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ARTICLE

Frequency control of crossover reactions in concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes: Specific roles of weak Lewis bases and solvent polarity

Arihiro Kanazawa* and Sadahito Aoshima*

Weak Lewis bases and solvent polarity are demonstrated to be highly responsible for the frequency of crossover reactions in the concurrent cationic vinyl-addition and ring-opening copolymerization of alkyl vinyl ethers (VEs) and oxiranes. Weak Lewis bases such as ethyl acetate and 1,4-dioxane promote crossover reactions from isobutylene oxide- or butadiene monoxide-derived propagating species to an alkyl VE monomer, potentially through the more frequent generation of carbocations via the ring opening of the oxonium ion. The specificity of the carbocation that results from the ring-opening reaction—a preference for VE monomers or an aversion to oxirane monomers—is another factor that changes the crossover frequency. Weak Lewis bases, however, have little effect on the relative reactivity of the VE-derived propagating species to each monomer. By contrast, solvent polarity has a significant effect on the promotion of the crossover from the VE-derived propagating end to an oxirane, while the frequency of the crossover from the oxirane-derived propagating end is not affected. In contrast to the two oxiranes, the reaction conditions have little effect on the copolymerization using isoprene monoxide, which is an oxirane that generates a more stable, resonance-stabilized carbocation through ring opening. The relative reactivities of VEs and oxiranes under various conditions are discussed in terms of the average number of each monomer unit in one block of the copolymers and in terms of the monomer reactivity ratios.

Introduction

The properties of copolymers, such as their thermal properties, solution properties, crystallinity, and degradability, are significantly affected by their monomer sequence distributions. Remarkable developments in controlled/living polymerization techniques have enabled syntheses of copolymers with various sequences, such as block, gradient, alternating, and periodic copolymers. In particular, forcible methods, including multistep or continuous monomer-feeding methods, are often employed for the synthesis of polymers such as block and gradient copolymers.[1] However, the native reactivities of monomers, or monomer reactivity ratios, are primarily responsible for the monomer sequence distributions of copolymers.[2] Therefore, copolymers with diverse distributions—multiblock, random, and alternating sequences—are purposefully generated when control over the monomer sequence distributions is achieved through a one-shot feed of monomers.

The sequence distribution in one-shot feed copolymerization may be governed by the reaction conditions in addition to the inherent monomer reactivities. In ionic vinyl-addition homopolymerization through carbocationic or carbanionic intermediates, the polymerization activity strongly depends on the reaction conditions, such as the solvent, catalyst, additive, and temperature. In copolymerization, however, the relative reactivities of monomers with similar structures [such as cationic copolymerizations between vinyl ethers (VEs) with different alkyl groups or between styrene derivatives with different substituents at the *p*-position] are negligibly dependent on the reaction conditions[3—5] because the reaction conditions similarly affect the reactivities of propagating species derived from similar monomers. In contrast, in copolymerizations of monomers with different structures (such as cationic copolymerization between a VE and a styrene derivative), the relative reactivities of monomers considerably differ depending on the reaction conditions.[3—11] Notably, the monomer reactivity ratios are greater than one in many cases, such as in reactions using 2-chloroethyl VE and *p*-methoxystyrene[4,5,8] or those using isobutylene and styrene.[6,9] These specific behaviors have partially been explained in terms of the "selective solvation" effect, although the details of these behaviors are not clear.[5—9]

In the copolymerization of two monomers with different structures, the reaction conditions strongly influence the monomer sequence distributions, in which the monomers generate different types of growing ends. This situation potentially occurs also in the concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl and cyclic monomers.[12,13] We recently developed the cationic copolymerization of alkyl VEs and oxiranes, which were previously considered to be incompatible with each other, based on the rational design of monomers and initiating systems.[14,15] An essential requirement for crossover reactions between monomers is the generation of a carbocationic propagating species through ring opening of the oxonium ion derived from an oxirane monomer. Thus, the monomer sequence distribution of the copolymer strongly depends on the frequency of carbocation generation from an oxirane, which is most likely related to the stability of the carbocation and to the nucleophilicity balance between the VE and oxirane monomers. Indeed, a reaction using isobutylene oxide (IBO) or isoprene monoxide (ISPO) generates multi-block-like or alternating-like copolymers, respectively, during copolymerization with isopropyl VE (IPVE).[15] The former oxirane generates a tertiary carbocation, whereas the latter oxirane affords a more stable, resonance-stabilized carbocation.

