Cationic Polymerization Behavior of Alkoxyallenes

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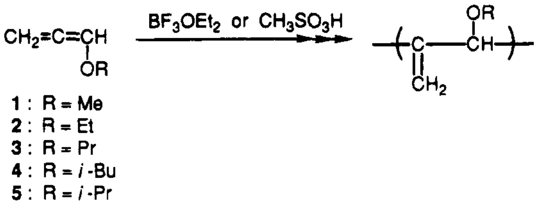
ABSTRACT: The alkoxyallenes (**1–5**) are polymerized by BF_3OEt_2 (2 mol %) or CH_3SO_3H (2 mol %) in dichloromethane at −50 °C. The cationic polymerizability of alkoxyallenes decreased in the following order: *i*-Pr > *i*-Bu > Pr > Et > Me. These results might be explained due to the electron-donating ability of the alkyl groups. The structures of all obtained polymers were formed by polymerizing only the 1,2-double bond of alkoxyallenes. The polymerization by BF_3OEt_2 decreased the content of the double bonds in the obtained polymer to 21–29 mol % of the theoretical content, whereas the polymerization by CH_3SO_3H suppressed the decrease of the double bond content in the obtained polymer.

Introduction

Cationic polymerization of a variety of vinyl monomers has been extensively developed, and further there has been much interest in the development of living cationic polymerization techniques for the synthesis of well-defined polymer structures in recent years.[1,2] However, no study has been reported on cationic polymerization of functional group-substituted allenes, which can be regarded as a kind of vinyl monomer having a cumulated carbon–carbon double bond, although the resulting polymers can be expected as functional polymers containing reactive *exo*-methylene groups attached to the polymer backbone.

We have recently developed work on the cationic polymerization of functional group-substituted allenes with the objective of an extension of our synthetic polymer chemistry of allene derivatives.[3] In a previous paper,[4] we have reported that methoxyallene (**1**) underwent cationic polymerization to afford a high molecular weight polymer by BF_3OEt_2 but a low molecular weight one by CH_3SO_3H. Both polymers consisted of repeat units derived by addition to the 1,2-double bond of allene. However, the content of the 2,3-double bonds in the resulting polymer decreased to 57–88 mol %, less than the theoretical amount, assuming that **1** was polymerized by only the 1,2-double bond in the polymerization by BF_3OEt_2, whereas in the polymerization by CH_3SO_3H the decrease of the 2,3-double bond content in the polymer was suppressed. This decrease of the olefin content in the polymer was speculated to involve both intra- and intermolecular reaction of a propagating cation with the 2,3-double bonds in the polymer.[4] Therefore, the olefin contents of the obtained polymers might be dependent on the nature of the initiator, the counterion, and the solvents.

In this paper, we wish to report the polymerization of some alkoxyallenes (**1–5**) by BF_3OEt_2 and CH_3SO_3H and discuss the effect of alkoxy groups on the olefin content, the molecular weight of the resulting polymers, and polymerization rate compared to the effect of alkoxy groups of vinyl ethers.



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Experimental Section

Measurements. ^1H NMR spectra were measured with a JEOL JNM-PMX 60si and JNM EX 90 spectrometer using CCl_4 or C_6D_6 as solvents. ^{13}C NMR spectra were also measured with a JNM EX90 or JNM-FX 100 spectrometer operating in the pulsed FT modes. Tetramethylsilane was used as an internal standard in CCl_4 or C_6D_6. FT-IR spectra were recorded on a JEOL JIR-5300. GPC was performed with a TOYO SODA CCP-8000 with a data processing system (eluent: THF, calibration: polystyrene standard). Conversion was estimated by GC analysis using the internal standard method (*n*-undecane) with a Shimazu GC-4CPF.

Preparation of Alkyl Propargyl Ethers. Alkyl propargyl ethers in this study were prepared from propargyl bromide and the corresponding alcohols in aqueous sodium hydroxide using tetrabutylammonium bromide (TBAB) as the phase transfer catalyst according to the reported method[5] under the conditions shown in Table 1.

