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Polymerization of Bicyclic Acetals. 13. Asymmetric-Selective Copolymerization of *rac*-4(e)-Bromo-6,8-dioxabicyclo[3.2.1]octane with Tribenzyllevoglucosan (1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose)

Masahiko Okada,* Hiroshi Sumitomo, and Takahito Hirasawa

Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan.

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ABSTRACT: Asymmetric-selective copolymerization of *rac*-4(e)-bromo-6,8-dioxabicyclo[3.2.1]octane (4(e)-BrDBO) with optically active tribenzyllevoglucosan (TBLG; 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose) was achieved in dichloromethane at −60 °C with antimony pentafluoride as an initiator. The unreacted 4(e)-BrDBO monomer in the copolymerization of the monomer mixtures of different compositions showed specific rotations of a positive sign, indicating that the D enantiomer of 4(e)-BrDBO was preferentially incorporated in the copolymer chain. The molar ratio of the D- and L-enantiomeric units of 4(e)-BrDBO in the copolymer (D/L ratio) was determined as a function of copolymer composition. The variation of the D/L ratio with copolymer composition was analyzed by the terminal model for terpolymerization. It was found that the growing chain end of a TBLG unit reacted with the D enantiomer of 4(e)-BrDBO about 4.2 times faster than it reacted with the L enantiomer. The asymmetric selection displayed by the chiral TBLG terminal unit is discussed.

The modes of steric control in stereospecific polymerization (stereoselective polymerization and asymmetric-selective polymerization) can be classified into two categories, that is, enantiomorphic catalyst site control and growing-chain control.[1] Most of the stereospecific polymerizations so far reported on various types of cyclic monomers such as epoxides, episulfides, lactones, and α-amino acid *N*-carboxy anhydride have been achieved by using coordination catalysts, and they are reasonably interpreted in terms of the enantiomorphic catalyst site-control mechanism. Some stereospecific polymerizations, for example, the polymerization of *tert*-butyloxirane by potassium *tert*-butoxide,[2,3] the polymerization of α-ethyl-α-phenyl-β-propiolactone by tetraethylammonium benzoate[4] and bis(triphenylphosphoranediyl)iminium acetate,[5] and the polymerization of D,L-α-amino acid *N*-carboxy anhydrides by trialkylaluminum,[6,7] tertiary amines,[8,9] and quaternary ammonium acetate,[10] can be accounted for by the growing-chain control mechanism.

Previously, we reported the first example for stereospecific ring-opening polymerization of racemic bicyclic acetals by a conventional cationic initiator:[11] The polymerization of *rac*-6,8-dioxabicyclo[3.2.1]octane (hereafter referred to as DBO) with boron trifluoride etherate as the initiator at low temperatures gave stereoregular polymers rich in isotactic diad. It was proved by the polymerization of enantiomerically unbalanced DBO monomer mixtures that the preferred formation of the isotactic sequence along the polymer chain is primarily ascribable to the enantiomer selection at the chiral growing chain end. Furthermore, a similar stereoregulation was observed in the ring-opening polymerization of 4(e)-bromo-6,8-dioxabicyclo[3.2.1]octane (4(e)-BrDBO) initiated with antimony pentafluoride or trifluoromethanesulfonic acid.[12] Also in this case, the enantiomer whose chirality was the same as that of a growing terminal unit was preferably incorporated into a polymer chain. These phenomena were interpreted in terms of steric and electronic repulsions between the active chain end and the approaching bulky monomer having two (DBO) or three (4(e)-BrDBO) asymmetric carbon atoms.

These findings prompted us to investigate copolymerization of racemic bicyclic acetals with optically active monomers in expectation that asymmetric-selective copolymerization would be achieved without using a chiral initiator. As the first approach, the present work deals with the copolymerization of *rac*-4(e)-bromo-6,8-dioxabicyclo[3.2.1]octane with optically active tribenzyllevoglucosan (TBLG; 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose) using antimony pentafluoride as initiator, with special emphasis on the enantiomer selection at the terminal TBLG unit.

