vinyl carbon bearing the isocyanide group is sufficient to block polymerization. Allyl isocyanide also failed to precipitate a polymer upon treatment with catalytic nickel(II) acetylacetonate in ethanol solution under conditions similar to those used for the polymerizations of vinyl isocyanides reported in this paper. Thus conjugation of the carbon–carbon double bond with the isocyanide group appears to facilitate polymerization.

Acknowledgment. We are indebted to the Minnesota Mining and Manufacturing Co. (3M) of St. Paul, MN, for support of this research. We are indebted to Dr. Paul Wang of the Science Research Laboratory of the 3M Co. for performing the molecular weight determinations reported in Tables I and II.

Registry No. MeCH═CHNC (homopolymer), 96806-12-1; Me$_2$C═CHNC (homopolymer), 96806-10-9; Me$_3$CCH═CHNC (homopolymer), 96806-07-4; PhCH═CHNC (homopolymer), 96806-08-5; PhMeC═CHNC (homopolymer), 96806-11-0; MesCH═CHNC (homopolymer), 96806-14-3; MeCH═CMeCH═CHNC (homopolymer), 96806-16-5; MeCH═CHNC (SRU), 98705-04-5; Me$_2$C═CHNC (SRU), 98705-05-6; Me$_3$CCH═CHNC (SRU), 98705-06-7; PhCH═CHNC (SRU), 98705-07-8; PhMeC═CNC (SRU), 98705-08-9; MesCH═CHNC (SRU), 98705-09-0; MeCH═CMeCH═CHNC (SRU), 98705-10-3; Ni(acac)$_2$, 3264-82-2; Ni(dpm)$_2$, 41749-92-2; NiCl$_2$, 7718-54-9; Co(acac)$_2$, 14024-48-7.

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Effect of Alkyl Groups on the Asymmetric Induction Copolymerization of Alkyl Vinyl Ethers with Indene Using (−)-Menthoxyaluminum Dichloride Initiator

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ABSTRACT: Copolymerizations of *tert*-butyl, isobutyl, *n*-butyl, isopropyl, and ethyl vinyl ethers with indene were undertaken with (−)-menthoxyaluminum dichloride as the initiator. The optically active copolymers were obtained and ether-cleaved with HBr gas. The optical rotation of the ether-cleaved copolymers was proportional to their values of $P_2(m_1m_2)$, the probability of an m_1m_2 diad sequence. The largest optical rotation per $P_2(m_1m_2)$ was obtained in the case of the ether-cleaved *tert*-butyl vinyl ether/indene copolymer. These results suggested that real asymmetric carbon atoms were introduced in the vinyl ether units and that the bulkiness of the alkyl group of the vinyl ethers played an important role in the asymmetric induction of this system. Furthermore, the mechanism of the asymmetric induction was discussed.

Introduction

We have been studying the asymmetric copolymerization of vinyl and α,β-disubstituted monomers.[1-7] In the cationic copolymerization of (−)-menthyl vinyl ether and indene,[3-5] the copolymers were still optically active after the removal of the chiral menthyl groups. The authors concluded that the addition of α,β-disubstituted monomer to a growing chain end during the propagation was sterically controlled by the chiral menthyl groups and one of the configurations was preferentially produced in the main chain.

In our previous paper,[8] we reported the copolymerization of isobutyl vinyl ether and indene initiated by (−)-menthoxyaluminum dichloride (1) and (−)-menthoxytitanium trichloride (2). From the linear relationship between the optical rotation and $P_2(m_1m_2)$ values of the copolymers, it was found that real asymmetric carbon atoms of the vinyl ether units were introduced under the influence of the chiral counteranion. The relative extent of the asymmetric copolymerization depended on solvents and initiators.

In this paper, the copolymerizations of several alkyl vinyl ethers and indene were carried out in cyclohexane using 1. To investigate the effect of alkyl groups of the vinyl ethers on asymmetric induction copolymerization, the copolymers were ether-cleaved.

