Polymerization of Bicyclic Acetals. 11. Steric Control in the Cationic Ring-Opening Polymerization of the Two Stereoisomers of 4-Bromo-6,8-dioxabicyclo[3.2.1]octane

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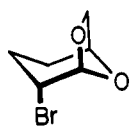
ABSTRACT: The present paper describes steric control in the cationic ring-opening polymerization of 4-bromo-6,8-dioxabicyclo[3.2.1]octane (4-BrDBO) as revealed by ^{13}C NMR analysis of the polymers obtained under various conditions (initiators, antimony pentafluoride and trifluoromethanesulfonic acid; solvent, methylene chloride; temperature, −90 to −30 °C) and of their reductive debromination products by tri-*n*-butylstannane. The polymers of the equatorially substituted monomer (4(e)-BrDBO) and its mixtures with the axial counterpart (4(a)-BrDBO) consisted of tetrahydropyran-2,6-diyloxymethylene backbone structures, indicating the exclusive occurrence of the C(5)–O(6) bond cleavage of the monomers in the polymerization. The polymerization of 4(e)-BrDBO at −60 °C or below gave stereoregular polymers consisting of "α-form" units and being rich in isotactic sequences of the D,L-enantiomeric units. In contrast, the polymerization of stereoisomeric mixtures of 4(a)-BrDBO and 4(e)-BrDBO provided stereoirregular polymers composed of "α-form" and "β-form" units even at a temperature as low as −90 °C. The α-form content in the polymers decreased with increasing 4(a)-BrDBO content in the initial monomer mixtures. These results are discussed in terms of enantiomer selection at growing chain ends and bromonium ion participation of a terminal 4(a)-BrDBO unit in propagation.

There have been numerous publications on the stereospecific ring-opening polymerization of various cyclic monomers, including epoxides, episulfides, lactones, and α-amino acid *N*-carboxy anhydrides.[1-4] Stereospecific polymerizations of these monomers have been performed in most cases by using coordinated catalysts, and they are satisfactorily interpreted in terms of the enantiomorphic catalyst site control mechanism.[2] Alternatively, some stereospecific polymerizations, for example, the polymerization of *tert*-butylethylene oxide by potassium *tert*-butoxide[5,6] and the polymerization of D,L-amino acid *N*-carboxy anhydrides by trialkylaluminum[7,8] and primary amines,[9,10] proceed through the growing chain control mechanism.[2]

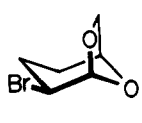
Previously, we reported the first example for stereospecific ring-opening polymerization of cyclic acetals by a conventional initiator:[11] In the polymerization of 6,8-dioxabicyclo[3.2.1]octane initiated with boron trifluoride etherate, stereoregular polymers having an isotactic dyad content of up to 84% were obtained at low temperatures. It was confirmed by D,L copolymerization experiments of enantiomerically unbalanced monomer that the preferred formation of the isotactic sequence along the polymer chain is primarily due to the stereoregulation displayed by the growing chain end.

Recently, we investigated the ring-opening polymerization of 4-bromo-6,8-dioxabicyclo[3.2.1]octane, with emphasis on the reactivities of its axially and equatorially substituted stereoisomers.[12] (Hereafter, they are referred to as 4(a)-BrDBO and 4(e)-BrDBO, respectively.) Whereas 4(e)-BrDBO underwent polymerization in the presence of antimony pentahalide and trifluoromethanesulfonic acid initiators to give relatively low molecular weight polymers, stereoisomeric mixtures of 4(a)-BrDBO and 4(e)-BrDBO were polymerized even with boron trifluoride etherate, which was an ineffective initiator for the polymerization of 4(e)-BrDBO to give rise to higher molecular weight polymers. The reactivity of 4(a)-BrDBO was higher than that of 4(e)-BrDBO over a wide range of reaction conditions. Furthermore, isomerization of 4(e)-BrDBO to 4(a)-BrDBO occurred during the polymerization above −30 °C, especially when trifluoromethanesulfonic acid was used as the initiator. These results were discussed from kinetic and thermodynamic standpoints in a previous paper.[12]

The present paper describes steric control in the ring-opening polymerization of 4-BrDBO as revealed by the ^{13}C NMR analysis of the polymers obtained under various conditions and their reductive debromination products.