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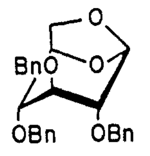
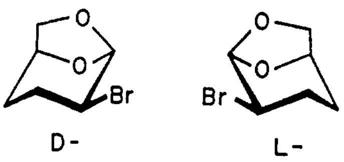


TBLG Bn, $-CH_2C_6H_5$
(OPTICALLY
ACTIVE)



4(e)-BrDBO
(RACEMIC)

Experimental Section

Materials. 4(e)-Bromo-6,8-dioxabicyclo[3.2.1]octane was prepared by the procedures described by Brown et al.[13] with slight modification. 3,4-Dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) was reduced with sodium borohydride in methanol to the corresponding alcohol. Subsequent bromination in carbon tetrachloride at 23 ± 3 °C under slightly reduced pressure by an aspirator in order to eliminate hydrogen bromide gave 4-bromo-6,8-dioxabicyclo[3.2.1]octane in a yield of 90%. The product was obtained as a mixture of the axially and equatorially substituted stereoisomers (4(a)-BrDBO:4(e)-BrDBO = 46:54 by gas chromatographic analysis). Since it was difficult to isolate each component by conventional methods, 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. It was dried over calcium hydride and distilled under reduced pressure before use (bp 78 °C (3 mmHg)).

Levoglucosan was obtained by the pyrolysis of microcrystalline cellulose under reduced pressure.[15] It was purified by recrystallization from ethanol and subsequently benzylated with sodium hydride and benzyl chloride in dimethylformamide. Crude tribenzyllevoglucosan (TBLG) was recrystallized three times from ethanol and then from a mixed solvent of *n*-hexane and dichloromethane (vol. ratio 2:1): mp 90.5–92.0 °C; $[\alpha]^{25}_D$ −31.0° (chloroform) (lit.[16] mp 90–91.5 °C; $[\alpha]^{25}_D$ −31.6° (chloroform)).

Copolymerization and Workup Procedures. Copolymerization was carried out in dichloromethane at −60 °C with antimony pentafluoride as the initiator. After the reaction was terminated by adding a small amount of pyridine, the reaction mixture was poured into a large volume of methanol to precipitate polymer. It was purified by repeated reprecipitation using dichloromethane and methanol as a solvent–precipitant pair followed by freeze-drying from benzene solution.

The methanol solutions used for the purification of the polymer were combined, and the solvents were removed by rotary evaporation. The residue was chromatographed on silica gel with a mixed solvent of *n*-hexane and ethyl acetate (vol. ratio 9:1) and subsequently with acetone as eluents to give unreacted 4(e)-BrDBO and TBLG, respectively.

Characterization. Copolymer compositions were determined by ^1H NMR and elemental analysis of the copolymer (determination of the composition of TBLG and total 4(e)-BrDBO) in combination with the measurement of specific rotation of the unreacted 4(e)-BrDBO monomer (determination of the proportion of the D and L enantiomers of 4(e)-BrDBO). ^1H and ^{13}C NMR spectra were recorded on JEOL FX-200 and FX-100 spectrometers operating at 200 and 25 MHz, respectively, on solutions in deuteriochloroform. Tetramethylsilane was used as the internal reference. Specific rotations of the copolymers and TBLG were measured in chloroform at 25 °C by a Jasco DIP 181 automatic polarimeter. Molecular weights of the copolymers were estimated by a Hitachi 634 gel permeation chromatograph (column, Shodex A80M, 1 m; eluent, chloroform; polystyrene standard).

Results and Discussion

Both 4(e)-BrDBO[12,17,18] and TBLG[16,19,20] undergo cationic homopolymerization at or below −60 °C to give polymers entirely consisting of the structural units in which the exocyclic oxygen atom is axially oriented to the tetrahydropyran ring, that is, the (1 → 6)-α-glycosidic residues in the terminology of carbohydrate chemistry. Therefore, the copolymerization of *rac*-4(e)-BrDBO with TBLG was carried out in dichloromethane at −60 °C with antimony pentafluoride as the initiator. Table I summarizes some of the results of the copolymerization.

