OUKA
The University of Osaka
Institutional Knowledge Archive

Title	Controlled Cationic Polymerization of 1-Methoxy-1,3-Butadiene: Long-Lived Species-Mediated Reaction and Control over Microstructure with Weak Lewis Bases
Author(s)	Togo, Yukinori; Kanazawa, Arihiro; Kanaoka, Shokyoku et al.
Citation	Journal of Polymer Science, Part A: Polymer Chemistry. 2018, 57(3), p. 288-296
Version Type	AM
URL	https://hdl.handle.net/11094/104809
rights	© 2018 Wiley Periodicals, Inc.
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

https://ir.library.osaka-u.ac.jp/

The University of Osaka

Controlled Cationic Polymerization of 1-Methoxy-1,3-Butadiene: Long-Lived Species-Mediated Reaction and Control over Microstructure with Weak Lewis Bases

Yukinori Togo, Arihiro Kanazawa, Shokyoku Kanaoka, and Sadahito Aoshima*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Correspondence to: Aoshima, S. (E-mail: aoshima@chem.sci.osaka-u.ac.jp)

((Additional Supporting Information may be found in the online version of this article.))

ABSTRACT

Controlled cationic polymerization of *trans*-1-methoxy-1,3-butadiene was achieved through the design of appropriate initiating systems, yielding soluble polymers with controllable molecular weights. The combined use of $SnCl_4$ or $GaCl_3$ as a Lewis acid catalyst and a weak Lewis base in conjunction with HCl as a protonogen resulted in efficient and controlled polymerization. The M_n values of the product polymers increased linearly along the theoretical line, which indicates that intermolecular crosslinking reactions negligibly occurred. In addition, the polymer microstructure was critically dependent on the weak Lewis base employed. In particular, the use of tetrahydrofuran as an additive resulted in the highest 4,1/4,3-structure ratio (96/4). Weak Lewis bases also affected the polymerization rates but exhibited unique trends that differed from their effects on the cationic polymerization of alkyl vinyl ethers.

KEYWORDS: cationic polymerization; controlled polymerization; diene; Lewis acid; microstructure

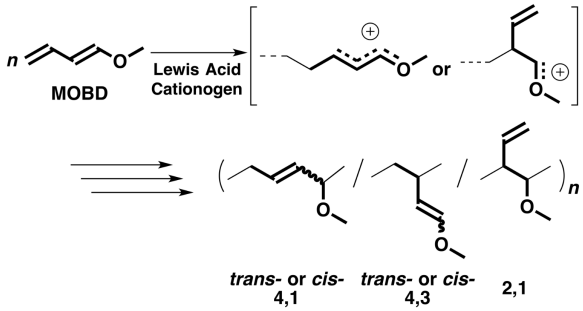
INTRODUCTION

The control of polymerization reactions of conjugated diene monomers has attracted much attention because the properties of the prepared polymers are elaborately designed through the microstructures that arise from the reaction modes, such as the 1,4-, 1,2, and 3,4-addition reactions, as well as from the *trans*- and *cis*-configurations in the main chain. In addition, block copolymerizations of dienes with various monomers afford copolymers with very attractive properties. Therefore, the main target of polymerization reactions of diene monomers should include simultaneous control of the polymer microstructures and reactions leading to “living”-type polymerization.

Important techniques that allow for precise control over the molecular weight (MW) and microstructure of a conjugated diene polymer include anionic and coordination polymerizations.[1] In anionic polymerization, the stable allyl-type propagating carbanions generating from diene monomers do not react with the olefin moieties, hence side reactions such as chain transfer reactions negligibly occurred to result in living polymerization reactions. In addition, the microstructure is relatively controlled through the reaction conditions (i.e., counterion, solvent, temperature, and additive). For example, polyisoprene with a *cis*-1,4-structure of >90% is produced using an alkyllithium initiator in a hydrocarbon solvent.[1] Because of these advantages, living anionic block copolymerization reactions involving diene monomers are industrially used for the synthesis of functional materials such as styrene-butadiene-styrene and styrene-isoprene-styrene triblock copolymers for

general use in our daily life. Another important development involves the use of metal catalysts for coordination polymerizations that control both the MW and microstructure of diene polymers.[2,3] Interestingly, very strict control over the microstructures, such as >99% of the 1,4-*cis*-structure, was achieved through the design of efficient catalysts using lanthanide metals.[4,5] However, little control over both MWs and microstructures has been achieved in cationic polymerizations because of frequent side reactions. The allyl-type carbocations that are generated from dienes, such as isoprene and 1,3-pentadiene, induce cyclization and branching reactions through intra- and intermolecular additions to the olefin structures in the main and side chains.[6–12] In contrast, cyclic diene monomers[13–15] such as cyclopentadiene and tetrahydroindene have been reported to generate polymers in controlled manners. The cyclic structures affected the reactivities of both the monomers and the propagating species to suppress side reactions. Another factor that may be responsible for the reactivity of diene monomers in cationic polymerization is the presence of a substituent on the conjugated structure. However, diene monomers other than hydrocarbons such as isoprene and butadiene have not been extensively investigated in cationic polymerization.

Therefore, we focused on *trans*-1-methoxy-1,3-butadiene (MOBD), which is a conjugated diene monomer with an electron-donating group. MOBD has a methoxy group at the 1-position, which will generate an alkoxy group adjacent to the propagating carbocation via attack of a cationic species on the 4- or 2-position (Scheme 1). These structures are similar to that of the carbocation generated in the cationic polymerization of alkyl vinyl ethers (VEs). However, the carbocation derived from the attack on the 4-position has a conjugated structure. 1-Alkoxy-1,3-butadienes have been reported to yield polymers through cationic mechanisms, but controlled polymerization has never been achieved.[16,17]



Scheme 1. Cationic polymerization of MOBD.