4(a)-BrDBO



4(e)-BrDBO

Experimental Section

Materials. 4-Bromo-6,8-dioxabicyclo[3.2.1]octane was obtained as a mixture of axially and equatorially substituted stereoisomers, 4(a)-BrDBO and 4(e)-BrDBO, from acrolein dimer by the procedure of Brown et al.[13] with a slight modification.[12] It was difficult to isolate each component by conventional methods such as fractional distillation and column chromatography. Therefore, the mixture was treated with sodium hydride in 1,2-dimethoxyethane to remove 4(a)-BrDBO as 6,8-dioxabicyclo[3.2.1]oct-3-ene,[14] and the unreacted 4(e)-BrDBO was recovered by fractional distillation. 4(e)-BrDBO thus obtained was confirmed to be free from 4(a)-BrDBO by ^{13}C NMR and gas chromatography.

Polymerization. Polymerization of pure 4(e)-BrDBO and its mixture with 4(a)-BrDBO was carried out in methylene chloride at temperatures ranging from −90 to −30 °C, with antimony pentafluoride and trifluoromethanesulfonic acid as the initiators. The polymerization and workup procedures were the same as those described in the previous paper.[12]

Characterization. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 25 MHz, deuteriochloroform and tetramethylsilane being used as the solvent and internal reference. Molecular weights of the polymers were measured by a Hewlett-Packard Model 302 vapor pressure osmometer in benzene solutions at 37 °C or by a Hitachi 634A gel permeation chromatograph (column, Shodex 80M, 1 m; eluent, chloroform).

Preparation of Tri-*n*-butylstannane. Tri-*n*-butylstannane was prepared according to the synthetic procedure for triphenylstannane:[15] Lithium aluminum hydride (0.80 g) and dry ethyl ether (75 mL) were placed in a three-necked flask equipped with a condenser, a dropping funnel, and a nitrogen gas inlet. With external ice cooling, tri-*n*-butylchlorostannane (17.0 g) was slowly added with magnetic stirring under a stream of nitrogen. After the addition of the reagent, the reaction mixture was stirred for a further 3 h at room temperature. Subsequently, water (50 mL) was cautiously added to the reaction mixture. The ether layer was washed twice with water and dried over anhydrous magnesium

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Table I
Polymerization of 4-Bromo-6,8-dioxabicyclo[3.2.1]octane[a]

monomer comp, %						polymer comp, %		
ax[b]	eq[b]	initiator	temp, °C	time, h	yield,[c] %	ax[d]	eq[d]	α form,[e] %
0	100	CF_3SO_3H	−30	48	72[f]	0	100	~100
37	63	CF_3SO_3H	−30	96	60	60	40	79
0	100	SbF_5	−60	24	85	0	100	97
42	58	SbF_5	−60	48	71	47	53	82
0	100	SbF_5[g]	−78	25	37	0	100	97
20	80	SbF_5[g]	−78	25	39	31	69	85
40	60	SbF_5[g]	−78	2.5	34	45	55	79
61	39	SbF_5[g]	−78	2.5	67[h]	69	31	78
0	100	SbF_5	−90	24	28	0	100	~100
42	58	SbF_5	−90	48	28	61	39	78

[a] Monomer, 5 mmol; solvent, CH_2Cl_2, 0.6 mL; initiator 5 mol % to monomer. [b] ax, 4(a)-BrDBO; eq, 4(e)-BrDBO. [c] Methanol-insoluble polymer. [d] ax, structural unit from 4(a)-BrDBO monomer; eq, structural unit from 4(e)-BrDBO monomer. [e] By ^{13}C NMR spectroscopy. [f] $M_n = 8.9 \times 10^3$. [g] Monomer, 10 mmol; solvent, CH_2Cl_2, 2.0 mL; initiator, 2 mol % to monomer. [h] $M_n = 4.3 \times 10^3$.

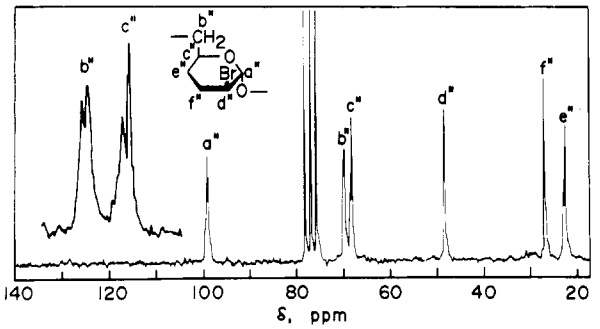


Figure 1. ^{13}C NMR spectrum of poly(3(a)-bromotetrahydropyran-6,2-diyloxymethylene) prepared at −90 °C with antimony pentafluoride: solvent, $CDCl_3$; temperature, 50 °C; 25 MHz; internal reference, Me_4Si.