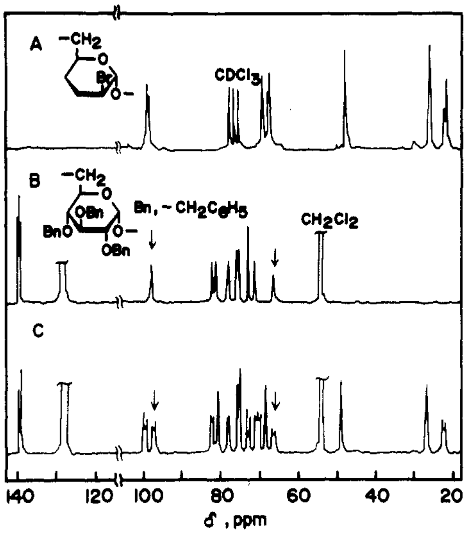


Figure 1. ^{13}C NMR spectra of (A) 4(e)-BrDBO homopolymer, (B) TBLG homopolymer, and (C) TBLG–4(e)-BrDBO copolymer (molar fraction of 4(e)-BrDBO, 0.52). Solvent: (A) $CDCl_3$, (B) $CHCl_2$ and (C) CH_2Cl_2 (external lock, D_2O). Internal reference, Me_4Si; 25 MHz.

The polymers obtained by the repeated reprecipitation using dichloromethane and methanol as a solvent–precipitant pair were readily soluble in benzene and chloroform, in sharp contrast to the insolubility of the homopolymer of 4(e)-BrDBO in the former solvent and the poor solubility in the latter solvent. The remarkable difference in the solubility is strongly indicative of the formation of a true copolymer.

A typical ^{13}C NMR spectrum of the copolymer of 4-(e)-BrDBO with TBLG is presented in Figure 1 along with the spectra of the homopolymers. In comparison with the spectrum of the homopolymer of TBLG, some of the signals due to the TBLG unit are split in the spectrum of the copolymer, as indicated with arrows. These splittings arise from the presence of TBLG–4(e)-BrDBO cross diads along the polymer chain and give additional support for the formation of the true copolymer.

As shown in Table I, the specific rotation of the 4(e)-BrDBO monomer recovered from the reaction mixture was of a positive value in each run. This is a clear indication that asymmetric selection occurs during the copolymerization. Since the optically pure L enantiomer of 4(e)-BrDBO ((1*R*,4*R*,5*S*)-4-bromo-6,8-dioxabicyclo[3.2.1]-octane in IUPAC nomenclature) has a specific rotation of +111° (chloroform, 25 °C),[18] the positive sign of the recovered monomer implies that the D enantiomer of 4-(e)-BrDBO is more favorably incorporated into the copolymer chain.

As a measure for evaluating the asymmetric selectivity in the copolymerization, the molar ratio of the D- and L-enantiomeric units in the copolymer, *D*/*L*, was adopted. Since the amount of methanol-soluble oligomeric products was negligibly small, the *D*/*L* ratio can be calculated on the basis of the observed specific rotation of the unreacted 4(e)-BrDBO monomer, the weight of each monomer in the feed, the copolymer yield, and the weight fraction of 4-(e)-BrDBO in copolymer by using eq 1.[21] The calculated values are listed in the last column in Table I.

$$\frac{D}{L} = \frac{M_2 - A(1 - [\alpha]/[\alpha]_0)}{M_2 - A(1 + [\alpha]/[\alpha]_0)} \tag{1}$$

Table I
Copolymerization of TBLG (M_1) with 4(e)-BrDBO (M_2)[a]