Experimental Section

Materials. Toluene, benzene, cyclohexane, methanol, and tetrahydrofuran (THF) were purified by the usual methods. Commericially available *l*-menthol (mp 43 °C, $[\alpha]_D$ −49.3° in ethanol, c = 0.1 g/L, l = 1.0 cm), ethylaluminum dichloride, tetralin, and bromine were used without further purification. Isopropyl vinyl ether (*i*-PrVE) and *tert*-butyl vinyl ether (*t*-BVE) were synthesized form *n*-butyl vinyl ether (*n*-BVE) and the corresponding alcohols with mercuric acetate as a catalyst according to Watanabe's method.[9] Ethyl vinyl ether (EVE), *n*-butyl vinyl ether (*n*-BVE), isobutyl vinyl ether (*i*-BVE), and indene (In) were commercial materials, distilled over sodium metal under vacuum before use. 1 ($[\alpha]_D$ −39.7° in toluene, c = 0.1 g/L, l = 1.0 cm) was prepared from *l*-menthol and ethylaluminum dichloride according to Furukawa's method.[10]

Copolymerization. Copolymerizations were carried out in polymerization tubes equipped with three-way ground-glass

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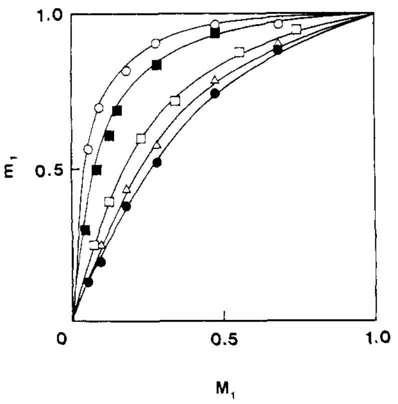


Figure 1. Composition curves of alkyl vinyl ethers (M_1) and indene (M_2) copolymers: (○) *t*-BVE; (■) *i*-PrVE; (□) EVE; (△) *n*-BVE; (●) *i*-BVE. The conversions were in the range 7.8–83.9%.

stopcocks. The required amounts of the monomers and solvent were placed in the tubes. A cyclohexane solution of 1 was added through a syringe under an atmosphere of nitrogen. After the polymerization period, the polymer solution was poured into a large amount of NH_3–methanol mixture to precipitate copolymers. The copolymers were purified by repeated reprecipitations with THF solvent and methanol precipitant to constant optical rotation. The composition of the copolymers was determined by elemental analysis.

Ether-Cleavage Reaction. The ether-cleavage reaction was carried out by blowing dry hydrogen bromide gas into a benzene solution of the copolymers according to the method described in our previous paper.[2]

Measurement. A Jasco DIP-4 polarimeter was used for D-line optical rotation measurements with filtered sodium light. Optical rotatory dispersion was obtained on a Jasco J-20 spectropolarimeter (c = 0.1 g/L, l = 1.0 cm). Viscosities were measured in an Ubbelohde viscometer in THF at 30 °C.

Results and Discussion

Copolymerization. Copolymerizations of *t*-BVE, *i*-BVE, *n*-BVE, *i*-PrVE, and EVE with indene were carried out in cyclohexane at 0 °C by 1. The copolymerizations were undertaken over a wide range of monomer feed ratios. The copolymers containing a high mole fraction of indene units were white powders. They became viscous liquids with increasing amounts of vinyl ether units. The softening point of the copolymers decreased with increasing contents of the monomeric units of the alkyl vinyl ethers. The intrinsic viscosity of the copolymers was in the range 0.07–0.23 dL/g. The copolymers are soluble in benzene, toluene, and THF and insoluble in methanol and *n*-hexane.

The composition curves of the copolymers are given in Figure 1. The composition of the copolymers was calculated with the values of elemental analysis (C and H). The monomer reactivity ratios were determined by the Fineman–Ross method. The r_1 and r_2 values were used to calculate the values of $P_2(m_1m_2)$, the probability of an m_1m_2 diad sequence.[11]

Optical Behavior of the Copolymers. The homopolymers of indene and alkyl vinyl ethers were optically inactive. The copolymers obtained with 1 have negative optical activity. The ORD's measured between 450 and 600 nm for the copolymers were simple dispersions. The relationships between the $[\alpha]_{450}$ values and the composition of the copolymers are shown in Figure 2. The curves are symmetric. In any case, the $[\alpha]_{450}$ values of the copolymers showed a maximum at 1:1 monomer molar ratio in the copolymers. The results may suggest that the copolymer containing alternative character shows the largest $[\alpha]_{450}$ value.