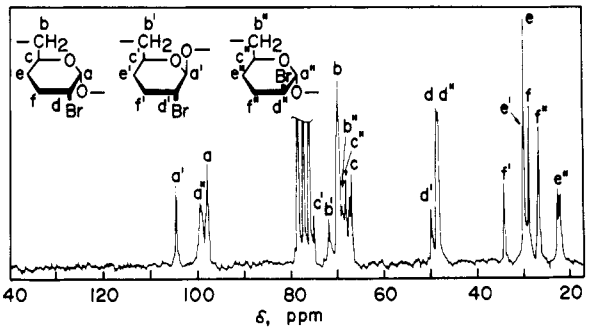


Figure 2. ^{13}C NMR spectrum of poly(3-bromotetrahydropyran-6,2-diyloxymethylene) prepared from a stereoisomeric mixture of 4(a)-BrDBO and 4(e)-BrDBO (42:58) at −90 °C with antimony pentafluoride: solvent, $CDCl_3$; temperature, 50 °C; 25 MHz; internal refernce, Me_4Si.

sulfate. The solvent was removed under reduced pressure, and the residue was rapidly distilled under vacuum to give tri-*n*-butylstannane, bp 55–61 °C (0.08 mmHg) (lit.[15] bp 68–74 °C (0.3 mmHg)).

Reductive Debromination of Poly(3-bromotetrahydropyran-6,2-diyloxymethylene). A sample of polymer (0.15 g), azobis(isobutyronitrile) (0.01 g), tetrahydrofuran (20 mL), and tri-*n*-butylstannane (1.2 g) were charged in this order in a three-necked flask equipped with a condenser and a nitrogen gas inlet. The mixture was stirred at reflux temperature for 25 h under a stream of nitrogen. The reaction mixture was concentrated by removing tetrahydrofuran under reduced pressure. Subsequent addition of *n*-hexane to the mixture precipitated the polymer. Unreacted reducing reagent and tri-*n*-butylbromostannane formed in the reaction were removed from the precipitated polymer by repeated washing with *n*-hexane. The polymer thus obtained was dried under vacuum to a constant weight.

Results

Polymerization of 4(e)-BrDBO and its mixture with 4(a)-BrDBO was carried out in methylene chloride at temperatures between −90 and −30 °C by using antimony pentafluoride and trifluoromethanesulfonic acid as initiators. Figure 1 shows a typical ^{13}C NMR spectrum of the polymer prepared from 4(e)-BrDBO at −90 °C with antimony pentafluoride. The simple pattern indicates that the polymer (IUPAC nomenclature: poly(3(a)-bromotetrahydropyran-6,2-diyloxymethylene) is composed almost entirely of a structural unit in which the exocyclic oxygen lies in the axial position of the tetrahydropyran ring (α form in the terminology of carbohydrate chemistry).

As clearly demonstrated in the expanded spectrum of the acetal carbon region, the signals a″, b″, c″, and e″ are split into two peaks with different intensities. By comparison of the chemical shifts of the polymer derived from racemic 4(e)-BrDBO with those of the optically active polymer of (+)-(1*R*,4*R*,5*S*)-4-bromo-6,8-dioxabicyclo-[3.2.1]octane, we have recently confirmed that these splittings arise from the dyad tacticity of the D,L-enantiomeric units along the polymer chain.[16] However, the difference in the chemical shifts of each signal pair is too small to allow an accurate determination of the dyad tacticity of the racemic polymer from the relative peak intensities of each signal pair. The difficulty was overcome by reductively debrominating the polymer obtained from 4(e)-BrDBO and analyzing the ^{13}C NMR spectrum of the product. This will be described in a later section.

Figure 2 presents the ^{13}C NMR spectrum of the polymer prepared from a stereoisomeric mixture of 4(a)-BrDBO and 4(e)-BrDBO (42:58) at −90 °C with antimony pentafluoride as the initiator. The spectrum is highly complicated by the presence of three structural units, that is, the α form and β form of 4(a)-BrDBO monomeric units and the α form of 4(e)-BrDBO monomeric units. (The β form is a structural unit in which the exocyclic oxygen is equatorially oriented to the tetrahydropyran ring.) On the basis of the assignments given in Figure 2, the α-form content was determined from the relative peak areas of a + a″ and a′.