M_1, g	M_2, g	F_2[b]	solv, mL	time, h	yield,[c] wt %	f_2[d]	M_n[e] × 10^{-4}	$[\alpha]^{25}_D$, deg polym[f]	$[\alpha]^{25}_D$, deg monom[g]	D/L[h]
5.83	0.29	0.10	10	0.20	17.6	0.07	1.7	+104.7	+7.3	3.3
5.18	0.58	0.20	10	0.33	27.2	0.17	2.4	+101.0	+15.2	2.7
4.54	0.87	0.30	8	3.0	15.4	0.35	1.0	+85.3	+6.6	1.8
2.16	0.97	0.50	4	2.0	29.2	0.52	1.3	+64.7	+8.5	1.4
1.30	1.35	0.70	4	0.67	32.8	0.67	1.0	+43.7	+2.1	1.1

[a] Solvent, CH_2Cl_2; initiator, SbF_5, 5 mol % to total monomers; temperature, −60 °C. [b] Mole fraction of M_2 in feed. [c] Methanol–insoluble polymer. [d] Mole fraction of M_2 in copolymer. [e] By gel permeation chromatography. [f] In $CHCl_3$. [g] Unreacted M_2 monomer, in C_2H_5OH. [h] Molar ratio of the D- and L-enantiomeric units of M_2 in copolymer.

where $A = M_2 - (M_1 + M_2)Yw_2/100$ and M_1 = the weight of TBLG in the feed, M_2 = the weight of 4(e)-BrDBO in the feed, Y = the copolymer yield (wt %), w_2 = the weight fraction of 4(e)-BrDBO in the copolymer, $[\alpha]$ = the observed specific rotation of the unreacted 4(e)-BrDBO monomer, and $[\alpha]_0$ = the specific rotation of optically pure (+)-4(e)-BrDBO ($[\alpha]^{25}_D$ + 111° (ethanol)[18]).

$$\begin{array}{ll}
\sim T^+ + T \xrightarrow{k_{TT}} \sim T^+ & \sim D^+ + T \xrightarrow{k_{DT}} \sim T^+ \\
 & \sim L^+ + T \xrightarrow{k_{LT}} \sim T^+ \\
\sim T^+ + D \xrightarrow{k_{TD}} \sim D^+ & \sim D^+ + D \xrightarrow{k_{DD}} \sim D^+ \\
 & \sim L^+ + D \xrightarrow{k_{LD}} \sim D^+ \\
\sim T^+ + L \xrightarrow{k_{TL}} \sim L^+ & \sim D^+ + L \xrightarrow{k_{DL}} \sim L^+ \\
 & \sim L^+ + L \xrightarrow{k_{LL}} \sim L^+
\end{array}$$

where T is TBLG, D is D-4(e)-BrDBO, L is L-4(e)-BrDBO, and k_{ij} is the rate constant (i, j = T, D, L).

If we consider the D and L enantiomers of 4(e)-BrDBO as independent comonomers, the copolymerization of TBLG with *rac*-4(e)-BrDBO can be treated as a terpolymerization system consisting of nine elementary propagation reactions. If we assume that the conventional terminal model is applicable to the present system, the instantaneous D/L ratio is given by eq 2.

$$\frac{dD}{dL} = \frac{k_{TD}[T^+][D] + k_{DD}[D^+][D] + k_{LD}[L^+][D]}{k_{TL}[T^+][L] + k_{DL}[D^+][L] + k_{LL}[L^+][L]} \qquad (2)$$

With decreasing molar fraction of 4(e)-BrDBO monomer in the feed, the propagation reactions involving both the 4(e)-BrDBO monomer and its oxonium ion occur much less frequently. This is another way of saying that with the decrease in the molar fraction of 4(e)-BrDBO units in the terpolymer, f_2, the diad fractions of consecutive 4(e)-BrDBO units (DD, DL, LD, and LL) become increasingly smaller. Thus

$$\lim_{f_2 \to 0} \frac{dD}{dL} = \frac{k_{TD}[D]}{k_{TL}[L]} \qquad (3)$$

Furthermore, at very low conversions, we may postulate that the concentration of the D enantiomer of 4(e)-BrDBO, [D], is equal to that of the L enantiomer, [L]. Therefore

$$\lim_{f_2 \to 0} \frac{dD}{dL} = \frac{k_{TD}}{k_{TL}} \quad \text{(at conversion} \approx 0) \qquad (4)$$