In this study, we aimed to control the cationic polymerization of MOBD and to examine the factors responsible for the control over the microstructures of the products. Through the design of initiating systems based on living cationic polymerization of alkyl VEs, the cationic polymerization of MOBD was demonstrated to proceed in a controlled manner with the use of $SnCl_4$ or $GaCl_3$ as a catalyst in conjunction with suitable additives and a protonogen. In addition, weak Lewis bases, such as an ester and ether, substantially affected the microstructures of the product polymers and the polymerization rates.

EXPERIMENTAL

Materials. 1-Methoxy-1,3-butadiene (Aldrich; 95%)[18] and ethyl acetate (Wako; >99.5%) were distilled twice over calcium hydride. Isobutyl VE (IBVE; TCI; >99.0%) was washed with 10% aqueous sodium hydroxide solution and then water and distilled twice over calcium hydride. Tetrahydrofuran (THF; Wako; >99.5%), 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. 2,6-Di-*tert*-butylpyridine (DTBP; Aldrich; >97%) was distilled twice over calcium hydride under reduced pressure. Dimethyl sulfide was distilled over calcium hydride and then sodium. 2,2'-Bipyridine (Nacalai Tesque, 99.5%) was used as received. nBu$_4$NCl (Fluka; ≥99.0%) was used without further purification and its stock solution in

dichloromethane was prepared. Dichloromethane (Wako; 99.0%), toluene (Wako; 99.5%), and hexane (Wako; 96.0%) were dried by passage through solvent purification columns (Glass Contour). Commercially available $SnCl_4$ (Aldrich; 1.0 M solution in heptane), $EtAlCl_2$ (Wako; 1.0 M solution in hexane), and HCl (Aldrich; 1.0 M solution in diethyl ether) were used without further purification. For $GaCl_3$, stock solution in hexane was prepared from anhydrous $GaCl_3$ (Aldrich; >99.999%). For $FeCl_3$, stock solution in diethyl ether was prepared from anhydrous $FeCl_3$ (Aldrich; 99.99%). The adduct of IBVE with HCl was prepared from the addition reaction of IBVE with HCl.[19] All chemicals except for dichloromethane, toluene, and 2,2'-bipyridine were stored in brown ampules under dry nitrogen.

Polymerization Procedure. The following is a typical polymerization procedure: A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ-206A; the blow temperature ~450 ºC) under dry nitrogen. Dichloromethane, ethyl acetate, and MOBD were added successively into the tube using dry syringes. After cooled to –78 ºC, a solution of HCl in dichloromethane containing a small amount of diethyl ether was added into the tube. The solution was kept at –78 ºC for 1 h. The polymerization was then started by adding an $SnCl_4$ solution in dichloromethane. After predetermined time, 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 removed under reduced pressure at 50 ºC and the residue was vacuum-dried for more than 6 h at room temperature. The monomer conversion was determined by gas chromatography (column packing material: PEG-20M-Uniport HP; GL Sciences Inc.) using heptane as an internal standard.

Characterization. The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 ºC with polystyrene gel columns [TSKgel GMH_{HR}-M $\times$ 2 or 3 (exclusion limit MW = 4×10^6; bead size = 5 μm; column size = 7.8 mm I.D. $\times$ 300 mm); flow rate = 1.0 mL min^{-1}] 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 the 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, $M_w/M_n \leq 1.1$). The absolute MW was determined using a GPC system composed of a pump (Viscotek VE 1122), polystyrene gel columns (TSKgel GMH_{HR}-M $\times$ 2), and a Viscotek TDA 305 triple detector [refractive index, laser light scattering (λ = 670 nm; 90º RALS and 7º LALS), and differential pressure viscometer] (eluent: THF). NMR spectra were recorded using a JEOL JNM-ECA 500 (500.16 MHz for ^1H and 125.77 MHz for ^{13}C). IR spectra were recorded using a JASCO FT/IR-6100 spectrometer.

RESULTS AND DISCUSSION

Controlled Cationic Polymerization of MOBD

Cationic polymerization of MOBD was first conducted under conditions suitable for living cationic polymerization of alkyl VEs.[20] An initiating system that consisted of a metal halide catalyst and a weakly Lewis basic additive was employed along with HCl as a protonogen in dichloromethane at –78 °C. Among the catalysts employed, $SnCl_4$ and $GaCl_3$ were effective for inducing controlled polymerization reactions (Figure 1; entries 1 and 5 in Table 1). In the presence of ethyl acetate, the polymerization of MOBD smoothly proceeded in a homogeneous state, producing polymers

Table 1. Cationic polymerization of MOBD under various conditions[a]

entry	cationogen	catalyst	weak Lewis base	solvent	temp.	time	conv. (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]
1	HCl	$SnCl_4$	ethyl acetate	CH_2Cl_2	–78	28 h	89	7.4	7.1	1.59
2			ethyl acetate	CH_2Cl_2	0	1 min	79	6.6	4.2	2.03
3			ethyl acetate	toluene	–78	6 h	61	5.1	3.2	8.09
4			none	CH_2Cl_2	–78	5 h	67	5.6	4.8	1.76
5		$GaCl_3$	ethyl acetate	CH_2Cl_2	–78	8 h	64	5.3	4.7	1.85
6			THF	CH_2Cl_2	–78	7 h	78	6.5	6.6	2.27
7		$EtAlCl_2$	ethyl acetate	CH_2Cl_2	–78	24 h	74	6.1	3.4	2.60
8		$FeCl_3$	ethyl acetate	CH_2Cl_2	–78	6 h	81	6.7	3.9	1.92
9	IBVE–HCl	$SnCl_4$	ethyl acetate	CH_2Cl_2	–78	1 h	32	2.7	3.7	1.66
10		$GaCl_3$	THF	CH_2Cl_2	–78	9 h	86	5.9	12.8	1.93

[a] $[MOBD]_0$ = 0.39 M, $[cationogen]_0$ = 4.0 mM, $[Lewis\ acid]_0$ = 5.0 mM, [additive] = 0.10 M, $[Et_2O]$ = 37 mM (for entries 1—8), [DTBP] = 5.0 mM (for $GaCl_3$), in CH_2Cl_2 at –78 °C. [b] Determined by GPC (polystyrene standards).

