also be indiscriminate in the selection of D and L monomers, since the 1°,2°-dimer VII is nearly equally threo and erythro.

Most of the isomeric dimer glycols were identified by comparison with synthetic samples. The successful syntheses for the 1°,2°-dimer glycols VIIe and VIIf and for the 2°,2°-dimer glycol VIII are outlined in Chart 1. Since the preparation of VIII utilized racemic tert-BuEO

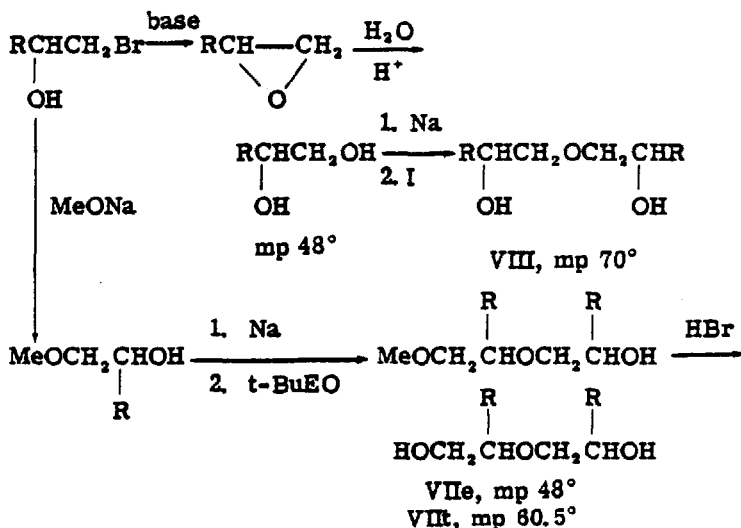


CHART 1. R = tert-Bu; Me = CH₃,

and racemic glycol, it should have produced a mixture of meso- and rac-VIII. We were unable to separate the mixture by recrystallization of GLC. This leaves the possibility open that the reaction to form dimer glycol may have been stereoselective for only one isomer. The synthesis of the dimer glycol VII led to isomers which were separable by distillation, recrystallization, or GLC, in contrast to the case of propylene oxide where the corresponding 1°,2°-dimer glycols were not resolvable. The identity of the erythro isomer VIIe was assumed from the fact that this isomer was 93-98% of the dimer glycol fraction from isotactic poly(tert-BuEO). A number of attempts to prepare the 1°,1°-isomer IX were unsuccessful so that the identification of the long-retention peak as IX must be regarded as tentative. The GLC characteristics of the glycols are summarized in Table 5.

TABLE 5. Some Properties of Dimer Glycols of tert-BuEO

Compound	GLC retention time (min)	Mp (°C)
VIII, synth	38.4	67.0-68.5
From degrad	38.4	66.0-68.5
VIIe, synth	48.8	45.5-48.0
From degrad	48.8	46.0-49.0
VIII, synth	52.1	58.0-60.5
From degrad	52.1	58.0-61.0
IX, from degrad	60	a

^aThis peak, appearing only for amorphous polymer from coordination catalysts, was always the least plentiful isomer (see Table 4) and we were not able to isolate enough to characterize the material by melting point or analysis.

II. STEREOSELECTION FACTORS IN BASE-CATALYZED POLYMERIZATIONS

The polymerization of tert-butylethylene oxide by potassium tert-butoxide has been found [4, 5] to give a crystalline polymer differing in configuration from that produced by coordination catalysts [4-6]. This behavior contrasts to that of phenyl glycidyl ether which gives crystalline polymer by base catalysis of the same isotactic configuration as by coordination catalysts [7, 8].

On the basis of NMR data, it was proposed that the configuration of crystalline base-catalyzed poly(tert-BuEO) was syndiotactic, with two skew conformations at the C-C backbone bond [5]. Tani and Oguni [9] have suggested the alternative possibility that the two sets of NMR lines for the backbone hydrogens arise from roughly equal numbers of isotactic and syndiotactic placements, although they made no decision between long blocks or a regular alternating sequence.