To confirm this, the optical rotation of the copolymers was plotted vs. the value of $P_2(m_1m_2)$ as shown in Figure 3. The $[\alpha]_{450}$ value of the copolymer is proportional to the value of $P_2(m_1m_2)$. This result reveals that the asymmetric carbon atoms were newly introduced to the diad sequence m_1m_2 in the copolymer main chain. The slope of the straight line ($[\alpha]_{450}/P_2(m_1m_2)$) gives the relative extent of asymmetric induction. The same linear relationship was observed in asymmetric induction copolymerization of *i*-BVE and indene using 1 or 2 as reported in our previous paper.[8]

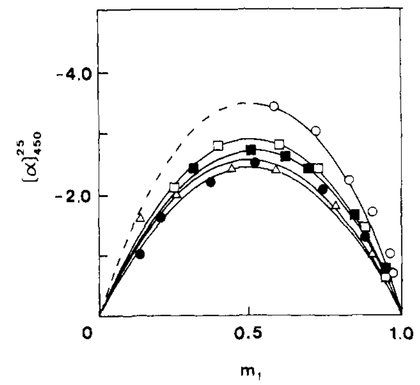


Figure 2. Relationship between $[\alpha]_{450}$ and the mole fraction (m_1) of alkyl vinyl ethers in the copolymers: (○) *t*-BVE; (■) *i*-PrVE; (□) EVE, (△) *n*-BVE; (●) *i*-BVE.

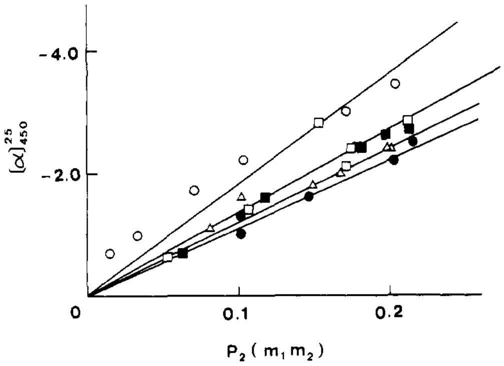


Figure 3. Relationship between $[\alpha]_{450}$ and the $P_2(m_1m_2)$ values of the copolymers: (○) *t*-BVE; (■) *i*-PrVE; (□) EVE; (△) *n*-BVE; (●) *i*-BVE.

The linear relationship suggests that the asymmetric induction did not occur on indene units. If the asymmetric carbon atoms of the indene units had been introduced, the relationship between the $[\alpha]_{450}$ values and $P_2(m_1m_2)$ values of the copolymers might not be linear. In addition, the ORD of the copolymers showed simple dispersions. The values of λ_c of the copolymers were about 220 nm. It suggests that there was no Cotton effect over the range 220–280 nm due to indene residues.

Smith et al.[12] reported that 1-substituted indans have Cotton effects near 270 nm associated with the ^1L_b transition of the benzene chromophore. It is concluded from Smith's and our results that asymmetric carbon atoms were not induced from the indene units. It is also clear from the linearity that the optical activity was not due to the *l*-menthoxy residues from the chiral initiator.

As shown in Figure 3, the slope for poly(*t*-BVE-*co*-In) is the largest and the one for poly(*i*-BVE-*co*-In) is in the lowest. In the case of the others, it is difficult to distinguish the slopes. As the contribution of alkyl groups to the optical rotation of the copolymers cannot be estimated quantitatively, it is not possible to compare directly the slopes for the relative extent of asymmetric induction.

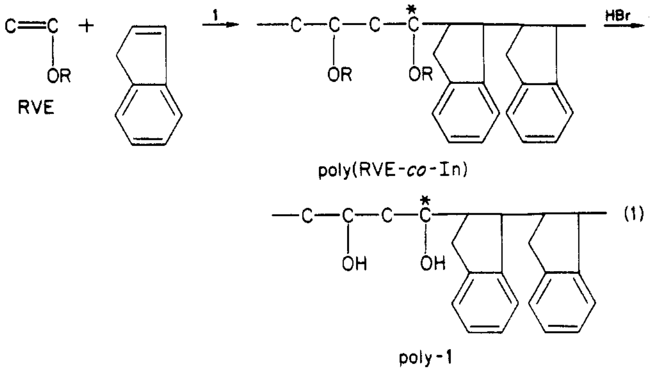
Synthesis of Ether-Cleaved Copolymers. For direct comparison of the effect of alkyl groups on asymmetric

Table I
Configurations of Optically Active Carbinols

carbinols $R_1R_2C^*(OH)H$						
R_1	R_2[a]	$[\alpha]_D$ neat	$[M]_D$ neat	optical purity, %	configuration	lit.
Me	*t*-Bu		+12		*S*	14
Et	*t*-Bu		−39		*S*	14
n-Pr	*t*-Bu		−55		*S*	14
n-Pr	C_6H_{11}	−1.39		8.1	*S*	13
n-Bu	*t*-Bu		−60		*S*	14
n-Bu	C_6H_{11}	−1.36		11.0	*S*	13
i-Pr	*t*-Bu		−14		*S*	14
i-Pr	C_6H_{11}	+0.21		2.1	*S*	13
D	*i*-Pr	−0.17		27.1	*R*	15
Me	Et	−0.97		7	*S*	15
Me	*i*-Pr	+0.87		16.3	*S*	15
Me	*t*-Bu	+0.95		12.4	*S*	15
Et	*i*-Pr	+6.05		61.7	*S*	15