Preparation of Alkoxyallenes 1–5. Alkoxyallenes **1–5** were prepared by the isomerization of the corresponding alkyl propargyl ethers with potassium *tert*-butoxide (30 mol %) according to the reported procedure[6] under the conditions shown in Table 2. All alkoxyallenes were distilled over sodium hydride before use.

Alkoxyallene **1**: ^1H NMR (CCl_4, TMS) δ 6.77 (t, 1H, $J = 6.0$ Hz), 5.47 (d, 2H, $J = 6.0$ Hz), 3.47 (s, 3H) ppm.

Alkoxyallene **2**: ^1H NMR (CCl_4, TMS) δ 6.62 (t, 1H, $J = 6.0$ Hz), 5.32 (d, 2H, $J = 6.0$ Hz), 3.53 (q, 2H, $J = 6.8$ Hz), 1.25 (t, 3H, $J = 6.8$ Hz) ppm.

Alkoxyallene **3**: ^1H NMR (CCl_4, TMS) δ 6.60 (t, 1H, $J = 6.0$ Hz), 5.30 (d, 2H, $J = 6.0$ Hz), 3.62 (d, 2H, $J = 7.0$ Hz), 1.63 (sixtet, 2H, $J = 7.0$ Hz), 0.97 (t, 3H, $J = 7.0$ Hz) ppm.

Alkoxyallene **4**: ^1H NMR (CCl_4, TMS) δ 6.62 (t, 1H, $J = 6.0$ Hz), 5.32 (d, 2H, $J = 6.0$ Hz), 3.23 (d, 2H, $J = 7.0$ Hz), 1.58–2.30 (m, 1H), 0.94 (d, 6H, $J = 7.0$ Hz) ppm.

Alkoxyallene **5**: ^1H NMR (CCl_4, TMS) δ 6.59 (t, 1H, $J = 5.9$ Hz), 5.37 (d, 2H, $J = 5.9$ Hz), 3.94 (septet, 1H, $J = 6.2$ Hz), 1.21 (d, 6H, $J = 6.2$ Hz) ppm.

Cationic Polymerization of alkoxyallenes 1–5 by BF_3OEt_2 or CH_3SO_3H. A typical procedure was carried out as follows. Cationic polymerizations of alkoxyallenes **1–5** (7 mmol) were carried out at −50 °C in the presence of BF_3OEt_2 (2 mol %) or CH_3SO_3H (2 mol %) in dry dichloromethane (12 mL) under an argon atmosphere. After the appropriate time, polymerization was quenched with ammoniacal methanol. The

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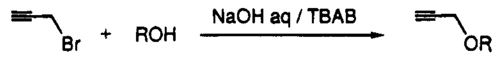
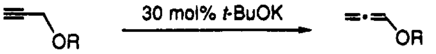
Table 1. Preparation of Alkyl Propargyl Ethers[a]



R	time, h	yield, %	bp, °C/Torr (lit.[5])
Me	7	77	57/760 (52–54/680)
Et	12	56	78–80/760 (76–78/680)
Pr	4	68	101/760 (96–96/680)
i-Bu	8	60	117–118/760
i-Pr	9	15	91/76 (87–89/680)

[a] $[\text{propargyl bromide}]_0 = 0.75$ M, $[\text{alcohol}]_0 = 0.75$ M, $[\text{NaOH}]_0 = 0.10$ M, $[\text{TBAB}]_0 = 0.25$ mM; the reaction was carried out at refluxing temperature.

Table 2. Preparation of Alkoxyallenes[a]



1-5

allene	R	temp, °C	time, h	yield, %	bp, °C/Torr (lit.[6])
1	Me	65	5	60	51–51.5/760 (51.5–52.5/760)
2	Et	25	4	46	78/760 (76–77/760)
3	Pr	25	1	48	56–56.5/149
4	*i*-Bu	25	1	40	71/144
5	*i*-Pr	25	0.5	48	91–92/760

[a] Reaction was carried out in bulk.