Degradation of this polymer by butyllithium has now shown it does indeed contain equal numbers of isotactic and syndiotactic placements as suggested by Tani and Oguni [9]. The results as summarized in Table 6 clearly show that this polymerization proceeds almost exclusively to form head-to-tail sequences, presumably due to highly preferential S_N2 attack at the primary carbon. It is also evident that the polymer has roughly equal amounts of isotactic and syndiotactic sequences, as indicated by the relative amounts of erythro- and threo-VII. The fact that the polymer, at least when prepared in bulk, is crystalline indicates that the equal proportions of VIIe and VIII cannot

TABLE 6. Dimer Glycols from Poly(tert-BuEO) (tert-BuOK Catalyst)

Polymer ^a	VIII	VII	VIIe (%) ^b
Bulk, Prep I	0.95	99.1	56.4
	1.37	98.6	58
	2.11	97.9	57.2
Prep II	3.95	98.1	54.8
	3.85	96.2	54.1
DMSO, Prep I	4.24	95.8	47.5
	4.37	95.6	48.1
Prep II	6.10	93.9	46.7
	9.16	90.9	49.1

^aThe bulk polymer is crystalline, while that prepared in DMSO is amorphous. Two different samples of each polymer were degraded two or three times each.

^bBased on VII only.

be due to atactic polymer sequences. The two alternatives would seem to be long blocks of isotactic and syndiotactic sequence in roughly equal amounts, or regularly alternating "iso,syn" sequences, i.e., regularly alternating isotactic and syndiotactic placements.

It seems highly unlikely that a single propagating species could produce crystalline block copolymers of isotactic and syndiotactic sequences without producing a great deal of atactic polymer as well. We therefore prefer the latter structure for the polymer. In fact, a reasonable mechanism for forming such a structure, involving chelation of ether groups by the potassium cation, is proposed below. The importance of ether groups in coordinating with cations has been demonstrated by Pederson [10] and is believed to be involved in the biological function of the macrocyclic antibiotics [11].

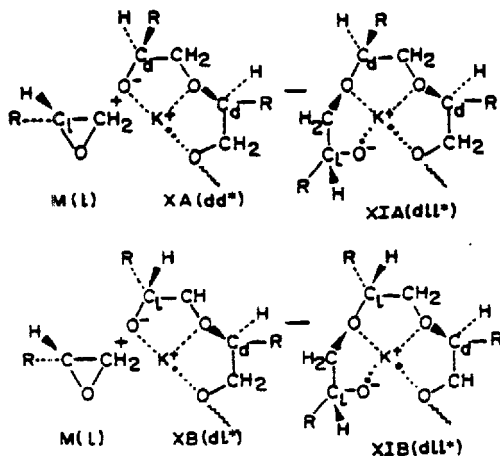
An interesting feature of the regular isosyn stereochemical sequence ddlddldl, etc., is that incoming configuration is always opposite to that of the penultimate unit at the growing end, i.e., $k_{ddl} \gg k_{ddd}$ and $k_{dll} \gg k_{dlld}$. Models approximating the transition state which account for such a sequence of relative reactivities are indicated below (XIA and XIB). These models assume that the growing chain end (XA or XB) will exist principally with an ion-pair bond between the terminal alkoxide anion and potassium cation and with the latter coordinated to at least two of the nearest ether oxygens. In the transition involving addition of a new monomer unit (M), the initial geometry will have the terminal O-, the primary oxirane carbon, and the oxirane oxygen in the essentially linear geometry required for an S_N2 displacement reaction at the

carbon. As the reaction proceeds, with negative charge developing on the oxirane oxygen, this oxygen will move as quickly and easily as possible to coordinate with the K^+ , as indicated by XIA (or XIB).