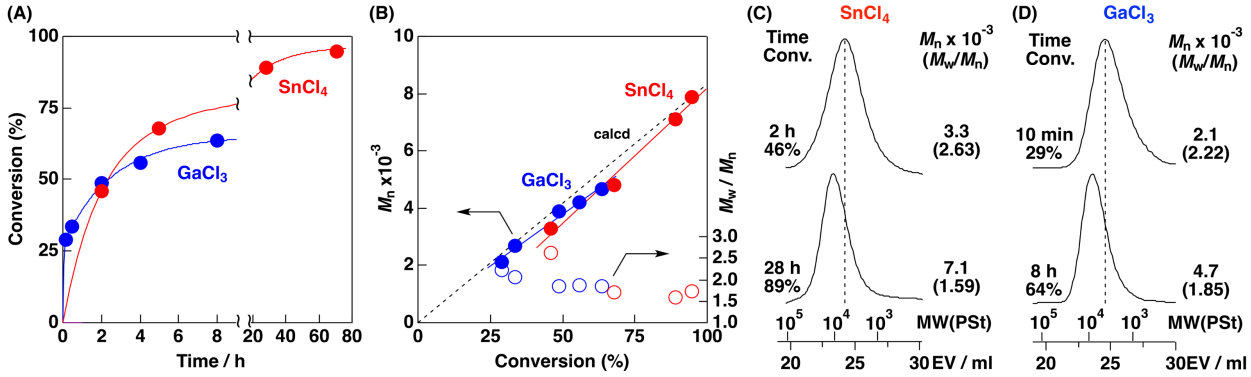


Figure 1. (A) Time-conversion curves, (B) M_n and M_w/M_n values for the polymerization of MOBD, and MWD curves of the polymers obtained with (C) $SnCl_4$ and (D) $GaCl_3$ {$[MOBD]_0$ = 0.39 M, $[HCl]_0$ = 4.0 mM, $[Lewis\ acid]_0$ = 5.0 mM, [ethyl acetate] = 0.10 M, $[Et_2O]$ = 37 mM, [DTBP] = 5.0 mM (for $GaCl_3$), in dichloromethane at –78 °C}.

with unimodal MWDs. The product polymers obtained with any catalyst were completely soluble in organic solvents, such as toluene and chloroform, indicating that intermolecular cross-linking reactions negligibly occurred during polymerization. The MWD curves of the products shifted toward higher-MW regions as the monomer conversion increased (Figures 1C and 1D), which indicates the generation of long-lived species. The M_n values of the polymers were in agreement with the theoretical values calculated on the basis of the monomer/protonogen ratios (Figure 1B). In addition, the M_n value based on polystyrene calibration was comparable to the absolute M_n value determined using a GPC system equipped with a light-scattering detector (M_n based on polystyrene standard = 7.1×10^3, absolute M_n = 7.7×10^3; entry 1 in Table 1). Moreover, the MWD curve also shifted toward a higher-MW region after the addition of a fresh feed of MOBD, which indicates that the polymerization occurred in a living manner (Figure S1).[21]

Suitable reaction conditions, including the temperature, solvents, additives, catalysts, and cationogen, were indispensable for the controlled polymerization of MOBD. The reaction at a higher temperature (0 °C)