The k_{TD}/k_{TL} ratio represents the asymmetric selectivity in the incorporation of the 4(e)-BrDBO enantiomers at the growing chain end of a TBLG unit. The asymmetric selectivity can be estimated by extrapolating the plots of D/L vs. f_2 to $f_2 = 0$ for the terpolymers obtained at the lowest conversions possible. However, it is experimentally difficult to determine the D/L ratios of the terpolymers obtained at such low conversions because the enantiomer unbalance in the remaining monomer is too small to be measured accurately. Therefore, we determined the D/L ratios of the terpolymers obtained at relatively high conversions (~30%) and analyzed the data with the aid of a computer.

The instantaneous composition for the present terpolymer is given by Alfrey and Goldfinger's equation (5).[22]

$$\begin{aligned}
&d[T]:d[D]:d[L] = \\
&[T]\left(\frac{[T]}{r_{DT}r_{LT}} + \frac{[D]}{r_{LD}r_{DT}} + \frac{[L]}{r_{DL}r_{LT}}\right)\left([T] + \frac{[D]}{r_{TD}} + \frac{[L]}{r_{TL}}\right): \\
&[D]\left(\frac{[T]}{r_{LT}r_{TD}} + \frac{[D]}{r_{TD}r_{LD}} + \frac{[L]}{r_{TL}r_{LD}}\right)\left(\frac{[T]}{r_{DT}} + [D] + \frac{[L]}{r_{DL}}\right): \\
&[L]\left(\frac{[T]}{r_{DT}r_{TL}} + \frac{[D]}{r_{TD}r_{DL}} + \frac{[L]}{r_{TL}r_{DL}}\right)\left(\frac{[T]}{r_{LT}} + \frac{[D]}{r_{LD}} + [L]\right)
\end{aligned} \qquad (5)$$

where [T], [D], and [L] are concentrations of TBLG, D-4(e)-BrDBO, and L-4(e)-BrDBO, respectively, and $r_{ij} = k_{ii}/k_{ij}$ and $r_{ji} = k_{jj}/k_{ji}$ (i, j = T, D, L) are monomer reactivity ratios for the respective binary copolymerizations.

Since the asymmetric selectivity k_{TD}/k_{TL} is afforded by r_{TL}/r_{TD}, we must determine the monomer reactivity ratios involved in eq 5. Two of the three pairs of monomer reactivity ratios for the three binary copolymerizations among TBLG, D-4(e)-BrDBO, and L-4(e)-BrDBO were determined experimentally: First, both r_{DL} and r_{LD} were evaluated to be 2.7 from the diad tacticity of the homopolymer of *rac*-4(e)-BrDBO obtained at −60 °C.[12] Second, r_{TL} and r_{LT} were estimated to be 3.8 and 2.3, respectively, from the diad fractions of the copolymer of TBLG and L-4(e)-BrDBO.[23] The third pair of monomer reactivity ratios, r_{TD} and r_{DT}, can be determined by using a computer simulation technique.

Because of relatively high conversions in the present case, Alfrey and Goldfinger's equation cannot be used directly to calculate copolymer composition. Therefore, Skeist's method[24] in combination with Alfrey and Goldfinger's equation was employed for the calculation. According to the computational procedures proposed by Chan and Meyer,[25] we have calculated the D/L ratios as a function of f_2 at 30% conversion, under the restriction that the TBLG content in the terpolymer is nearly equal to that in the monomer feed as observed experimentally. In this calculation, r_{TD} and r_{DT} were used as variables, while r_{DL}, r_{LD}, r_{TL}, and r_{LT} were kept constant as described above.