In the context of our studies on concurrent cationic copolymerization, we have aimed to control the crossover frequency through tailoring the reaction conditions. A strategy for frequency control is to modulate the ring-opening step of the copolymerization because the crossover reactions from an oxirane-derived propagating end to a VE monomer are thought to be completely dependent on the generation of the carbocation through ring opening. A candidate additive is a weak Lewis base that nucleophilically attacks the oxonium ion to promote ring opening but does not form a covalent bond with the propagating species. In fact, weak Lewis bases, such as esters and ethers, do not disturb cationic polymerization and have been beneficially employed as an "added base" for the living cationic polymerization of various vinyl monomers; the major roles of the additives are to stabilize the propagating carbocation and to adjust the Lewis acidity of the catalyst through acid-base interactions.[16,17] In addition, the copolymerizations of VEs and oxiranes are examined in different solvents to determine the effect of solvent polarity on the crossover efficiency. The relative reactivities of monomers under different conditions are primarily discussed in terms of the average number of each monomer unit in one block of copolymers and in terms of the monomer reactivity ratios.

Experimental Section

Materials. IPVE (Wako; 97.0+%) and ethyl vinyl ether (EVE; TCI; >98.0%) were washed with 10% aqueous sodium hydroxide solution and then water, and distilled twice over calcium hydride. IBO (TCI; >97.0%), butadiene monoxide (BDO; Alfa Aesar; 98%), ISPO (Alfa Aesar; 97%), and ethyl acetate (Wako; >99.5%) were distilled twice over calcium hydride. 1,4-Dioxane (Wako; >99.5%), diethyl ether (Wako; >99.5%), and ethylene glycol dimethyl ether (glyme; Nacalai Tesque; 99.0%) were distilled over calcium hydride and then lithium aluminum hydride. Diethylene glycol dimethyl ether (diglyme; TCI; >99.0%) was distilled over calcium hydride and then lithium aluminum hydride under reduced pressure. Dichloromethane (Wako; 99.0%) and hexane (Wako; 96.0%) were dried by passage through solvent purification columns (Glass Contour). $B(C_6F_5)_3$ (Aldrich; 95%) was used without further purification after preparing its stock solution in dichloromethane. All chemicals except for dichloromethane were stored in brown ampules under dry nitrogen.

Polymerization Procedures. The following is a typical polymerization procedure using ethyl acetate as an additive. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the blow temperature ~450 °C) under dry nitrogen. Dichloromethane, hexane, ethyl acetate, IPVE, and IBO were added successively into the tube using dry syringes. The polymerization was started by the addition of a prechilled 10 mM $B(C_6F_5)_3$ solution in dichloromethane at −78 °C. After 5 h, the reaction was terminated with methanol containing a small amount of an aqueous ammonia solution. The quenched mixture was diluted with hexane and washed with water. The volatiles were then removed under reduced pressure at 50 °C to yield a polymer. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport HP for IPVE, EVE, and IBO; GL Sciences Inc.) using hexane as an internal standard, except for the ISPO and BDO systems. The monomer conversions for the ISPO and BDO systems were determined by the gravimetry and ^{1}H NMR integral ratios.

Acid Hydrolysis. The acid hydrolysis of the polymers was conducted with 0.5 M HClaq in 1,2-dimethoxyethane at room temperature for 1 h (sample: ~1 wt%). The quenched mixture was diluted with dichloromethane and washed with an aqueous sodium hydroxide solution and water, successively. The volatiles were removed under atmospheric pressure at room temperature for several days or under reduced pressure for several hours.
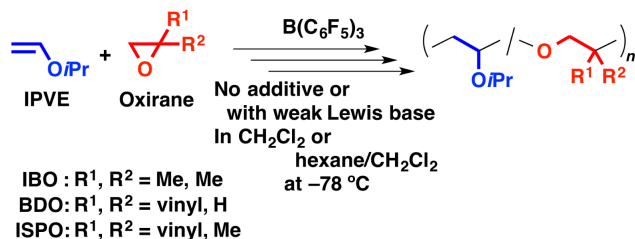
Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [TSKgel GMH$_{HR}$-M × 2 or 3 (exclusion limit molecular weight = 4×10^6; bead size = 5 μm; column size = 7.8 mmI.D. × 300 mm) or TSKgel MultiporeH$_{XL}$-M × 3 (exclusion limit molecular weight = 2×10^6; bead size = 5 μm; column size = 7.8 mmI.D. × 300 mm); flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; M_n = 577—1.09×10^6, $M_w/M_n \leq 1.1$). NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ^{1}H) spectrometer.