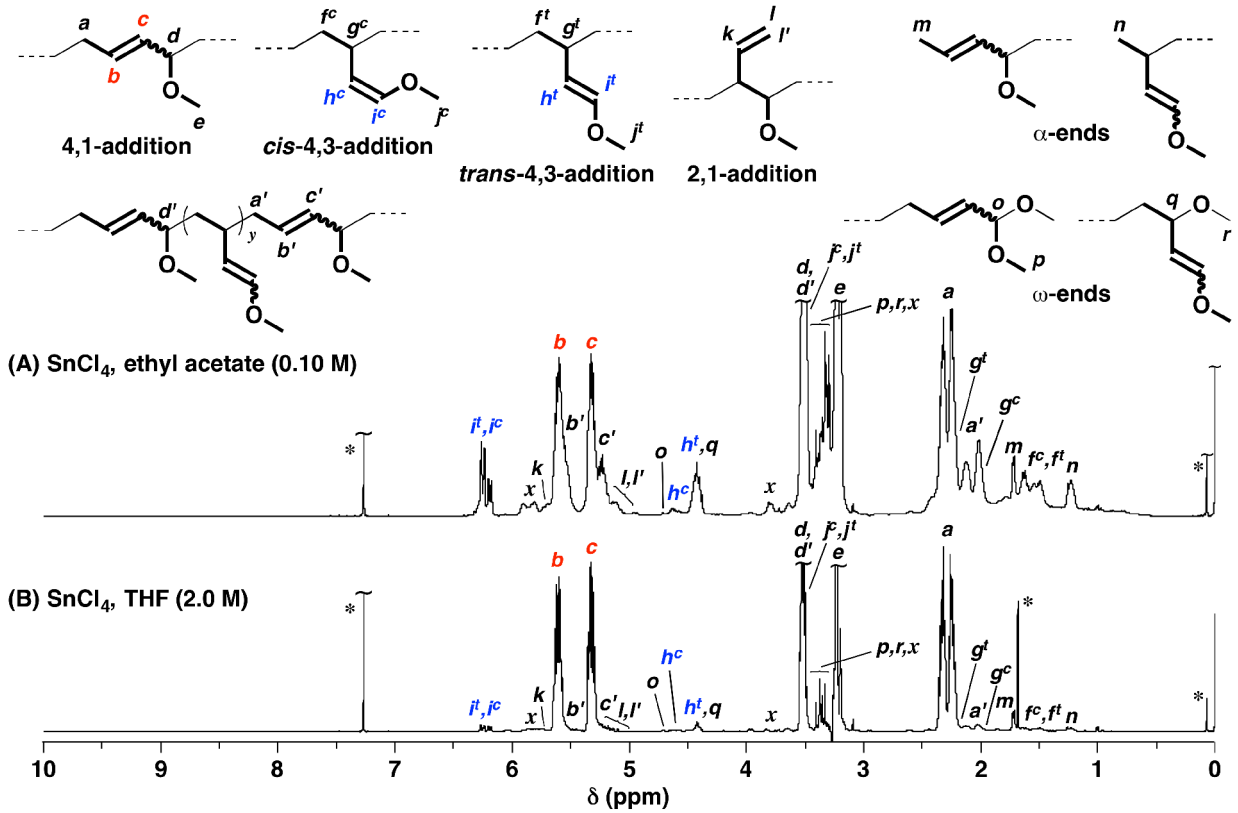


Figure 2. ^{1}H NMR spectra of poly(MOBD)s obtained with $SnCl_4$ in the presence of (A) ethyl acetate (entry 1 in Table 1; entry 6 in Table 2; entry 6 in Table 4) or (B) THF (entry 3 in Table 2); in $CDCl_3$ at 30 ºC (* water, grease, and solvent; see Scheme S1 for peaks *x*).

proceeded at a higher rate and produced a polymer with a broader MWD (entry 2) compared to that of the polymer produced by the reaction at –78 °C. In addition, the use of toluene instead of dichloromethane as a solvent resulted in the generation of a product with a very broad MWD (entry 3). Side reactions such as Friedel–Crafts reaction with toluene were not confirmed via NMR analysis of the product. The reaction in the absence of ethyl acetate (containing 37 mM of diethyl ether derived from the HCl solution) generated a product with a slightly lower MW and a broader MWD (entry 4). The polymerization using $EtAlCl_2$ or $FeCl_3$ as a catalyst also yielded polymers with lower M_n values (entries 7 and 8). In contrast, when IBVE–HCl, which is an adduct of IBVE with HCl, was employed as a cationogen in place of HCl, the reaction yielded products with MWs greater than the theoretical values (entries 9 and 10; see entries 1 and 6 for comparison, respectively). In particular, an M_n value that is twice as large as the calculated value was obtained when $GaCl_3$ was used as a catalyst, which indicates low initiation efficiency from IBVE–HCl.

^{1}H NMR analysis of the product obtained with the $SnCl_4$/ethyl acetate system (Figure 2A; see Figures S2–S5 for ^{13}C and 2D NMR spectra) indicated that the polymer was primarily generated via 4,1- and 4,3-addition reactions. In addition, the number of structures resulting from the 4,1-addition reaction (peaks *a*, *b*, *c*, *d*, and *e*)[22] was more than three times the number resulting from the 4,3-addition reaction (peaks *f*, *g*, *h*, *i*, and *j*) under all of the investigated polymerization conditions. The peaks assigned to the structure derived from the 2,1-addition reaction (peaks *k*, *l*, and *l'*) were also observed; however, their integral ratios were much

smaller than those of the peaks of the aforementioned structures. A very small amount (approximately 10%) of the *cis*-isomer in the employed monomer reagent[18] is most likely responsible for the generation of the 2,1-addition structure, as previously reported for the polymerization of a mixture of *trans*- and *cis*-1-ethoxy-1,3-butadiene.[17] Therefore, the microstructure analysis suggests that the propagation reaction primarily occurred through the addition of a monomer at the 4-position to the carbocationic species, which has a resonance structure. The preferential formation of the 4,1-structure over the 4,3-structure is due to the nature of the propagating carbocation. The positive charge may be preferentially located on the 1-position compared to the 3-position, and/or the steric hindrance around the 1-position may be smaller than that around the 3-position. In addition, the higher reactivity or the higher energy of the enol ether moiety resulting from the 4,3-addition reaction compared to that of the alkyl-substituted olefin moiety resulting from the 4,1-addition reaction may be responsible for the preferential formation of the 4,1-structure.

The most likely side reactions in the polymerization were the intramolecular or intermolecular reactions of the propagating species with the carbon–carbon double bonds in the polymer chains. In particular, the propagating carbocation may react with the side-chain moiety that results from the 4,3-addition reaction. This reaction is due to the alkoxy group with an adjacent double bond, which is similar to the structure of a β-alkyl substituted VE, possessing a greater electron density compared to other structures, such as those generated from the 4,1-addition reaction. An estimate based on the ^{1}H NMR spectra of the product polymers suggested that these intramolecular or intermolecular reactions might occur. However, the ratio is calculated to be, at most, approximately 10%, even though the ratio depends on the employed reaction conditions. The values were estimated on the basis of a comparison of the integral ratios of the unsaturated (4–7 ppm) and saturated (1–4 ppm) regions. Peaks *x* in the spectra (Figure 2) are assigned to the protons of the cyclic structure that result from the intramolecular cyclization reaction (see Scheme S1).

The Effects of Weak Lewis Bases on the Microstructure and the Polymerization Rate