Table I summarizes some of the results of the polymerization of 4-BrDBO with different isomer compositions. Comparison of the compositions of the initial monomer with those of the polymerized monomer indicates that the reactivity of 4(a)-BrDBO is higher than that of 4(e)-BrDBO. It is noteworthy that the α-form content of the polymer decreases with increasing 4(a)-BrDBO content in the initial monomer. In addition, the formation of the polymer having an appreciable amount of the β form from a stereoisomeric mixture of 4(a)-BrDBO and 4(e)-BrDBO even at a temperature as low as −90 °C is noticeable. This

Table II
Reductive Debromination of Poly(3-bromotetrahydropyran-6,2-diyloxymethylene)[a]

polymn condn		polymer comp, %		polymer,	Bu_3SnH,	AIBN,	time,	debrominated polymer	
initiator	temp, °C	ax[b]	eq[b]	g	g	mg	h	α form,[c] %	iso dyad,[d] %
CF_3SO_3H	−30	0	100	0.15	1.14	10	25	~100	66
SbF_5	−60	0	100	0.19	1.44	20	60	~100[e]	73
SbF_5	−90	0	100	0.11	0.83	10	60	~100[f]	76
CF_3SO_3H	−30	60	40	0.15	1.16	10	25	79	
SbF_5	−60	47	53	0.15	1.10	11	25	78	
SbF_5	−90	61	39	0.08	0.70	6	25	75	

[a] In tetrahydrofuran (20 mL) under reflux. [b] ax, structural unit from 4(a)-BrDBO monomer; eq, structural unit from 4(e)-BrDBO monomer. [c] By ^{13}C NMR spectroscopy (acetal carbon). [d] By ^{13}C NMR spectroscopy (methine carbon). [e] $M_n = 4.1 \times 10^3$. [f] $M_n = 8.5 \times 10^3$.

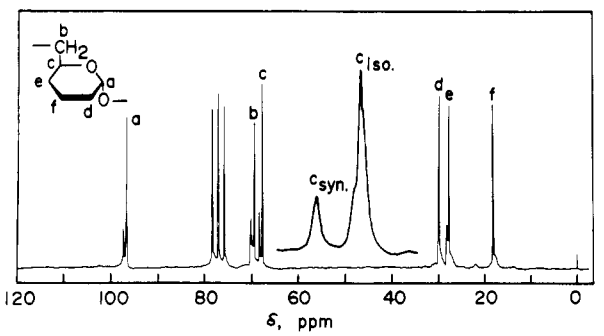


Figure 3. ^{13}C NMR spectrum of the reductive debromination product of poly(3(a)-bromotetrahydropyran-6,2-diyloxymethylene) prepared at −90 °C: solvent, $CDCl_3$; temperature, 50 °C; 25 MHz; internal reference, Me_4Si.

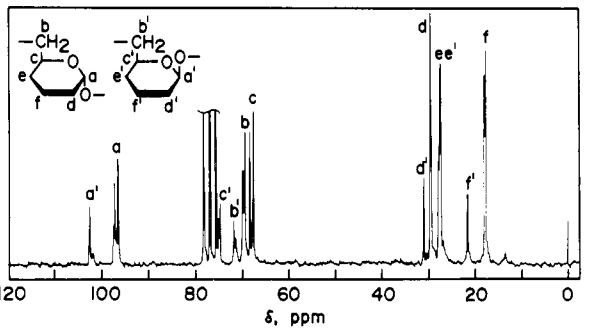


Figure 4. ^{13}C NMR spectrum of the reductive debromination product of poly(3-bromotetrahydropyran-6,2-diyloxymethylene) prepared from a stereoisomeric mixture of 4(a)-BrDBO and 4(e)-BrDBO (42:58) at −90 °C: solvent, $CDCl_3$; temperature, 50 °C; 25 MHz; internal reference, Me_4Si.

is of significance from a mechanistic point of view, because polymers consisting entirely of α-form units are generally formed in the polymerization of 6,8-dioxabicyclo[3.2.1]-octane and its derivatives, including 4(e)-BrDBO, at such a low temperature.[11,12] Therefore, the formation of the stereoirregular polymers from monomer mixtures of 4(a)-BrDBO and 4(e)-BrDBO strongly suggests that the axially oriented bromine atom in 4(a)-BrDBO plays an important role in the propagation step.