Results and Discussion

Cationic Copolymerization of IBO with IPVE

The cationic copolymerization of IPVE with IBO was first conducted using $B(C_6F_5)_3$ as a Lewis acid catalyst in the absence or presence of ethyl acetate at –78 ºC (Scheme 1). The solvents used were dichloromethane alone or a mixture of hexane and dichloromethane. Cationogens were not used because adventitious water functions as a protonogen through activation by $B(C_6F_5)_3$. The polymerization reactions proceeded under all reaction conditions, affording polymers with unimodal molecular weight distributions (MWDs) (Figure 1, black curves). ^{1}H NMR analyses of the products (Figure 2) indicated that the copolymerizations occurred through crossover reactions between the two monomers. The peak at 4.7–4.8 ppm (peak 8) was assigned to acetal structures derived from the crossover reactions from IPVE to IBO, and the peak at 0.9 ppm (peaks 13 and 17) was assigned to the methyl protons of the structure resulting from the crossover from IBO to IPVE. A portion of the latter crossover reactions occurred after hydride shift isomerization,[14] and their frequency appeared to be dependent on the reaction conditions.[18] In addition, acid hydrolysis of the copolymers yielded products with lower molecular weights and unimodal MWDs (Figure 1, purple curves). The clean shifts of the MWD curves suggest that the copolymerization products were composed of copolymers containing acid-labile acetal structures in their main chains.

Interestingly, differences in the polymerization conditions significantly affected the numbers of IPVE and IBO units
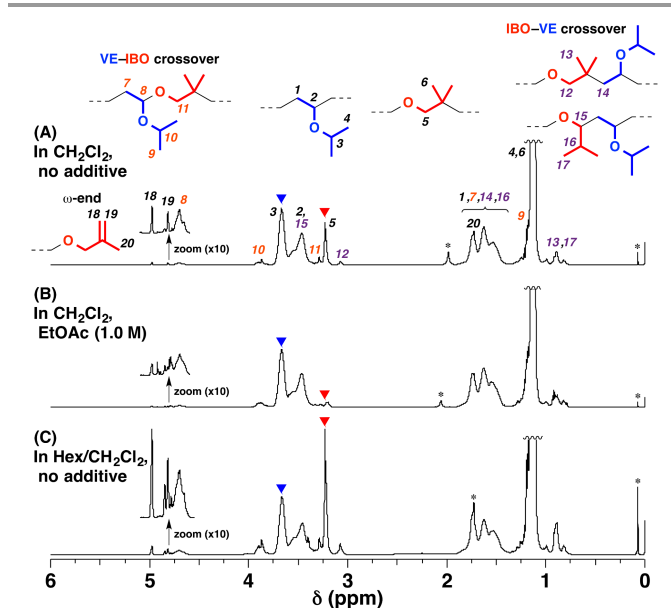

Figure 2. ^{1}H NMR spectra of the copolymerization products of IPVE and IBO: (A) entry 1, (B) entry 3, and (C) entry 5 in Table 1 (the heights of the spectra were standardized based on the peaks with blue inverted triangle; * water, grease).

contained in one block, that is, the crossover frequency. The peak ratios of the methine protons of the IPVE side chains (peak 3, blue inverted triangle) and the methylene protons of the IBO units (peak 5, red inverted triangle) are clearly different in the ^{1}H NMR spectra (Figure 2), the heights of which were standardised based on the former peak. The average number of each unit in one block was calculated from the integral ratios of these peaks and the peaks for the structures derived from the crossover reactions (Table 1). The copolymer obtained in the absence of any additives in dichloromethane (entry 1) was composed of IPVE and IBO blocks with averages of 22 and 4.8 units, respectively. The product generated in the presence of ethyl acetate (entry 3) had a comparable number of IPVE units in one block (average of 16 units), but the number of IBO units in one block was considerably smaller (average of 1.6 units). The average number of IBO units in one block of the product obtained using a smaller amount of ethyl acetate (entry 2)