On the basis of the investigation of the effects of the reaction conditions on the microstructure of the product polymers, the weak Lewis bases were primarily responsible for the ratio of the 4,1- and 4,3-structures. The results of the cationic polymerization of MOBD using $SnCl_4$ in the presence of various weak Lewis bases are listed in Table 2. High 4,1/4,3 ratios were achieved when THF was employed as an additive. The polymerization in the presence of 0.10 M THF yielded a product with a 4,1/4,3 ratio of 91/9 (entry 1), which is a higher ratio than that obtained in the presence of ethyl acetate (77/23, entry 6). In addition, when the concentration of THF was increased to 1.0 M (entry 2) or 2.0 M (entry 3; Figure 2B for the ^{1}H NMR spectrum of the product), the highest 4,1/4,3 ratio (96/4) was attained. However, different cyclic and acyclic ethers [i.e., 1,4-dioxane (entry 10) and diethyl ether (entry 11)] were less effective for controlling the microstructure and yielded products with 4,1/4,3 ratios of 80/20 and 78/22, respectively. In addition, the 4,1/4,3 ratio did not increase in the presence of a larger quantity of ethyl acetate (entry 7). Furthermore, the 4,1/4,3 ratios of the products with ethyl acetate, 1,4-dioxane, or diethyl ether were comparable to the ratios of the products obtained in the absence of an additive (80/20, entry 13; containing 37 mM of diethyl ether derived from the HCl solution), which suggests that these weak Lewis bases only modestly affect the microstructure compared to the effect of THF. The polymer produced with glyme had a higher 4,1/4,3 ratio of 90/10 (entry 12), which was in contrast to the cases using ethyl acetate, 1,4-dioxane, and diethyl ether.

Table 2. Effects of weak Lewis bases, solvent, and temperature on the microstructure of poly(MOBD)[a]

entry	additive	[additive]	solvent	temp.	time	conv. (%)	$M_n \times 10^{-3}$ (calcd)	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	4,1-/4,3-unit ratio[c]
1	THF	0.10 M	CH_2Cl_2	–78	2 h	84	7.0	4.2	2.31	91/9
2		1.0 M	CH_2Cl_2	–78	30 min	83	6.9	5.4	1.95	96/4
3		2.0 M	CH_2Cl_2	–78	10 min	81	6.7	6.1	1.76	96/4
4		1.0 M	toluene	–78	6 h	63	5.2	2.7	2.91	95/5
5		1.0 M	CH_2Cl_2	–40	3 min	86	7.1	4.8	2.01	96/4
6[d]	ethyl acetate	0.10 M	CH_2Cl_2	–78	28 h	89	7.4	7.1	1.59	77/23
7		2.0 M	CH_2Cl_2	–78	2 h	55	4.5	3.2	1.98	77/23
8[d]		0.10 M	toluene	–78	6 h	61	5.1	3.2	8.09	82/18
9[d]		0.10 M	CH_2Cl_2	0	1 min	79	6.6	4.2	2.03	88/12
10	1,4-dioxane	2.0 M	CH_2Cl_2	–78	30 min	34	2.9	1.9	4.84	80/20
11	Et_2O	2.0 M	CH_2Cl_2	–78	5 h	82	6.9	3.3	2.25	78/22
12	glyme	1.0 M	CH_2Cl_2	–78	30 min	48	4.0	2.1	2.28	90/10
13[d]	none	–	CH_2Cl_2	–78	5 h	67	5.6	4.8	1.76	80/20

[a] $[MOBD]_0$ = 0.39 M, $[HCl]_0$ = 4.0 mM, $[SnCl_4]_0$ = 5.0 mM, $[Et_2O]$ = 37 mM. [b] Determined by GPC (polystyrene standards). [c] Determined by ^1H NMR. [d] Entries 6, 8, 9, and 13 are the same samples to entries 1, 3, 2, and 4 in Table 1, respectively.

Table 3. Effects of various additives on the microstructure of poly(MOBD)[a]

entry	additive	4,1/4,3-ratio[b]
1	Me_2S (5.0 mM)	93/7
2	2,2'-bipyridine (5.0 mM)	76/24
3	DTBP (5.0 mM)	80/20
4	nBu$_4$NCl (8.0 mM)	82/18

[a] $[MOBD]_0$ = 0.39 M, $[HCl]_0$ = 4.0 mM, $[SnCl_4]_0$ = 5.0 mM, $[Et_2O]$ = 37 mM. in dichloromethane at –78 °C. See Table S1 for the conversion values and MWs. [b] Determined by ^1H NMR.

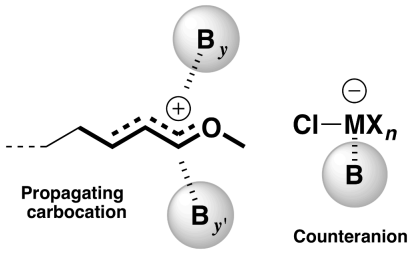


Figure 3. Plausible roles of weak Lewis bases (B: weak Lewis base).

The reaction in the presence of dimethyl sulfide (entry 1 in Table 3) yielded a 4,1/4,3 ratio that was comparable to that obtained using THF. Interestingly, a very small amount of dimethyl sulfide was sufficient to increase the amount of 4,1-structure. The reaction in the presence of a larger amount (10 mM) of dimethyl sulfide did not proceed, likely because of deactivation of the catalysts through interaction with the very strong Lewis base. Unlike Me_2S, other additives (2,2'-bipyridine, DTBP, and nBu$_4$NCl) were inefficient for increasing the 4,1/4,3 ratio (entries 2—4 in Table 3).

Weak Lewis bases affect the 4,1/4,3 ratios of the product polymers through interaction with the propagating carbocation and/or through coordination to the counteranion[23] (Figure 3). Because of these weak Lewis base functions, the direction in which a monomer adds to the propagating carbocation might be restricted. In these cases, the size and basicity of the weak Lewis base may affect the degree of the restriction.

The solvent polarity and temperature moderately affected the microstructure of the obtained poly(MOBD)s. The polymerization of MOBD using $SnCl_4$ in toluene, which is a less polar solvent, in the presence of ethyl acetate yielded a polymer with a 4,1/4,3 ratio (82/18, entry 8) slightly larger than that produced in dichloromethane. In addition, polymerization at a higher temperature (0 °C) resulted in an increase in the 4,1/4,3 ratio (88/12, entry 9). However, in the presence of THF, the solvent polarity and temperature negligibly affected the microstructure of the product polymers (entries

4 and 5). Comparable 4,1/4,3 ratios were obtained in toluene (95/5) or at a higher temperature (96/4). The effects of the solvent polarity and temperature would be marginal under conditions that allow for a high level of control over the microstructure of poly(MOBD)s. In contrast to the effects of solvent and temperature, the Lewis acid catalysts did not affect the 4,1/4,3 ratio. Products with similar 4,1/4,3 ratios were obtained using $SnCl_4$, $GaCl_3$, $FeCl_3$, and $EtAlCl_2$ (Table 4).