It should be pointed out that the models XIA (ddl^*) and XIB (dll^*) are diastereoisomeric. They would not be expected to have equal energies, nor equal rates of formation. What is essential is that the rate of formation of XIA (ddl^*) be considerably greater than that of ddd^* (which would give *iso,iso* sequences) and that the rate of formation of XIB (dll^*) be considerably greater than that of dld^* (which would give *syn, syn* sequences).

In order to clarify the steric features which would lead to the expectation of the observed regular *iso, syn* sequences, consider the model XA. Note that in the two fused rings, the planes of the two five-membered rings have a sharp angle, dictated largely by the COC bond angle. Each ring has a tert-butyl group, one on a carbon α to the ring junction, one on a carbon β to the ring junction. Models indicate that the van der Waals radii of an α -*cis*-tert-butyl group and an α' *cis* hydrogen would overlap by about 2.0 Å and thus α -*cis*-tert-butyl would be strongly disfavored compared to α -*trans*-. A β -*cis*-tert-butyl group would fail to overlap α' (or β') hydrogens by ca. 0.2-0.5 Å and so would be disfavored but little compared to a β -*trans*-tert-butyl. It is on this basis that we have chosen the indicated conformations of XA and XB with the α -tert-butyl *trans* to the adjacent ring.

Model XIA does involve an α -*cis*-tert-butyl placement of the central tert-butyl group. However, the alternative of adding a D monomer to give *iso, iso* sequences would involve an α -*cis*-tert-butyl- β -*cis*-tert-butyl interaction. This would be strongly disfavored because of a



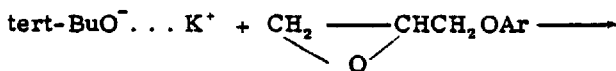
severe interference ($\sim 2.5 \text{ \AA}$) of the van der Waals radii of two tert-butyl groups.

For model XIB, there is a mildly unfavorable β -cis-tert-butyl interaction for the central tert-butyl group. However, if the D monomer were to add, giving syn,syn sequences, there would be a second mildly unfavorable β -cis-tert-butyl interaction.

A simplified statement of the stereochemistry producing preferred iso,syn sequences is that 1) the models XA and XB have their conformation dictated by preference for the α -tert-butyl to be trans and 2) the transition states XIA and XIB then select monomer to put the incoming β -tert-butyl in a β -trans position.

The failure to obtain a crystalline polymer from tert-BuEO by tert-BuOK polymerization in DMSO is in accord with the hypothesis that chelated structures X and XI are important in determining stereoselection. With HMPT as solvent amorphous polymer is also produced, but in this case the molecular weight is not lowered, as it is by chain transfer with DMSO molecules. The strongly polar DMSO or HMPT molecules, with a strong negative field around the oxygen atom, would tend to displace the less polar ether oxygens from the K^+ in X and XI. Similarly, the observation that dicyclohexyl-18-crown-6 macrocyclic ether [10] produced amorphous polymer also fits with the importance of chelation to stereoselection. The 18-crown-6 ethers have strong tendencies to coordinate with potassium and would thus markedly diminish its capacity to order the structure of the growing polymer chain as shown in models X and XI.

On the basis of the fact that polymerization of phenyl glycidyl ether (PGE) in DMSO with potassium tert-butoxide as catalyst gave increased (although low) yields of crystalline, acetone-insoluble isotactic polymer with increased catalyst concentration, it was suggested that ion-pair association of K^+ with the growing alkoxide unit in base-catalyzed polymerization was important in promoting stereoselection [7]. It was also suggested that chelation of this K^+ with adjacent ether groups including the aryl ether was involved [5].