Scheme 1. Cationic copolymerization of IPVE and oxiranes.
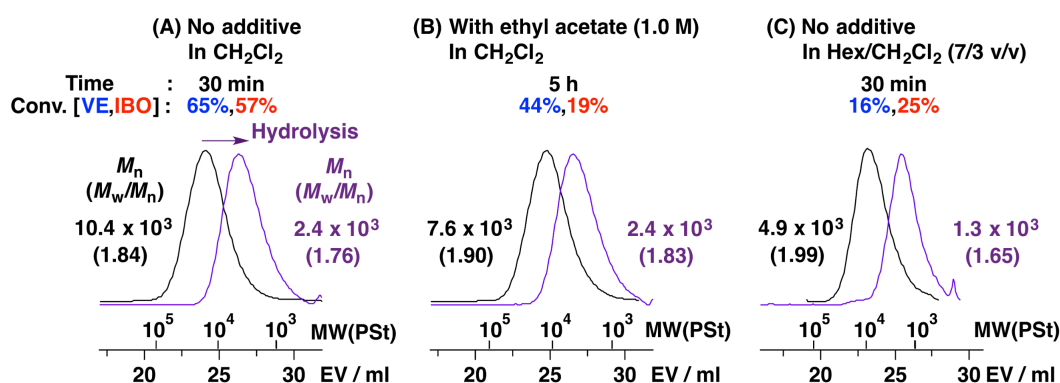

Figure 1. MWD curves of the copolymerization products of IPVE and IBO (black curves) and their hydrolysis products (purple curves): (A) entry 1, (B) entry 3, and (C) entry 5 in Table 1.

Table 1. Cationic Copolymerizations of IPVE and Oxiranes Under Various Reaction Conditions.[a]

entry	oxirane	additive	solvent (v/v)	time	VE conv (%)[b]	oxirane conv (%)[b]	$M_n \times 10^{-3 c}$	M_w/M_n[c]	VE–oxirane crossover per chain[d]	av no. of VE units per one block[d]	av no. of oxirane units per one block[d]
1	IBO (0.22 M)	None	CH_2Cl_2	0.5 h	65	57	10.4	1.84	4.9	22	4.8
2		EtOAc (0.2 M)	CH_2Cl_2	2 h	65	39	11.5	1.78	6.8	22	2.4
3		EtOAc	CH_2Cl_2	5 h	44	19	7.6	1.90	4.0	16	1.6
4		None	hexane/CH_2Cl_2 (5/5)	0.5 h	42	54	8.1	2.07	4.4	14	5.4
5		None	hexane/CH_2Cl_2 (7/3)	0.5 h	16	25	4.9	1.99	3.0	9.8	4.8
6		1,4-Dioxane	CH_2Cl_2	5 h	36	13	6.7	1.79	3.1	13	2.2
7		Et_2O	CH_2Cl_2	1 h	49	41	6.8	1.79	3.5	18	3.5
8		glyme	CH_2Cl_2	5 h	52	33	6.1	1.77	2.6	21	1.5
9		diglyme	CH_2Cl_2	5 h	66	50	6.1	1.85	2.8	22	1.4
10	BDO (0.75 M)	None	CH_2Cl_2	4 h	16	9	2.9	2.95	4.1	5.5	3.4
11		EtOAc	CH_2Cl_2	17 h	6	3	1.0	1.64	1.8	4.7	2.2
12		None	hexane/CH_2Cl_2 (7/3)	17 h	11	18	1.4	3.14	2.8	2.5	4.2
13	ISPO (0.75 M)	None	CH_2Cl_2	1 h	11	18	2.5	2.84	7.3	1.6	2.5
14		EtOAc	CH_2Cl_2	17 h	14	23	1.7	3.06	6.2	1.3	2.0
15		None	hexane/CH_2Cl_2 (7/3)	4 h	10	17	1.9	3.68	6.1	1.4	2.4