[a] C_6H_{11} = cyclohexyl group.

induction, the side-chain ether-cleavage reaction was carried out with HBr gas. The ether-cleaved copolymers were white powders, soluble in THF, DMF, Me_2SO, and benzene, and insoluble in methanol and *n*-hexane. The intrinsic viscosity of the ether-cleaved polymers was in the range 0.06–0.19 dL/g. The infrared spectra of the original and ether-cleaved copolymers were compared. The original copolymer gave an absorption band at 1070–1150 cm^{-1} due to the side-chain ether group. After the removal of these ether groups, the absorption band at 1070–1150 cm^{-1} disappeared and one appeared at 3200–3400 cm^{-1} due to the hydroxy group. The results of elemental analysis were in agreement with theoretical values for ether-cleaved poly(*n*-BVE-*co*-In). Anal. Calcd for $(C_2H_4O)_{0.43}(C_9H_8)_{0.57}$: C, 76.3; H, 8.1. Found: C, 76.1; H, 8.1. From the above results the ether-cleavage reaction took place completely.



R=alkyl group, RVE=alkyl vinyl ether

Optical Behavior of Ether-Cleaved Copolymers. After the removal of the alkyl groups, the copolymers had a negative optical activity. The optical rotation of the ether-cleaved copolymers was about half that of the corresponding copolymers. The ORD measured between 450 and 600 nm for the ether-cleaved copolymer was a simple dispersion. The value of λ_c for the copolymer was about 220 nm, which was the same as that of the original copolymer.

The $[\alpha]_{450}$ values of the ether-cleaved copolymers were proportional to their values of $P_2(m_1m_2)$ in a similar manner to the original copolymers (Figure 4). The largest slope was obtained with ether-cleaved poly(*t*-BVE-*co*-In). In the case of the others, it is difficult to distinguish the slopes. These results suggest that the bulkiness of the alkyl groups of these vinyl ethers played an important role in the asymmetric induction of this system. Further discussion on this aspect will be given later.

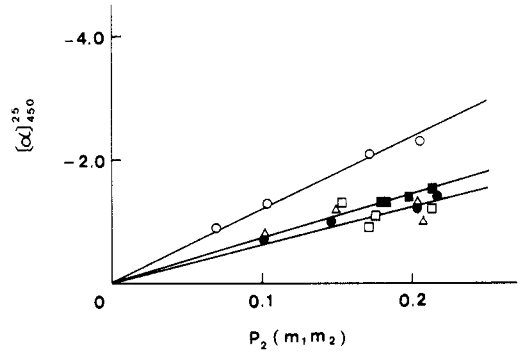
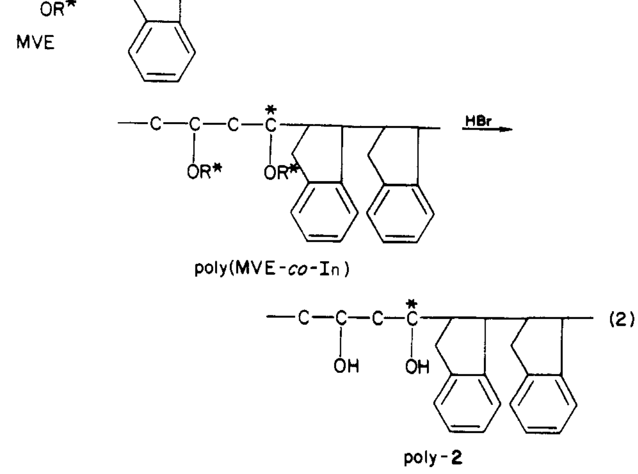


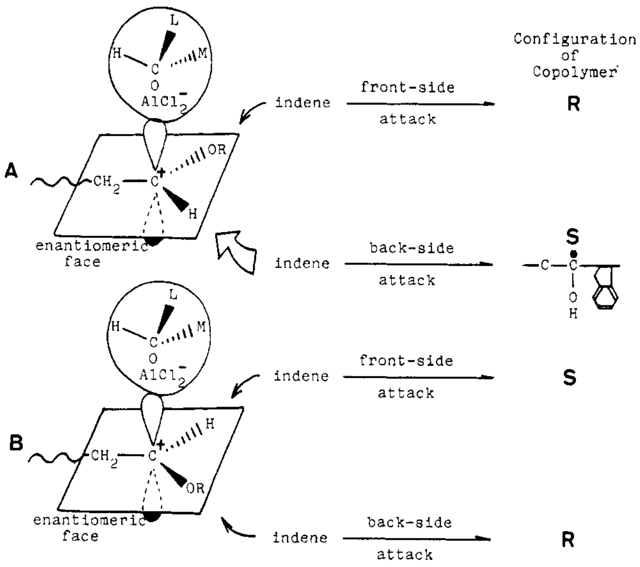
Figure 4. Relationship between $[\alpha]_{450}$ and the $P_2(m_1m_2)$ of the ether-cleaved copolymers: (○) *t*-BVE; (■) *i*-PrVE; (□) EVE; (△) *n*-BVE; (●) *i*-BVE.