Table 3. Cationic Polymerization of Alkoxyallenes by BF_3OEt_2[a]

allene[b]	time, h	conv, %[c]	yield, %[d]	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	olefin content, mol %[f]
1	6	100	38[g]	23000[h]		76 (75)[i]
2	3	100	28	10000	1.84	72 (78)[i]
3	3	100	54	5400	2.38	79
4	3	100	55	4800	2.53	71
5	4	100	41	3800	2.13	73 (73)[i]

[a] 2 mol % at −50 °C. [b] $[\text{allene}]_0 = 0.60$ M in CH_2Cl_2. [c] Estimated by GC (internal standard: *n*-undecane). [d] Insoluble in methanol. [e] Estimated by GPC (based on PSt). [f] The content of the 2,3-double bond in the polymer estimated by ^1H NMR. [g] Insoluble in *n*-hexane. [h] Peak top value of GPC. [i] Wijs method.

quenched reaction mixture was diluted with dichloromethane (40 mL), subsequently washed with aqueous sodium bicarbonate and brine, and then dried over anhydrous magnesium sulfate. The dried solution was evaporated under reduced pressure to obtain the polymer. The polymer was purified by dissolution into dichloromethane followed by precipitation with methanol (except for polymerization of **1** which used *n*-hexane) containing a small amount of triethylamine. M^* (peak top value of GPC elution curve) and $\bar{M}_n$ of the polymer were estimated by GPC analysis.

Poly **1**: IR (KBr) 1652, 1456, 1186, 1088, 1003, 930 cm^{-1}; ^1H NMR (C_6D_6, TMS) δ 5.60 (s, 2H), 4.53 (s, 1H), 3.33 (s, 3H) ppm; ^{13}C NMR (C_6D_6, TMS) δ 146.5 ($C{=}CH_2$), 114.9 ($C{=}CH_2$), 81.8 ($CH{-}O$), 57.3 (OCH_3) ppm.

Poly **2**: IR (KBr) 1652, 1444, 1190, 1086, 987, 930 cm^{-1}; ^1H NMR (C_6D_6, TMS) δ 5.68 (s, 2H), 4.68 (s, 1H), 3.65–3.58 (m, 2H), 1.20 (s, 3H) ppm; ^{13}C NMR (C_6D_6, TMS) δ 147.3 ($C{=}CH_2$), 114.6 ($C{=}CH_2$), 80.1 ($CH{-}O$), 65.3 (OCH_2CH_3), 15.7 (CH_3) ppm.

Poly **3**: IR (KBr) 1650, 1465, 1087, 1051, 985, 922 cm^{-1}; ^1H NMR (CCl_4, TMS) δ 5.30 (bs, 2H), 4.20 (bs, 1H), 3.30 (bs, 2H), 1.93–0.55 (m, 5H) ppm; ^{13}C NMR (C_6D_6, TMS) δ 147.3 ($C{=}CH_2$), 114.8 ($C{=}CH_2$), 80.3 ($CH{-}O$), 71.9 ($-OCH_2CH_2CH_3$), 23.8 ($OCH_2CH_2CH_3$), 11.1 (CH_3) ppm.

Poly **4**: IR (KBr) 1651, 1471, 1188, 1084, 1024, 993, 930 cm^{-1}; ^1H NMR (CCl_4, TMS) δ 5.27 (s, 2H), 4.18 (s, 1H), 3.13 (bs, 1H), 2.17–1.27 (b, 2H), 1.22–0.57 (m, 6H) ppm; ^{13}C NMR (C_6D_6, TMS) δ 147.2 ($C{=}CH_2$), 115.1 ($C{=}CH_2$), 80.3 ($CH{-}O$), 77.3 (OCH_2CH), 29.4 (OCH_2CH, 19.9 (CH_3) ppm.

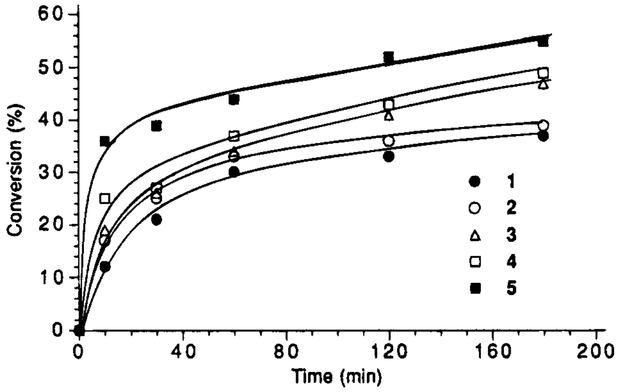


Figure 1. Time–conversion curves for the polymerizations of **1–5** by BF_3OEt_2-NEt_3 in dichloromethane at −50 °C. $[M]_0 = 0.30$ M; $[BF_3OEt_2]_0 = 1.0$ mol %; $[NEt_3]_0 = 0.25$ mol %.