XII, Ar = C_6H_5

XIII, Ar = $p\text{-CH}_3C_6H_4$

XIV, Ar = $p\text{-CH}_2OC_6H_4$

XV, Ar = $p\text{-ClC}_6H_4$

XVI, Ar = $2,6\text{-(CH}_3)_2C_6H_3$

XVII, Ar = $2,4,6\text{-(CH}_3)_3C_6H_2$

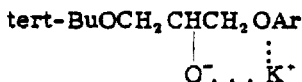


TABLE 7. Preparation and Properties of Poly(phenyl Glycidyl Ethers)

Substance	By Et ₂ Zn-H ₂ O		By tert-BuOK, cryst				Amorphous				
	% benzene yield	Mp (°C)	[η]	Major x-ray spacings (Å)	Mp (°C)	Major x-ray spacings (Å)	[η] (mol wt) ^f	% Sp yield (°C)			
H	96	200-203	1.12	8.0, 8.5, 4.1, 3.8	96-102	8.0, 4.7, 4.1, 3.8	0.08 (6400)	80	60-72	0.07	
p-Me	90	200-205	1.0	4.6, 4.1, 3.5	105-112	4.6, 4.1, 3.5	0.08 (12,000)	75	50-65	0.05	
p-MeO	98	190-200	1.0	4.5, 4.1, 3.7, 3.4	36 ^{c,d}	113-115	4.6, 4.2, 3.9, 3.6	0.1 (17,000)	64	75-85	0.08
p-Cl	74	185-192	2.09	7.5, 4.5, 4.0	None		(5500)	98	Semi-solid	0.04	
2,6-Me ₂	85	125	1.04	6.9, 4.0	None		(3900)	82	Semi-solid		

^aAnalysis: Calculated for C₁₁H₁₄O₂: C, 74.19; H, 7.86. Found: C, 73.90; H, 7.88.

^bIn DMSO, 12%, mp 105-112°.

^cIn DMSO, 14%, mp 110-115°; in HMPT, 6%; in bulk with dicyclohexyl-18-crown-6 added equivalent to catalyst, 6.7%, mp 110-115°.

^dThe crystalline polymer from Et₂Zn or tert-BuOK showed bands at 1352, 1150, 890, and 870 cm⁻¹ in KBr which were not present in CHCl₃ or CS₂ solutions nor in the acetone-soluble polymer from tert-BuOK nor in polymer prepared in DMSO or HMPT or with dicyclohexyl-18-crown-6 added. The latter polymers were all amorphous glasses, softening point ~75-90°.

^eIn benzene at 30°, dl/g.

^fBy Mechrolab Vapor Osmometer.

Evidence in support of chelation by the aryl ether group in PGE has been obtained by polymerization of analogs of PGE in which suchelation would be enhanced (p-methyl- and p-methoxy-) or inhibited (p-chloro- and 2,6-dimethyl-). As seen in Table 7, the p-methoxy derivative (Hammett $\sigma = -0.27$) gave more crystalline polymer than did the p-methyl ($\sigma = -0.17$), while the p-chloro ($\sigma = +0.23$) gave no polymer of sufficient isotacticity to be insoluble in acetone at room temperature. A negative σ constant would be expected to enhance the ability of the aryl ether to coordinate with potassium while a positive σ constant would have the opposite effect. Two o-methyl groups, while promoting the basicity of the aryl ether electronically, would be expected to offer strong steric interference with chelation.

Even XIV, which gave 36% of crystalline polymer in bulk polymerizations, gave only 14% in DMSO and 6% in HMPT. It was also shown that dicyclohexyl-18-crown-6 macrocyclic ether reduced the amount of crystalline polymer formed from XIV from 36 to 7%.

The experimental evidence thus supports the view that chelation of ion-paired K^+ at the growing chain end promotes stereoselection in favor of isotactic sequences. The evidence indicates that coordination at the aryl ether oxygen is important. In fact, this extra ether oxygen must be crucial in directing the propagation isotactically rather than in the regular isosyn sequence found for polymerization of tert-butylethylene oxide by the same catalyst under the same conditions. Actually the only modification necessary in models XA and XIA is to recognize that the aryl ether group in incoming monomer could coordinate to K^+ in XA only if the aryl ether group were (D configuration), leading to an isotactic sequence (ddd*) in XIA.

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