Reductive debromination of the polymers of 4-BrDBO was undertaken in order to confirm their backbone structures. Tributylstannane, which has been recently used with success for the reductive dechlorination of poly(vinyl chloride),[17-19] was chosen as a reducing reagent, since dehalogention by this reagent takes place via a radical mechanism[15] and hence it does not require the energetically unfavorable flipping of the tetrahydropyran ring in a polymer chain unlike S_N2 reactions. The reductive debromination was carried out in tetrahydrofuran at reflux temperature in the presence of a small amount of azobis(isobutyronitrile). The reaction proceeded smoothly to give a perfectly debrominated polymer in quantitative yield.

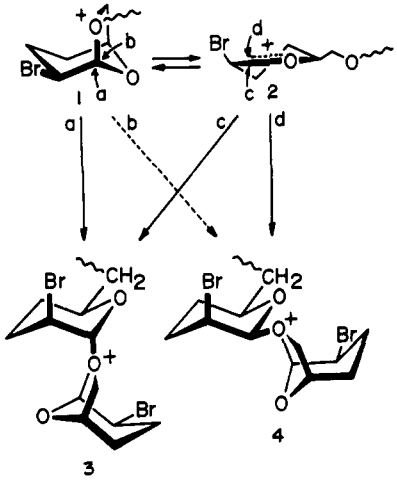
The ^{13}C NMR spectrum of the debromination product of the polymer prepared from 4(e)-BrDBO at −90 °C with antimony pentafluoride is shown in Figure 3. The signal pattern is essentially identical with that of poly(tetrahydropyran-2,6-diyloxymethylene) consisting of α-form units prepared by the low-temperature polymerization of 6,8-dioxabicyclo[3.2.1]octane with boron trifluoride etherate as the initiator.[11] This provides definite evidence that the polymer obtained from 4(e)-BrDBO is composed of the tetrahydropyran-2,6-diyloxymethylene backbone structures and that the bond cleavage of the monomer occurs exclusively at the C(5)–O(6) bond.

In the ^{13}C NMR spectrum of the debrominated polymer, the signals a, b, c, and e are split into two peaks of different intensities. Previous work has confirmed that the higher field peak of each signal pair is ascribable to the dyad structures of D,D or L,L consecutive units (isotactic dyad), whereas the lower field peak is assignable to the dyad structures of the D,L-enantiomeric pair (syndiotactic dyad).[20] As the expanded spectrum of the signal c demonstrates, the two peaks are well separated, from which the dyad tacticity of the polymers can be evaluated. Since the reductive debromination proceeds completely under the reaction conditions employed and the tacticity of the polymer is not altered by this procedure, it is safely postulated that the tacticity of the debrominated polymer is equal to that of the original polymer.

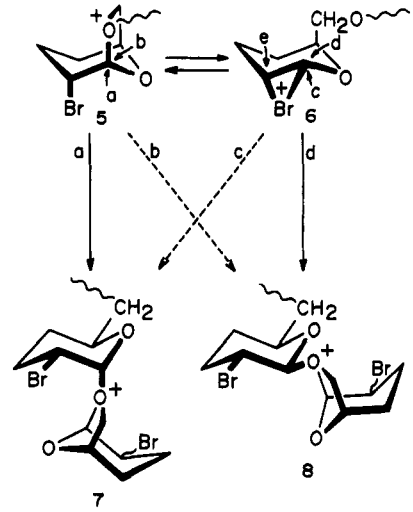
Figure 4 presents the ^{13}C NMR spectrum of the reductive debromination product of the polymer derived from a stereoisomeric mixture (4(a)-BrDBO:4(e)-BrDBO = 42:58). Compared with the spectrum in Figure 3, there appear several additional signals assignable to the β-form unit. The coexistence of α-form and β-form units in a polymer chain makes the ^{13}C NMR pattern complicated, particularly in the acetal carbon region.[11] Thus the chemical shifts are affected not only by the dyad sequences of the D- and L-enantiomeric units but also by the sequences of α-form and β-form units. Therefore, the dyad tacticity of the polymers containing an appreciable amount of the β-form unit cannot be determined by this method.