In Figure 2 are shown the observed and calculated D/L vs. f_2 curves. The calculated curve, which approximately simulated the observed curve, was obtained with the parameters of $r_{TD} = 0.9$ and $r_{DT} = 1.3$. Therefore, the k_{TD}/k_{TL} value in the present terpolymerization was calculated to be 4.2. This means that the growing chain end of a TBLG unit reacts with the D enantiomer of 4(e)-

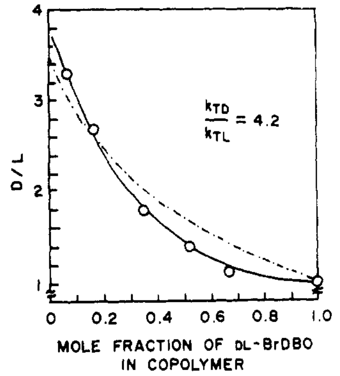


Figure 2. Relationship between the molar ratio of the D- and L-enantiomeric units of 4(e)-BrDBO in the copolymer (*D*/*L* ratio) and the TBLG-4(e)-BrDBO copolymer composition. Polymerization conditions: solvent, CH_2Cl_2; initiator, SbF_5, 5 mol% to total comonomers; temperature, −60 °C; conversion, ~30%. (○) Experimental; (-·-) calculated by using the following parameters: $r_{DL} = 2.7$, $r_{LD} = 2.7$, $r_{TL} = 3.8$, $r_{LT} = 2.3$, $r_{TD} = 0.9$, and $r_{DT} = 1.3$. (See text.)

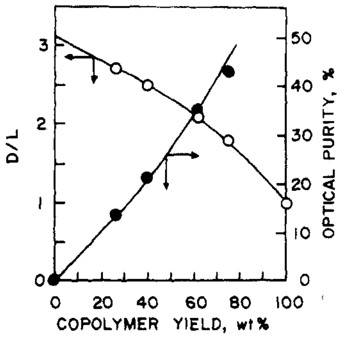


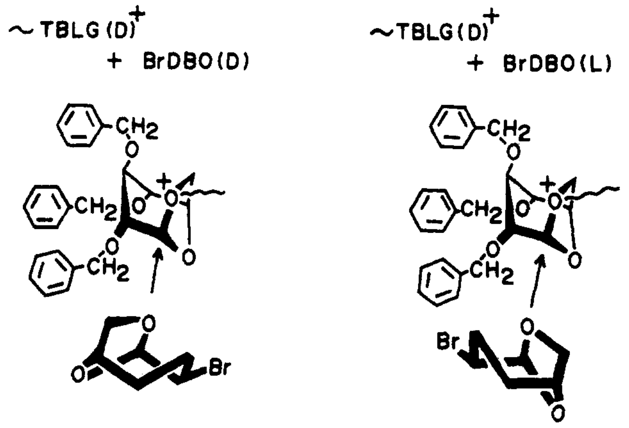
Figure 3. Dependences of the *D*/*L* ratio in copolymer (○) and the optical purity of unreacted 4(e)-BrDBO monomer (●) on the yield of TBLG–4(e)-BrDBO copolymer (molar fraction of 4(e)-BrDBO in feed, 0.20). Polymerization conditions: solvent, CH_2Cl_2; initiator, SbF_5, 5 mol % to total comonomers; temperature, −60 °C. Both curves were calculated by using the parameters given in the caption of Figure 2.

BrDBO 4.2 times faster than it reacts with the L enantiomer.

Figure 3 presents the variations of the optical purity of the unreacted 4(e)-BrDBO monomer and the *D*/*L* ratio of the terpolymer with the conversion of 4(e)-BrDBO at a fixed initial monomer feed (molar fraction of 4(e)-BrDBO, 0.20). The following two points are noticeable. First, the optical purity of the unreacted monomer increased monotonously with increasing copolymer yield. In other words, the unreacted monomer in the reaction mixture became increasingly enriched in the less reactive L enantiomer. Second, the ratio of the D-enantiomeric units to the L-enantiomeric units of 4(e)-BrDBO incorporated into the terpolymer chain decreased with increasing copolymer yield. The observed plots are on, or very close to, the curves calculated by using the monomer reactivity ratios described above.[26] The agreement supports that the aforementioned treatment is reasonable.