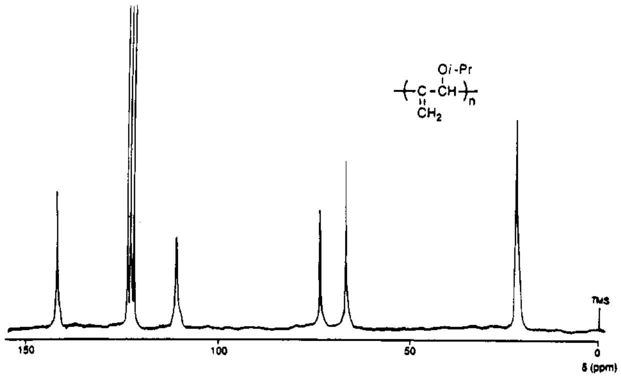


Figure 2. ^{13}C NMR spectra of poly **5**.

Poly **5**: IR (KBr) 1650, 1471, 1174, 1122, 1057, 989, 924 cm^{-1}; ^1H NMR (C_6D_6, TMS) δ 5.48 (s, 2H), 4.45 (s, 1H), 3.75 (s, 1H), 1.22 (s, 6H) ppm; ^{13}C NMR (C_6D_6, TMS) δ 148.4 ($C{=}CH_2$), 115.7 ($C{=}CH_2$), 76.7 ($CH{-}O$), 69.7 ($OCH(CH_3)_2$), 22.9 (CH_3) ppm.

Estimation of Polymerization Rate. Polymerization of alkoxyallenes **1–5** (5 mmol) was carried out at −50 °C in the presence of BF_3OEt_2 (1 mol %), NEt_3 (0.25 mol %), and *n*-undecane (0.1 g) as an internal standard in dry dichloromethane (16 mL) under an argon atmosphere. After a predetermined interval, the polymerization was terminated with ammoniacal methanol. Conversion was determined from the residual monomer concentration measured by gas chromatography with *n*-undecane as an internal standard.

Results and Discussion

Cationic Polymerizations of 1–5 by BF_3OEt_2. Methoxy- (**1**), ethoxy– (**2**), propoxy– (**3**), isobutoxy- (**4**), and isopropoxyallenes (**5**) were prepared according to the slightly modified Kucherov[5] and Aren[6] procedures. The cationic polymerizations of alkoxyallenes **1–5** were carried out at −50 °C by using BF_3OEt_2 (2 mol %) in dry dichloromethane under an argon atmosphere. The results are shown in Table 3. Furthermore, to compare the polymerization rates of **1–5** the polymerization was carried out at −50 °C with BF_3OEt_2 (1 mol %)–NEt_3 (0.25 mol %) in dry dichloromethane under an argon atmosphere, and their time–conversion curves (Figure 1) were established by monitoring the consumption of **1–5**.

As shown in Table 3, all alkoxyallenes polymerized by BF_3OEt_2 yielded methanol insoluble polymers except for the polymerization of **1**. The ^1H and ^{13}C NMR spectra of poly **5** were shown in Figures 2 and 3. As shown in Figure 2, ^{13}C NMR spectra exhibited five carbon signals at δ 22.9 (CH_3), 69.7 ($OCH(CH_3)_2$), 76.7

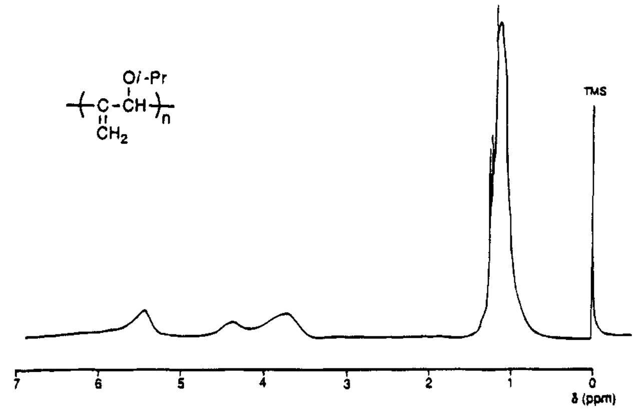


Figure 3. ^{1}H NMR spectra of poly **5**.