Table II summarizes the results of the reductive debromination and the determination of the stereoregularity of the polymers. The α-form contents of the debromination products evaluated from the relative peak areas of the acetal carbons were in good agreement with those of the original polymers within the accuracy of the measurement. This proves the validity of the previous assignments of the ^{13}C NMR spectrum of the polymers prepared from 4-BrDBO.[12] The isotactic dyad content of poly(3(a)-bromotetrahydropyran-6,2-diyloxymethylene) derived from 4(e)-BrDBO varies from 66 to 76%, depending upon the reaction conditions. The polymer having the highest iso-

Scheme I
Propagation Processes in the
Polymerization of 4(e)-BrDBO



Scheme II
Bromonium Ion Participation in the Propagation
Involving a 4(a)-BrDBO Terminal Unit



tactic content was obtained in the polymerization at −90 °C with antimony pentafluoride as the initiator.

Discussion

As described in the foregoing section, the polymers obtained from 4(e)-BrDBO, especially those obtained at lower temperatures, were almost entirely composed of α-form units. This is a clear indication that the polymerization of 4(e)-BrDBO proceeds through an S_N2-type mechanism involving a trialkyloxonium ion (1) (Scheme I); i.e., monomer attacks the acetal carbon of the oxonium ion from the opposite side of the C–O$^+$ bond (arrow a) to give the α-form unit (3). At higher temperatures, unimolecular cleavage of the trialkyloxonium ion 1 to an oxacarbenium ion (2) may occur to some extent. In that case, monomer attacks the oxacarbenium ion 2 from both sides of the nearly planar ring (arrows c and d) to afford α-form and β-form units (3 and 4). However, the participation of the oxacarbenium ion 2 in the polymerization of 4(e)-BrDBO, if any, is of minor importance even at −30 °C, since the α-form contents of the polymers were 97% or higher. This is in marked contrast to the cationic polymerization of unsubstituted 6,8-dioxabicyclo[3.2.1]octane, in which polymers containing 10–20% β-form units were generally formed at −30 °C.[21] The higher β-form content of the polymer, in other words, a significant contribution of the oxacarbenium ion in the polymerization of 6,8-dioxabicyclo[3.2.1]octane, seems to be correlated with its higher ring-opening reactivity compared with that of the 4-bromo derivative as revealed by acid-catalyzed hydrolysis.[12]

In the polymerization of stereoisomeric mixtures of 4(a)-BrDBO and 4(e)-BrDBO, the α-form contents of the polymers obtained at −78 °C decreased with increasing 4(a)-BrDBO fraction in the monomer feed (Table I). Furthermore, a polymer consisting of 78% α-form and 22% β-form units was obtained from a steroisomeric mixture of 4(a)-BrDBO and 4(e)-BrDBO (42:58) at −90 °C, whereas a polymer entirely consisting of α-form units was produced from pure 4(e)-BrDBO under similar conditions. These findings unequivocally indicate that the axially oriented bromine atom of 4(a)-BrDBO affects the steric course of the propagation significantly.

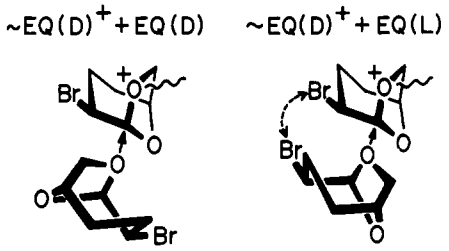
A possible mechanism for the propagation involving the growing chain end of 4(a)-BrDBO is proposed in Scheme II. It seems likely that the propagating species, which is reasonably assumed to be a trialkyloxonium ion (5), is in equilibrium with a bromonium ion (6). Such neighboring group participation of the bromine atom[22] probably takes place relatively easily, since the bromine atom and the oxonium oxygen atom in 5 are in the anti position. The trialkyloxonium ion 5 is attacked by monomer exclusively from the direction opposite to the C–O$^+$ bond (arrow a) to give the α-form unit (7). In contrast, the bromonium ion 6 is ring opened by the attack of monomer from the opposite direction of one of the C–Br$^+$ bonds as arrow d shows, thus leading to the formation of the β-form unit (8) in a polymer chain. The alternative bond cleavage of the bromonium ion by the attack of monomer from the opposite direction of the other C–Br$^+$ bond (arrow e) would produce a 2-bromotetrahydropyran-6,3-diyloxymethylene unit in a polymer chain. However, this possibility can safely be excluded on the basis of the finding that the reductive debromination products of the polymers obtained from stereoisomeric mixtures of 4(a)-BrDBO and 4(e)-BrDBO were entirely composed of tetrahydropyran-2,6-diyloxymethylene repeating units as described in the previous section.