The observed enantiomer selectivity ($k_{TD}/k_{TL} = 4.2$) is somewhat higher than that calculated from the diad tacticity of the polymer in the homopolymerization of *rac*-4(e)-BrDBO under similar conditions, where the active chain end of a given chirality reacts with the enantiomer of the same chirality 2.7 times (−60 °C) and 3.2 times (−90 °C) faster than it reacts with the enantiomer of the opposite chirality.[12] Recently, Penczek et al.[5] analyzed the kinetics of the anionic polymerization of enantiomerically unbalanced α-methyl-α-phenyl-β-propiolactone initiated

Scheme I
Possible Mode of Asymmetric Selection of 4(e)-BrDBO Enantiomers at the Growing Chain End of a TBLG Unit in the Copolymerization of TBLG with 4(e)-BrDBO



with bis(triphenylphosphoranediyl)iminium acetate, and they determined the rate constants for the homopropagation (k_{ph}) and cross propagation (k_{pc}) considering the *R* and *S* enantiomers as comonomers. The ratio of k_{ph}/k_{pc} was 1.7 at 25 °C in dichloromethane.

Stereospecific ring-opening polymerization of cyclic monomers by the growing-chain control mechanism ordinarily requires coordination of monomer and growing chain to counterion or helix formation. In the cationic polymerization of bicyclic acetals, such coordination to the counteranion seems unlikely because of the nucleophilic character of the monomers. Furthermore, to our knowledge, (1→6)-α-linked polysaccharides and their derivatives do not assume a helical conformation in solution. Therefore, it is reasonable to postulate that the asymmetric-selective copolymerization as well as stereospecific homopolymerization arises from the enantiomer selection at the chiral growing chain end.

Let us consider the cross propagation between a TBLG growing chain end and the D or L enantiomer of 4(e)-BrDBO. Both TBLG and 4(e)-BrDBO are rigid bicyclic monomers having bulky and polar substituents, and hence there occur steric and electronic repulsions when 4(e)-BrDBO approaches the active center of the terminal TBLG oxonium ion. According to molecular model inspection, in the reaction of the TBLG terminal unit with the D enantiomer of 4(e)-BrDBO as illustrated in Scheme I (left), steric and electronic repulsions between the TBLG terminal unit and the incoming monomer become minimum when the monomer takes a spatial arrangement in which the bromine atom is far from the bulky benzyloxy groups of the terminal unit. On the other hand, when the TBLG oxonium ion reacts with the L enantiomer of 4(e)-BrDBO, the most preferable approach of the monomer to the growing chain end seems to be that as illustrated in Scheme I (right), even though appreciable steric and electronic repulsions between the axial benzyloxy group of the TBLG terminal unit and the bromine atom of the monomer cannot be avoided. When the L enantiomer approaches the oxonium ion in such a way as to avoid these repulsions, alternative and more severe repulsions unavoidably occur between the methylene group of the 7 position of the monomer and the ring oxygen atom of the TBLG terminal unit. Therefore, the propagation between the TBLG oxonium ion and the D enantiomer of 4(e)-BrDBO is energetically more favorable than that between the TBLG oxonium ion and the L enantiomer of 4(e)-BrDBO. As a consequence, the D enantiomer is incorporated preferentially in the copolymer chain. In the interpretation above, only the interactions between the TBLG terminal unit and incoming monomer have been taken into account for the sake of simplification. Penultimate and even more remote untis may contribute, to some extent, to the enantiomer selection at the growing chain end, but their effects cannot be evaluated by the aforementioned analytical procedure.