(*C*H—O), 115.7 (C=*C*H$_2$), and 148.4 (*C*=CH$_2$) ppm. Further, ^{1}H NMR spectra (Figure 3) showed four kinds of signals, *i.e.*, assignable to the methyl protons at δ 1.22, the isopropoxy methine proton at 3.75, the methine proton at 4.45, and the vinyl protons at 5.48 ppm. And then it was shown in Figure 3 that the ratio of *exo*-methylene and methine protons of the polymer was decreased in the theoretical ratio. These results were assumed to be caused by the intermolecular cyclization of the propagating species and the grafted reaction, the same as in the cationic polymerization of methoxyallene.[4] Accordingly, the structures of the obtained polymers seemed to be mainly polymerized 1,2-double bonds of all alkoxyallenes (eq 1). Molecular weights of the obtained polymers decreased in the following order: **1** > **2** > **3** > **4** > **5**, although the polymerization rate increased in the order **1** < **2** < **3** < **4** < **5**. The content of the 2,3-double bonds in the polymer was found to be 70−79%, irrespective of the alkoxy groups, by ^{1}H NMR and the titration method using iodine chloride the reagent developed by Wijs.[8]

The observed effects of the alkoxy groups of **1**−**5** on the molecular weight and the polymerization rate are very similar to those of the alkyl vinyl ethers;[7,9] with the increasing electron-donating ability of the alkoxy group, the molecular weight decreased but the polymerization rate increased. Accordingly, on the basis of the reported interpretation of the behavior of the cationic polymerization of alkyl vinyl ethers by a Lewis acid,[7,9] the decrease of the molecular weight seems to be attributed to the increased facility of chain transfer reaction of a propagating cation to the alkoxy group of allene monomer and/or allene polymer with the increasing stability of alkyl cations: $\mathrm{Me}^+ < \mathrm{Et}^+ < \mathrm{Pr}^+ < i\text{-}\mathrm{Bu}^+ < i\text{-}\mathrm{Pr}^+$, which is the same as the order of electron-donating ability. An increase of the polymerization rate may be accounted for by both the increased electron density of allene's carbon−carbon double bond and the increased stability of the propagating cation in the order of **1** < **2** < **3** < **4** < **5**.

Although the olefin content values of the 2,3-double bonds in the polymer were not strongly influenced by the alkoxy group of **1**−**5**, only the GPC elution curve of the polymer of **1** started from the very high molecular weight region, contrary to the polymer obtained from **2**−**5** (Figure 4). These differences imply that the decrease of the olefin content in the polymers of **2**−**5** may be interpreted in terms of only the intramolecular cyclization of the propagating cation to the 2,3-double bond in the polymer, since the very high molecular weight region of the polymer of **1** has been reported in the previous paper[4] to indicate the grafted polymer formed by the intermolecular reaction of a propagating cation with the 2,3-double bond in another polymer. Consequently, alkoxy groups that are more bulky than the methoxy group may be assumed to suppress the intermolecular side reaction of the propagating cation but not to affect the intramolecular side reaction of it.

[a] 2 mol % at −50 °C. [b] [allene]$_0$ = 0.60 M in CH$_2$Cl$_2$. [c] Estimated by GC (internal standard: *n*-undecane.) [d] Insoluble in methanol. [e] Estimated by GPC (based on PSt). [f] The content of the 2,3-double bond in the polymer estimated by ^{1}H NMR. [g] Insoluble in *n*-hexane. [h] Wijs method.