As for the trialkyloxonium ion 1 of 4(e)-BrDBO, neighboring group participation of its equatorially oriented bromine atom is less likely to take place, because the bromine atom and the oxonium oxygen atom in 1 are located on the same side of the tetrahydropyran ring. Therefore, the formation of a considerable amount of β-form units, even at lower temperatures, in the polymerization of stereoisomeric mixtures of 4(a)-BrDBO and 4(e)-BrDBO is reasonably interpreted in terms of the neighboring group participation of the axially oriented bromine atom of a 4(a)-BrDBO terminal unit.

As demonstrated in Table II, the polymers derived from 4(e)-BrDBO are, more or less, rich in isotactic dyad, although the stereoregularity is not so high. The preferential formation of an isotactic sequence in a polymer chain must be induced by the growing chain end control mechanism,[2] since the initiators used are devoid of asymmetrical factors. Thus the enantiomer whose chirality is the same as that of a growing terminal unit tends to be incorporated into a polymer chain preferentially. A similar phenomenon was observed in the polymerization of 6,8-dioxabicyclo-[3.2.1]octane initiated with boron trifluoride etherate, and the growing chain end control mechanism was proved by the D,L copolymerization of enantiomerically unbalanced monomer mixtures.[11]

A possible mechanism for the enantiomer selection at the growing chain end is illustrated in Scheme III. When the D enantiomer of 4(e)-BrDBO approaches the oxonium

Scheme III
Possible Mode of the Enantiomer Selection at the Growing Chain End in the Polymerization of 4(e)-BrDBO (EQ)



ion of the D-enantiomeric unit in such a way that the dipole moments of the two tetrahydropyran rings are oriented in the opposite direction, there is relatively small electronic repulsion between the bromine atom of the incoming monomer and the lone pair orbital of the oxygen atom of the terminal unit. On the other hand, when the L enantiomer attacks the oxonium ion of the D-enantiomeric unit, there occurs repulsion between the bromine atom of the incoming monomer and the bromine atom of the terminal unit. When the monomer approaches the active center in such a way as to avoid the repulsion, alternative electronic repulsion between the bromine atom of the incoming monomer and the lone pair orbital of the oxygen atom of the terminal unit becomes unavoidable. Therefore, the propagation between the monomer and the terminal unit of the same chirality should occur more readily than the propagation between the monomer and the terminal unit of the opposite chirality, thus producing a stereoregular polymer that is rich in isotactic dyad.

In conclusion, the polymerization of 4(e)-BrDBO proceeds through an oxonium ion intermediate at low temperatures to give stereoregular polymers consisting entirely of α-form units and being rich in isotactic sequences of their D,L-enantiomeric units. In contrast, the polymerization of stereoisomer mixtures of 4(a)-BrDBO and 4(e)-BrDBO gives rise to stereoirregular polymers composed of both α-form and β-form units even at −90 °C due to the participation of the bromonium ion intermediate of a 4(a)-BrDBO terminal unit in the propagation.

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Steric Control in the First Step of the Isospecific Ziegler–Natta Polymerization of Propene

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ABSTRACT: Our recent model of the catalytic site in heterogeneous Ziegler–Natta catalysts has been employed to study the first step in the polymerization of propene when the alkylating group is CH_3, C_2H_5, or i-C_4H_9. The computations indicate, in agreement with experimental data obtained by Zambelli and co-workers, that the placement of the first group is stereoirregular in the case of CH_3, but becomes partially stereospecific in the case of C_2H_5 and is totally isospecific in the case of i-C_4H_9. This trend is due to the fixed chiral orientation of the first C–C bond of alkyl groups bulkier than CH_3 induced by steric interactions with the local environment of the catalytic site. That orientation, in fact, determines different nonbonded interactions depending on the presented monomer face.

Introduction

In previous papers[1-3] we have studied, through extensive computations the role played by nonbonded interactions at model catalytic sites in determining the stereospecificity and regiospecificity of heterogeneous Ziegler–Natta catalysts. We concluded that, in the framework of the model, the isospecificity of the reaction is mainly due to the fixed chiral orientation of the first C–C bond of the reactive end of the growing polymeric chain. Although some specific features of the isotactic steric control depend on the

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