[a] $[IPVE]_0 = 0.75$ M, $[oxirane]_0 = 0.22$ (IBO) or 0.75 (BDO and ISPO) M, $[B(C_6F_5)_3]_0 = 1.0$ mM, [weak Lewis base] = 0 or 1.0 M (except for entry 2), in dichloromethane or hexane/dichloromethane at −78 ºC. Smaller amounts of IBO compared to IPVE were used because some copolymers that were obtained using larger amounts of IBO precipitate during copolymerization reactions due to long IBO units. [b] Monomer conversions for copolymerizations of IPVE and IBO were determined by gas chromatography. However, values for IBO conversion in several runs were lower than the values estimated from gravimetry and the ^{1}H NMR integral ratios in the products, indicating that side reactions yielded volatile products and/or a part of residual IBO monomer was decomposed after quenching. [c] By GPC (polystyrene calibration). [d] Determined by ^{1}H NMR for entries 1—9 or by ^{1}H NMR and M_n(GPC) values for entries 10—15.

was 2.4, which is between the above two values, suggesting that ethyl acetate affects the polymerization behavior. However, the number of IBO units in one block was not affected by the solvent polarity (average of 5.4 and 4.8 units in hexane/dichloromethane with volume ratios of 5/5 and 7/3, respectively; entries 4 and 5), whereas the number of IPVE units in one block decreased as the solvent polarity decreased (average of 14 and 9.8 units).

The monomer reactivity ratios under different conditions were then determined to further investigate the effects of a weak Lewis base and solvent polarity. The copolymer composition plots are shown in Figure 3A. The monomer reactivity ratios presented in Table 2 were obtained from these data using the Kelen–Tüdõs method.[19,20] The r_1 and r_2 values for copolymerization in the absence of additives in dichloromethane were 2.4 and 7.3, respectively,[15] which indicates that both monomers preferentially undergo homopropagation reactions. However, the r_2 value considerably decreased to 0.35 in the presence of ethyl acetate, although the r_1 value, 1.9, was compatible with the value for the copolymerization in the absence of additives. An r_2 value of less than one suggests that IBO-derived propagating species prefer crossover reactions in the presence of ethyl acetate. However, the r_1 value decreased to 0.98 in hexane/dichloromethane (7/3 v/v), although the r_2 value, 7.0, was similar to the value in dichloromethane. These values appear to accurately reflect the crossover frequencies that were expected from the average numbers of monomer units

in one block as shown in Table 1 (entry 5). The results suggest that a weak Lewis base facilitates the crossover reaction from IBO to IPVE and that the solvent polarity affects the crossover frequency from IPVE to IBO.

To investigate the effect of a weak Lewis base in more detail, copolymerizations were conducted in the presence of various weak Lewis bases (Table 1, entries 6—9). 1,4-Dioxane, a cyclic ether with a basicity comparable to that of ethyl acetate,[21—25] similarly affected the polymerization, affording polymers with small numbers of IBO units in one block (2.2; entry 6). The monomer reactivity ratios for copolymerization in the presence of 1,4-dioxane ($r_1 = 1.2$ and $r_2 = 0.41$; Table 2) were comparable to those in the presence of ethyl acetate, although the r_1 value was also lower, as expected from the smaller average number of IPVE units in one block (13). In contrast, diethyl ether was not as effective as the two weak Lewis bases (entry 7). A polymer obtained in the presence of diethyl ether had 3.5 IBO units on average, which is less than that obtained in the absence of additives but greater than those obtained in the presence of either ethyl acetate or 1,4-dioxane. The monomer reactivity ratios, r_1 of 2.3 and r_2 of 6.4, also support this result (Table 2). The weaker effect of diethyl ether is consistent with its role in the living cationic polymerizations of vinyl monomers using various Lewis acids.[16,17,26] Although the basicity of diethyl ether, which was estimated from several scales[21—25] such as the donor number and the hydrogen-bond basicity, is comparable to those of ethyl acetate and 1,4-dioxane,
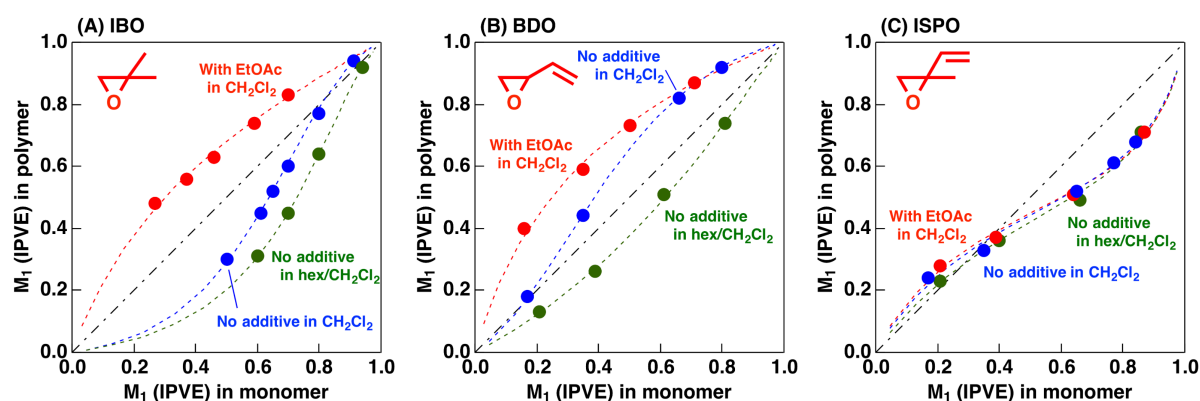
Figure 3. Copolymer compositions for the cationic copolymerizations of IPVE and oxiranes (see Table 2 for the monomer reactivity ratios obtained from these data; broken curves: drawn using the *r* values obtained by the Kelen–Tüdõs method; dashed-dotted lines: azeotropic lines; the copolymerization results used for the plots are listed in Table S1 in the ESI).