Table 4. Effects of Lewis acids on the microstructure of poly(MOBD)[a]

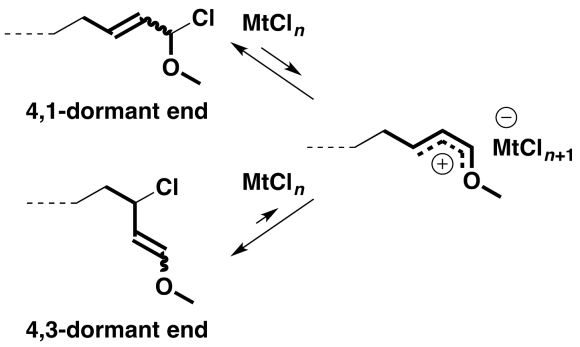
entry	additive	Lewis acid	4,1/4,3-ratio[b]
1[c]	THF	$SnCl_4$	91/9
2		$GaCl_3$	92/8
3		$FeCl_3$	92/8
4	1,4-dioxane	$SnCl_4$	79/21
5		$GaCl_3$	78/22
6[c]	ethyl acetate	$SnCl_4$	77/23
7		$GaCl_3$	79/21
8[c]		$FeCl_3$	78/22
9		$EtAlCl_2$	78/22

[a] $[MOBD]_0$ = 0.39 M, $[HCl]_0$ = 4.0 mM, $[Lewis\ acid]_0$ = 5.0 mM, [additive] = 0.10 M, $[Et_2O]$ = 37 mM. in dichloromethane at –78 ºC. See Table S2 for the conversion values and MWs. [b] Determined by ^1H NMR. [c] Entries 1 and 6 are the same samples to entries 1 and 6 in Table 2, respectively. Entry 8 is the same sample to entry 8 in Table 1.

Weak Lewis bases also affected the polymerization rates but exhibited trends that differed from their effects on the polymerization of alkyl VEs. Cationic polymerizations of alkyl VEs using metal chloride catalysts in the presence of THF proceed much slower compared to reactions in the presence of ethyl acetate or 1,4-dioxane. For example, the monomer conversion in the cationic polymerization of IBVE using $GaCl_3$ reached ca. 50% in ~10 min, < 1 s, and < 2 s in the presence of THF, ethyl acetate, and 1,4-dioxane, respectively ($[IBVE]_0$ = 0.76 M, $[IBVE–HCl]_0$ = 4.0 mM, $[GaCl_3]_0$ = 5.0 mM, [weak Lewis base] = 1.0 M, in toluene at 0 °C).[24] The greater moderation by THF is most likely due to the stronger interaction between the Lewis acid catalyst (and/or the propagating carbocation) and THF compared to when a weaker Lewis base is used. In contrast to the polymerization rate of alkyl VEs, the polymerization rate of MOBD in the presence of THF was much larger than that in the presence of ethyl acetate or 1,4-dioxane. In addition, the reaction with a larger amount of THF (2.0 M) proceeded much faster than that with a smaller amount (0.10 M).

The unique trends in the polymerization rates of MOBD may be partially related to the difference in the reactivity of the 4,1- and 4,3-type dormant species with carbon–chlorine bonds (Scheme 2). Because the dormant species with the 4,1-structure are activated more easily than those with the 4,3-structure, the polymerization proceeds faster under conditions that yield high 4,1/4,3 ratios of the main chain structures. In these cases, weak Lewis bases are responsible for the 4,1/4,3 ratio of the dormant species in a manner similar to their effects on the main chain structure. Specifically, the 4,1/4,3 ratios in the main chain structures of the resulting polymers may be closely related to the 4,1/4,3 ratios of the dormant species formed during polymerization because the main chain structures and the dormant species are formed through the addition of a monomer or a chlorine atom (anion), respectively, to a carbocationic species with a resonance structure (however, the higher reactivity of the 4,1-type dormant species than the 4,3-counterpart likely caused the accumulation of the latter; see Figure S7). Therefore, both the highest 4,1/4,3 ratio and the highest polymerization rate were achieved in the presence of THF. Another possible explanation is that THF assists the activation of the dormant species via nucleophilic attack on the carbon atom adjacent to the chlorine atom or the carbon at the γ-position. The abstraction of the Cl anion by the catalyst and the nucleophilic attack by THF would occur via a concerted mechanism. In any case, the polymerization rates are most likely governed by the balance between these effects and the degree of moderation of the catalyst activity due to interactions with the weak Lewis bases. In particular, a strong Lewis base such as

dimethyl sulfide may affect the polymerization rate primarily through the latter effect.



Scheme 2. The 4,1- and 4,3-type dormant species that generate during the cationic polymerization of MOBD.

The difference in the reactivity between the 4,1- and 4,3-dormant ends would also be responsible for the relatively broad MWDs of the product polymers. When the 4,3-type dormant ends are harder to cleave compared to the 4,1-type dormant ends, uneven propagation reactions will occur, yielding a product with a broader length distribution of the polymer chains. Such disproportion of chain lengths among polymer chains is significant in the early stage of polymerization, which is probably responsible for the larger MWDs of the products obtained at lower monomer conversion. However, the M_n values of the products will agree with the calculated values as long as undesired reactions are suppressed and the initiation efficiency is quantitative.