Table I gives the sign of the optical rotation and the absolute configuration of the optically active carbinols synthesized by several investigators.[13-15] Carbinols such as *tert*-butylethyl-, ethylisopropyl-, and cyclohexyl-*n*-propylcarbinols may be regarded as a model compounds of poly-1. These carbinols with a negative sign of optical rotation have the *S* configuration. From the results, it seems likely that poly-1 has preferentially the *S* configuration. Previously, we copolymerized (−)-methyl vinyl ether (MVE) and indene and obtained optically active poly(MVE-*co*-In).[3-5] The ether-cleaved poly(MVE-*co*-In) (hereinafter abbreviated poly-2) was still optically active.



R* = *l*-menthyl group

Scheme I



The optical rotation of poly-**2** was proportional to the values of $P_2(m_1m_2)$. The largest slope was obtained from the copolymer that was copolymerized with BF_3OEt_2 in toluene. It was concluded that asymmetric carbon atoms were introduced on the polymer main chain.

We have claimed that the optical rotation of poly-**1** and poly-**2** depends upon the amounts of m_1m_2 diad sequence. The final product (poly-**1**) has partially the alternating sequence, m_1m_2 consisting of the vinyl alcohol and indene units (eq 1). Poly-**2** obtained in a previous paper[4] had partially the alternating sequence $-CH_2-CH(OH)-In-$ (eq 2), which was substantially the same as that of poly-**1**. So we can directly compare the optical activity of poly-**1** with that of poly-**2**.

The largest $[\alpha]_{450}/P_2(m_1m_2)$ value for poly-**1** obtained from poly(*t*-BVE-*co*-In) was −11.5°. On the other hand, the value for poly-**2** reported in a previous paper[4] was −690°. The above results suggested that the asymmetric induction ability of the menthoxy groups, which were located at the growing chain ends as counteranions (Scheme I), was 1/60th of that of those groups covalently bonded on the vinyl groups (eq 2).

The alternative conformations (A and B) of the ion pairs of the growing chain end, which contain enantiomeric faces, are shown in Scheme I. Steric hindrance between the alkyl group and the L and M substituents of the chiral counteranion dominates the thermodynamic stabilities of A and B. A is probably more stable than B. The difference in the stabilities increases as the alkyl groups become larger. The difference causes asymmetric induction copolymerization.

The counteranion would hinder the approach of an attacking monomer from the same side (front-side attack),[16] whereas indene attacks the growing cation chain end from the opposite side of the anion (back-side attack). As A may be more stable than B, it would be expected that poly-**1** has the S configuration. This aspect is supported by the fact that poly-**1** obtained had preferentially the *S* configuration, as mentioned above.

The stability of A and B is influenced by solvents. As we had reported in a previous paper,[8] in the copolymerization of *i*-BVE and indene using **1** and **2**, the optical rotation of the copolymer was affected by the dielectric constant of solvents used. The largest $[\alpha]_{450}/P_2(m_1m_2)$ value was obtained by copolymerization in cyclohexene. In dichloroethane, asymmetric induction copolymerization did not occur. As the polarity of the polymerization medium decreased, the Coulombic interaction of the propagating ion and chiral counteranion became greater. Consequently the difference between the stability of A and B increased, and the reaction of eq 4 in Scheme I took place preferentially.

Registry No. 1, 17676-43-6; *t*-BVE, 926-02-3; *i*-BVE, 109-53-5; *n*-BVE, 111-34-2; *i*-PrVE, 926-65-8; EVE, 109-92-2; (*t*-BVE)·(indene) (copolymer), 98542-15-5; (*i*-PrVE)·(indene) (copolymer), 98542-16-6; (EVE)·(indene) (copolymer), 98542-17-7; (*n*-BVE)·(indene) (copolymer), 98542-18-8; (*i*-BVE)·(indene) (copolymer), 93610-86-7; indene, 95-13-6.

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