Table 2. Monomer Reactivity Ratios for Cationic Copolymerizations of VEs and Oxiranes.[a]

M_1	M_2	additive	solvent (v/v)	r_1	r_2
IPVE	IBO	None	CH_2Cl_2	2.4	7.3
		EtOAc	CH_2Cl_2	1.9	0.35
		None	Hex/CH_2Cl_2 (7/3)	0.98	7.0
		1,4-Dioxane	CH_2Cl_2	1.2	0.41
		Et_2O	CH_2Cl_2	2.3	6.4
IPVE	BDO	None	CH_2Cl_2	3.8	1.5
		EtOAc	CH_2Cl_2	2.6	0.28
		None	Hex/CH_2Cl_2 (7/3)	0.75	1.9
IPVE	ISPO	None	CH_2Cl_2	0.24	0.56
		EtOAc	CH_2Cl_2	0.22	0.50
		None	Hex/CH_2Cl_2 (7/3)	0.23	0.69

[a] By the Kelen–Tüdõs method. See Figures S1 and S2 for the $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$ plots. See Figures 3 and S2 for the copolymer composition curves.

diethyl ether moderated the polymerization activity considerably less fairly than did ethyl acetate and 1,4-dioxane, potentially because of a weaker interaction with a Lewis acid and/or the propagating carbocation.[17] Acyclic ethers with multiple ether bonds, however, effectively functioned in a manner similar to that of ethyl acetate and 1,4-dioxane. Copolymers obtained in the presence of glyme (entry 8) and diglyme (entry 9) possessed low numbers of IBO units in one block: 1.5 and 1.4, respectively. These acyclic ethers also exhibited similar or larger moderating effects on the cationic polymerizations of vinyl ethers compared to ethyl acetate and 1,4-dioxane.[26] The IBO polymer also possesses similar ether groups in its main chain, but the dimethyl groups located at the carbon atoms adjacent to oxygen atoms most likely suppressed the function of the ether due to steric hindrance.

Copolymerization using EVE, which is a vinyl ether monomer that is less reactive than IPVE, also supported the promotion effect of a weak Lewis base on the crossover frequency from IBO to VE (Figure 4). The monomer reactivity ratios, r_1 and r_2, for copolymerization in the absence of

additives were 0.08 and 8.7, respectively. The very small r_1 value is due to the lower reactivity of EVE to the EVE-derived propagating carbocation compared to that of IBO, which may reflect the native nucleophilicity of each monomer. In contrast to the large difference in reactivity, the r_2 value significantly decreased to 0.80 in the presence of ethyl acetate, while the r_1 remained small (0.23). The results indicate that the IBO-derived propagating species prefers EVE in the presence of ethyl acetate, as in the case of the IPVE system.
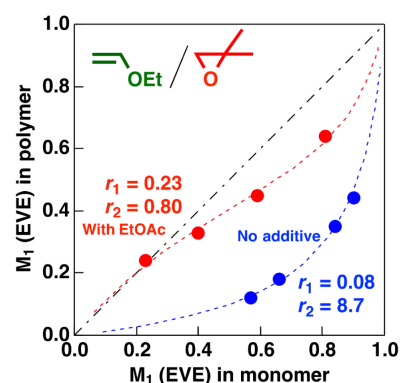