Cationic Copolymerization of MOBD with IBVE: Unique Reactivity of MOBD

To further examine the reactivity of MOBD, cationic copolymerization with IBVE was conducted under conditions that are effective for the controlled polymerization of MOBD (Figure 4). When $SnCl_4$ was used as a catalyst, both MOBD and IBVE were consumed at comparable rates to achieve a conversion of approximately 85% in 8 h, which resulted in polymers with unimodal MWDs. The M_n values of the products increased linearly, which indicates the generation of long-lived species. The ^{13}C NMR spectrum of the copolymer (Figure 5) exhibited a peak that was assigned to the methylene carbon of the MOBD unit in the IBVE–MOBD sequence, suggesting that the copolymerization occurred through crossover reactions between the two monomers. The

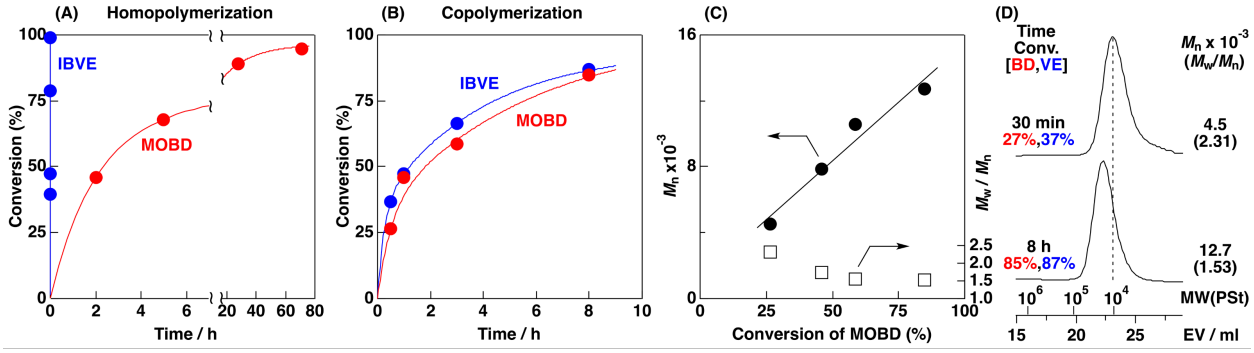


Figure 4. Time–conversion curves for (A) the homopolymerizations and (B) the copolymerization of MOBD and IBVE, (C) M_n and M_w/M_n values, and (D) MWD curves of the copolymers {$[MOBD]_0$ = 0.39 M, $[IBVE]_0$ = 0.39 M, $[HCl]_0$ = 4.0 mM, $[SnCl_4]_0$ = 5.0 mM, [ethyl acetate] = 0.10 M, $[Et_2O]$ = 37 mM, in dichloromethane at –78 ºC}.

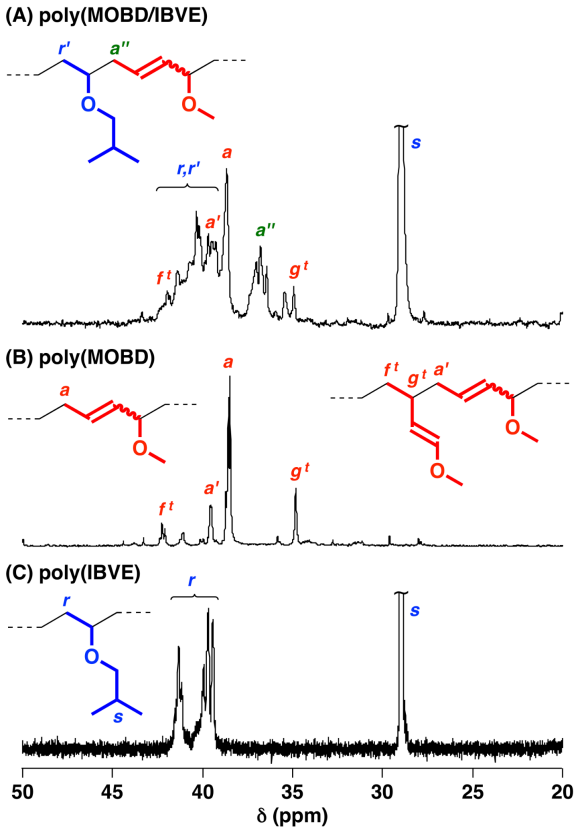
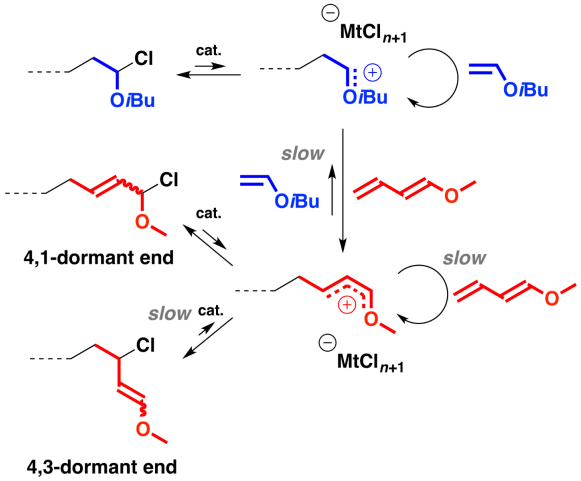


Figure 5. ^{13}C NMR spectra of (A) poly(MOBD-*co*-IBVE) (the upper sample in Figure 4D), (B) poly(MOBD) [obtained with $SnCl_4$ in the presence of ethyl acetate (0.10 M); M_n(GPC) = 4.8 × 10^3, M_w/M_n(GPC) = 1.70] and (C) poly(IBVE) [obtained with $SnCl_4$ in the presence of 1,4-dioxane (1.0 M); M_n(GPC) = 17.8 × 10^3, M_w/M_n(GPC) = 1.07]; in $CDCl_3$ at 30 ºC (see Figure S2A for the spectra at a wider region).

monomer reactivity ratios were determined to be r_{MOBD} = 0.68 and r_{IBVE} = 1.2 using the Kelen-Tüdõs method[25,26] (Figure S8). These values indicate that both monomers have comparable reactivities in the copolymerization reactions.