In summary, asymmetric-selective copolymerization *rac*-4(e)-BrDBO with optically active TBLG was achieved in dichloromethane at −60 °C without using a chiral initiator. In this copolymerization, the D enantiomer of 4-(e)-BrDBO, whose chirality was the same as that of the optically active comonomer TBLG, was preferentially incorporated in the copolymer chain. Such asymmetric selection originates from the difference in the reactivities of the growing chain end of the chiral TBLG unit toward the D and L enantiomers of 4(e)-BrDBO, and it is principally ascribable to the steric and electronic interactions between the asymmetric environment created by the chiral terminal TBLG unit and the rigid bicyclic 4(e)-BrDBO monomer having three asymmetric centers in addition to the polar bromine substituent.

Registry No. TBLG, 10548-46-6; (TBLG)·(4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]octane) (copolymer), 98819-28-4; 4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]octane, 84621-97-6.

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(21) The molar ratio of the D- and L-enantiomeric 4(e)-BrDBO units in the copolymer, D/L, is represented by eq i

$$\frac{D}{L} = \frac{(M_2/2) - Af_D}{(M_2/2) - A(1 - f_D)} \tag{i}$$

where M_2, A, and f_D are the weight of 4(e)-BrDBO in feed, the weight of unreacted 4(e)-BrDBO and the fraction of the D enantiomer in the unreacted 4(e)-BrDBO. (A is calculated by the equation shown below eq 1.) Since f_D is given by eq ii

$$f_D = \frac{1}{2}\left(1 - \frac{[\alpha]}{[\alpha]_0}\right) \tag{ii}$$

one obtains eq 1 from eq i and ii.

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(24) Skeist, I. *J. Am. Chem. Soc.* **1946**, *68*, 1781. Change in copolymer composition with conversion is given by eq iii

$$\ln (1 - m) = \int_{f_1^0}^{f_1} \frac{df_1}{F_1 - f_1} \tag{iii}$$

where m, f_1 and F_1 are conversion, monomer composition, and instantaneous copolymer composition, respectively. This equation is applicable to any copolymerization and terpolymerization as long as the relation between f_1 and F_1 is given.

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(26) The curves in Figure 3 were calculated as follows: With the use of monomer reactivity ratios given in the text, copolymer composition at any conversion and therefore the D/L ratio can be determined by Skeist's equation in combination with Alfrey and Goldfinger's equation. The optical purity of the remaining 4(e)-BrDBO can be readily calculated from the copolymer composition and conversion.

Polysilane High Polymers with Olefinic Side Groups: Syntheses, Properties, and Addition of Hydrogen Halides

Harald Stüger[1] **and Robert West***

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

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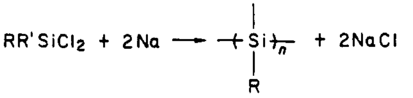
ABSTRACT: Three polysilane polymers containing alkene substituent groups were prepared by sodium condensation of dichlorosilanes: poly[(2-(3-cyclohexenyl)ethyl)methylsilylene] (**3**) and copolymers of this with phenylmethylsilylene (**1**) and *n*-propylmethylsilylene units (**2**). These polymers undergo cross-linking when irradiated with UV light or heated to 200 °C in vacuo. Addition of HCl or HBr to **1** or **2** in the presence of Lewis acid catalysts gave the corresponding chlorine- or bromine-containing polymers, with little degradation of the polysilane backbone.

Introduction

Recently several different substituted polysilane polymers have been prepared[2] by the reaction of dichlorosilanes RR′SiCl$_2$ with sodium in refluxing toluene (eq 1). Properties, molecular weights, and yields of the products are strongly dependent on the substituents R and R′. All of these polymers are soluble in common organic solvents and can be formed into a variety of shapes by molding, casting, or potting. They also show strong UV absorption and are easily degraded by UV irradiation[3] or heating to high temperatures.[4] Some of them also can be cross-linked by UV irradiation[3] or by heating them in the presence of vinylsilanes and free radical initiators.[5] Because of these



$$RR'SiCl_2 + 2Na \longrightarrow -\!\!\!\left[\underset{R}{\overset{R'}{\underset{|}{\overset{|}{Si}}}}\right]_n\!\!\!- + 2NaCl \tag{1}$$

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