Figure 4. Copolymer compositions for the cationic copolymerizations of EVE and IBO (broken curves: drawn using the *r* values obtained by the Kelen–Tüdõs method; dashed-dotted lines: azeotropic lines; the copolymerization results used for the plots are listed in Table S1 in the ESI).

The unique reaction behaviors in the presence of a weak Lewis base can potentially be explained through the following two reasons: (1) a weak Lewis base promotes the ring-opening reaction of the IBO-derived oxonium ion to generate a carbocation (reaction *f* in Scheme 2), and (2) the generated carbocation has a preference for VE monomers or an aversion to oxirane monomers (reactions *d* and *e*). The latter was also suggested by our previous study on copolymerizations using various oxiranes.[15] A possible role for a weak Lewis base in promoting ring opening is shown in Scheme 3. A basic group, such as a carbonyl group or an ether group, nucleophilically attacks the carbon atom adjacent to the cationically charged

oxygen atom of the oxonium ion, which generates a ring-opened carbocationic species. The subsequent stabilization of the carbocation through interactions with the carbonyl group may be another role for a weak Lewis base in promoting ring opening. The promotion of ring-opening reactions of oxiranes by the combination of a Lewis acid and Lewis base has been reported in many studies.[27,28] The majority of those studies employed Lewis acids with two vacant sites, such as Si(IV) and Sn(IV) compounds, and suggested that a Lewis base promotes the reactions via coordination to the vacant site of an oxirane-coordinated Lewis acid. In contrast, the Lewis acid used in this study, $B(C_6F_5)_3$, has only one vacant site and coordinates a hydroxyl group abstracted from adventitious water during the initiation step. Thus, a Lewis base most likely functions during cationic polymerization in a considerably different manner than that in previous studies of ring-opening reactions.
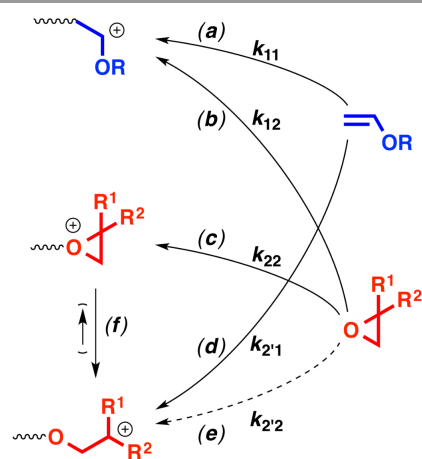
Scheme 2. Propagation reactions for the concurrent cationic vinyl-addition and ring-opening copolymerization of vinyl ethers and oxiranes.
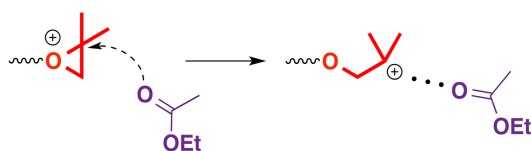
Scheme 3. Possible roles of a weak Lewis base: The promotion of the ring-opening reaction via the nucleophilic attack by the carbonyl group of ethyl acetate and/or the stabilization of the resulting carbocation through the interaction with the carbonyl group (a counteranion is omitted).

The effect of solvent polarity on the relative reactivities of the VE- and oxirane-derived propagating species appears to be unexplained at the present stage. The rate for cationic vinyl-addition homopolymerization generally decreases with decreasing solvent polarity, most likely because the propagating carbocation is less stabilized in a less polar medium. Thus, a smaller r_1 value in a less polar solvent may indicate that the propagating oxonium ion species derived from crossover from the VE-derived carbocation to an oxirane is more stable and more easily generated compared to the VE-derived carbocation that is generated through homopropagation.