Interestingly, the consumption rate of IBVE in the copolymerization with MOBD was significantly smaller compared to the rate in the homopolymerization, even though MOBD was consumed at comparable rates in both polymerizations. The conversion of IBVE reached 99% in 30 s in the homopolymerization, and a conversion of 87% was achieved in 8 h in the copolymerization under the same conditions. The significant retardation of the IBVE consumption in the copolymerization may be due to the stability of the MOBD-derived carbocation and/or the reactivity of the MOBD-derived dormant species (Scheme 3). In the former case, the propagation reactions through the addition reactions of the IBVE or MOBD monomers to the MOBD-derived carbocation are slow because of the high stability or low electrophilicity of the carbocation resulting from the delocalization of the positive charge. In the latter case, the low concentration of the propagating carbocations, which results from infrequent formation of the propagating carbocations from the 4,3-type dormant ends derived from MOBD, is responsible for the slow copolymerization reaction. Because the 4,3-type dormant end is much less frequently activated compared to other dormant ends, such as the 4,1-type and the IBVE-derived ends, most of the propagating chains are almost exclusively 4,3-type dormant ends. The copolymerization results suggest that the diene structure is responsible for the unique reactivity of MOBD.



Scheme 3. Possible mechanisms for the copolymerization of MOBD and IBVE.

CONCLUSIONS

Cationic polymerization of MOBD was demonstrated to proceed in a controlled manner using an initiating system composed of $SnCl_4$ or $GaCl_3$ and a weak Lewis base at –78 °C. Soluble polymers with theoretical MW values were obtained, which indicated that the polymerization proceeded without accompanying side reactions, such as crosslinking reactions. In addition, weak Lewis bases were responsible for the control over the microstructure of the product polymers. A very high 4,1/4,3 ratio of 96/4 was achieved when THF was employed as an additive. In addition, the polymerization rates depended on the weak Lewis bases but exhibited trends that differed from those of the polymerization of alkyl VEs. The effect of weak Lewis bases on the polymerization rates may also be related to the 4,1/4,3 ratio in the main chain. The results obtained in this study will lead to more precise control over the MW and microstructure of the products of cationic polymerizations of various diene monomers.

ACKNOWLEDGEMENTS

This work was partially supported by JSPS KAKENHI Grant Numbers 17H03068 and 26708014.

REFERENCES AND NOTES

1. R. P. Quirk In Polymer Science: A Comprehensive Reference; K. Matyjaszewski; M. Möller, Eds; Elsevier B. V.: Amsterdam, **2012**; vol. 3.17.
2. Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1.
3. P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404.
4. N. Ajellal, L. Furlan, C. M. Thomas, O. L. Casagrande Jr, J.-F. Carpentier, *Macromol. Rapid Commun.* **2006**, *27*, 338.
5. L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.* **2007**, *46*, 1909.
6. S. Ouardad, M.-E. Bakleh, S. V. Kostjuk, F. Ganachaud, J. E. Puskas, A. Deffieux, F. Peruch, *Polym. Int.* **2012**, *61*, 149.
7. S. Ouardad, A. Deffieux, F. Peruch, *Pure Appl. Chem.* **2012**, *84*, 2065.
8. N. G. Gaylord, B. Matyska, K. Mach, J. Vodehnal, *J. Polym. Sci., Part A-1* **1966**, *4*, 2493.
9. K. Hasegawa, R. Asami, T. Higashimura, *Macromolecules* **1977**, *10*, 592.
10. C. Vautrin-Ul, F. Pla, A. Petit, *Macromol. Symp.* **1997**, *119*, 197.
11. J.-M. Santarella, E. Rousset, S. Randriamahefa, A. Macedo, H. Cheradame, *Eur. Polym. J.* **2000**, *36*, 2715.
12. S. Ouardad, T. Lebarbé, A. Deffieux, F. Peruch, *Polym. Chem.* **2013**, *4*, 407.
13. M. Ouchi, M. Kamigaito, M. Sawamoto, *Macromolecules* **2001**, *34*, 3176—3181.
14. N. Mizuno, K. Satoh, M. Kamigaito, Y. Okamoto, *Macromolecules* **2006**, *39*, 5280.
15. S. Kobayashi, C. Lu, T. R. Hoye, M. A. Hillmyer, *J. Am. Chem. Soc.* **2009**, *131*, 7960.
16. M. Otsuki, T. Masuda, T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1157.
17. T. Fueno, T. Tsunetsugu, K. Arimoto, J. Furukawa, *J. Polym. Sci., Part A-1* **1971**, *9*, 163.
18. The MOBD monomer that was employed in this study is composed mostly of *trans*-isomer but contains a small amount (approximately 10%) of *cis*-isomer.
19. T. Higashimura, M. Kamigaito, M. Kato, T. Hasebe, M. Sawamoto, *Macromolecules* **1993**, *26*, 2670.
20. S. Aoshima, S. Kanaoka, *Chem. Rev.* **2009**, *109*, 5245.
21. Block copolymerization with IBVE was also feasible using $SnCl_4$ under the conditions similar to those for Figure 1 ($[IBVE]_0$ = 0.39 M, $[MOBD]_{added}$ = 0.39 M *;* $M_n = 15.4 \times 10^3$, M_w/M_n = 1.26).
22. Non-negligible amounts of *cis*-4,1-structures would be generated unlike the cationic polymerization of 1-ethoxy-1,3-butadiene (reference 17). See Figure S6 for the details.
23. A. Kanazawa, S. Shibutani, N. Yoshinari, T. Konno, S. Kanaoka, S. Aoshima, *Macromolecules* **2012**, *45*, 7749.

24. A. Kanazawa, S. Kanaoka, S. Aoshima, *Macromolecules* **2009**, *42*, 3965.
25. T. Kelen, F. Tüdõs, *React. Kinet. Catal. Lett.* **1974**, *1*, 487.
26. J. P. Kennedy, T. Kelen, F. Tüdõs, *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2277.