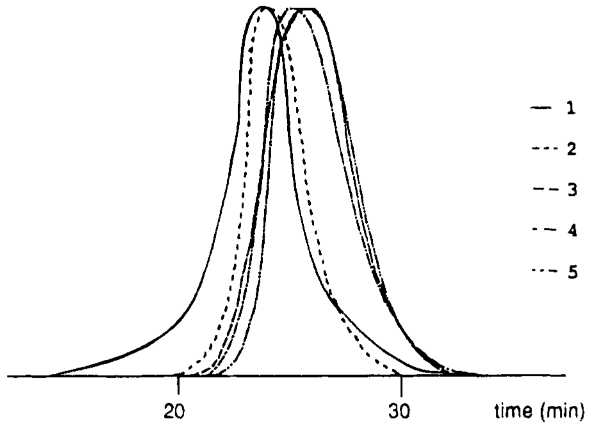


Figure 4. GPC elution curves of the obtained polymers on the cationic polymerization of alkoxyallenes **1**−**5** by BF$_3$OEt$_2$ (2 mol %) at −50 °C in dichloromethane.

Table 4. Cationic Polymerization of Alkoxyallenes by CH$_3$SO$_3$H[a]

allene[b]	time, h	conv, %[c]	yield, %[d]	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]	olefin content, mol %[f]
1	6	59	12[g]	1000	5.33	94 (90)[h]
2	8	76	6	3500	2.23	90
3	8	60	15	6800	2.51	96
4	8	58	14	6700	1.50	92
5	8	83	9	2000	1.44	95

[a] 2 mol % at −50 °C. [b] [allene]$_0$ = 0.60 M in CH$_2$Cl$_2$. [c] Estimated by GC (internal standard: *n*-undecane.) [d] Insoluble in methanol. [e] Estimated by GPC (based on PSt). [f] The content of the 2,3-double bond in the polymer estimated by ^{1}H NMR. [g] Insoluble in *n*-hexane. [h] Wijs method.

Cationic Polymerization of 1−**5 by CH$_3$SO$_3$H.** We have reported that the high olefin content of polymer **1** (94 mol %) was obtained by the polymerization with CH$_3$SO$_3$H, contrary to the polymerization by BF$_3$OEt$_2$.[4] However, the yield and the molecular weight of the resulting polymer were lower than those obtained by polymerization with BF$_3$OEt$_2$. Therefore, we examined the cationic polymerization of **2**−**5** with CH$_3$SO$_3$H, which can be expected to have a higher ability toward cationic polymerization. The cationic polymerizations of **1**−**5** were carried out at −50 °C in the presence of CH$_3$SO$_3$H (2 mol %) in dry dichloromethane under an argon atmosphere. These results are summarized in Table 4.

All alkoxyallenes underwent polymerization to yield methanol insoluble polymers except for **1**, although the polymerizations only reached a relatively low conversion, as shown in Table 4, even after 8 h of reaction time. ^{1}H and ^{13}C NMR and IR spectra of the polymers were very similar to those of the corresponding polymers obtained by BF$_3$OEt$_2$ and supported the fact that all of the 1,2-double bonds of **1**−**5** were consumed. The olefin content values of the 2,3-double bonds in the polymer were estimated to be more than 90 mol % by ^1H NMR in all cases. The molecular weights of the resulting polymers increased in the order **1** < **2** < **3** but decreased in the order **3** > **4** > **5**. It should be noted that the molecular weights of the polymers obtained from **3** and **4** were higher than those of the corresponding polymers obtained by BF_3OEt_2, and the olefin content of the polymer obtained from **3** increased to 96 mol %; it was very close to the ideal structure representing polymerization exclusively at the 1,2-double bond.

As mentioned in the previous paper,[4] higher olefin content obtained from the polymerization with CH_3SO_3H seems to be attributed to a poorly electrophilic and bulk propagating species involving a strong interaction of the propagating cation and the gegenion $CH_3SO_3^-$. These bulky propagating species may be also partially responsible for the different observed effect of the alkoxy group on the molecular weight, compared to the polymerization by BF_3OEt_2. Thus facility of the chain transfer reaction affecting the molecular weight may be interpreted by both stability of the alkyl cations, which increases in the order **1** < **2** < **3** < **4** < **5** as mentioned in the polymerization by BF_3OEt_2, and the steric hindrance in the chain transfer reaction of the bulky propagating species to the alkyl groups of the monomer and/or the polymer, which seems to decrease in the order **1** > **2** > **3** > **4** > **5**.

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