Cationic Copolymerization of BDO or ISPO with IPVE

To further examine the effects of a weak Lewis base and solvent polarity on crossover frequency, copolymerizations with IPVE were conducted using two other oxiranes: BDO and ISPO. Because these oxiranes have a vinyl group attached directly to their three-membered ring, the oxonium ions derived from the oxiranes easily induce ring-opening reactions to afford allyl-type, resonance-stabilized carbocations. In fact, our previous study[15] demonstrated that efficient crossover reactions proceed between these oxiranes and VEs to yield copolymers. In this study, the reactions were performed in the presence of ethyl acetate in dichloromethane and in the absence of additives in hexane/dichloromethane (7/3 v/v).

As expected, BDO exhibited behaviors similar to that of IBO during copolymerization with IPVE. The average numbers of IPVE and BDO in one block differed among the copolymers (entries 10—12 in Table 1; see Figure S3 for ^1H NMR spectra of the products). The monomer reactivity ratios determined for the copolymerizations under these conditions (Figure 3B and Table 2) clearly reflected the crossover frequencies that were deduced from the average numbers of units in one block. The r_1 and r_2 values were 3.8 and 1.5, respectively, for the reaction in the absence of additives in dichloromethane. The use of ethyl acetate lowered the r_2 value, whereas the r_1 value remained similar ($r_1 = 2.6$ and $r_2 = 0.28$). However, the r_1 value was smaller in hexane/dichloromethane, although the r_2 was similar to that in dichloromethane alone ($r_1 = 0.75$ and $r_2 = 1.9$). The results indicate that a weak Lewis base and solvent polarity affect the copolymerizations of BDO in a manner similar to that of IBO.

In contrast to the BDO and IBO cases, copolymerization using ISPO proceeded through crossover reactions of comparable frequencies irrespective of the reaction conditions (entries 13—15 in Table 1; see Figure S4 for ^1H NMR spectra of the products). The numbers of IPVE and ISPO units in one block of each copolymer were small under all conditions. The average numbers of 1.3–1.6 and 2.0–2.5 for IPVE and ISPO units, respectively, suggest that crossover reactions frequently occurred during copolymerizations to yield products with an alternating tendency. Both the r_1 and r_2 values were less than one in all cases (Figure 3C and Table 2), which supports the occurrence of frequent crossover reactions.

The specificity of ISPO may arise from the nature of the carbocation that is generated via ring opening of the oxonium ion. The carbocation derived from ISPO is more stable than that derived from IBO or BDO.[29,30] Due to this stability, most of the ISPO-derived oxonium ions may undergo ring opening to generate carbocations, even in the absence of a weak Lewis base. Moreover, the specificity of the oxirane-derived carbocation, i.e., the preference of VE monomers or the aversion of oxirane monomers, leads to preferential crossover reactions from the ISPO-propagating end to IPVE, resulting in r_2 values less than one. The reason for the ineffectiveness of solvent polarity is not clear, but the native tendency of the IPVE-

derived propagating species to undergo frequent crossover reactions to ISPO would mask the effect of solvent polarity.

Conclusion

In conclusion, weak Lewis bases and solvent polarity significantly affect the relative reactivities of vinyl ethers and oxiranes in concurrent cationic vinyl-addition and ring-opening copolymerization. Weak Lewis bases such as esters and ethers promote crossover reactions from the VE-derived propagating end to IBO, potentially because weak Lewis bases nucleophilically attack the oxonium ion to promote the ring-opening reaction and because the generated carbocation exhibits a preference for a VE monomer or an aversion to an oxirane monomer. Solvent polarity has little effect on the crossover from the IBO-derived propagating end to a VE but increases the frequency of crossover from the VE-derived propagating end to IBO. In addition, copolymerization using BDO depends on the reaction conditions, similar to the IBO case, but the crossover frequency in the copolymerization using ISPO negligibly changes, irrespective of the reaction conditions. The results obtained in this study will lead to the precise sequence-control—from multiblock to alternating structures—of copolymers produced via the concurrent cationic copolymerization of vinyl and oxirane monomers.

Acknowledgments

References and Notes

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† Electronic Supplementary Information (ESI) available: Polymerization data and ^{1}H NMR spectra. See DOI: 10.1039/b000000x/

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