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Precise Synthesis of End-Functionalized Poly(vinyl chloride) with Butyllithium

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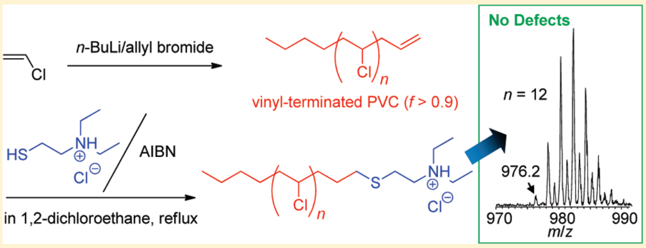
Supporting Information

ABSTRACT: The polymerization of vinyl chloride (VC) with *n*- or *tert*-butyllithium (*n*- or *tert*-BuLi) in the presence of allyl bromide (ABr) was evaluated for synthesizing the vinyl-terminated poly(vinyl chloride) macromonomer (PVCM). The structure of the product was based on the ^{1}H NMR and H−H COSY spectra. The functionality of the vinyl group was over 90%. To determine the detailed structure of PVCM, a MALDI-TOF-MS analysis of the PVCM derivative (PVC-DEA·HCl) obtained by the thiol−ene reaction of the macromonomer with 2-(diethylamino)ethanethiol hydrochloride was conducted. The MALDI mass spectrum of PVC-DEA·HCl in the absence of any ionizers exhibited only one series of ions repeating at an interval of 62 Da (which was the repeating VC unit), and the mass distribution agreed well with the calculated value of PVC-DEA·H$^+$ without any defect structures. The syndiotactic rich PVC was found to be synthesized by the polymerization of VC with BuLi in the presence of ABr. Especially, the obtained PVCM using *tert*-BuLi (ABr/BuLi = 10) was the most syndiotactic polymer (*rr* > 80%).



INTRODUCTION

Precision polymerization is an important method for polymer architecture with control of the molecular weight, stereoregularity, and chain-end structure of the polymer and has been well-developed regardless of the polymerization mechanisms.[1−3] Although molecular weight control of the poly(vinyl chloride) (PVC) has been achieved by the polymerization of vinyl chloride (VC) with butyllithium (BuLi),[4] half-titanocene/MAO,[5] Cu^0,[6] or Na$_2$S$_2$O$_4$[7] in this decade, the main-chain regularity and stereoregularity were not well-developed.

It was reported that the PVC obtained using BuLi or the half-titanocene/MAO catalyst had no defect structures introduced in a free-radical polymerization. On the other hand, the poly(vinyl chloride) macromonomer (PVCM) with a well-defined structure has not been synthesized, although a macromonomer having a vinyl group was synthesized by the reaction of a living polymer with allyl bromide (ABr).[8,9] In this study, the polymerization of VC with BuLi as the initiator and ABr as the end-functionalizer was investigated. The effect of ABr on the polymerization of VC with BuLi was also discussed.

EXPERIMENTAL SECTION

Materials. VC (Sumitomo Seika) was used after drying over calcium hydride. The *n*-hexane solution of *n*-BuLi (Kanto Chemical) and the *n*-pentane solution of *tert*-BuLi (Kanto Chemical) were used as received. ABr (Wako Pure Chemical) was distilled before use. Benzoyl peroxide (BPO, Nakarai Chemical) and *N*,*N*-dimethylaniline (DMA, Wako Pure Chemical) were used without further purification. All other reagents were used after purification by conventional methods.

Polymerization Procedure. A Y-shaped glass tube with a rubber septum for introducing the reagents into the tube by a syringe and with a connection to a vacuum system was used for charging the reagents. The tube was heated by a burner to dry the inside wall of the tube. The required amounts of reagents were charged into the tube using syringes through the rubber septum at −78 °C. In a typical case, VC (50 mL, 0.79 mol) was introduced into the tube at −78 °C by vacuum distillation, and then a 1.65 mol/L solution of *n*-BuLi (5.0 mL, 8.25 mmol) and ABr (0.7 mL, 8.1 mmol) was charged. After all reagents were charged, the tube was sealed off under high vacuum. The polymerization was carried out in a thermostat bath at a constant temperature for a given time. After the polymerization, the contents of the tube were poured into a large amount of methanol containing a small amount of hydrochloric acid to precipitate the polymer formed. The product was isolated and dried under high vacuum at room temperature overnight. The polymer yield was determined by a gravimetric method.

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Table 1. Synthesis of PVCM at −30 °C for 24 h[a]

entry	initiator	[ABr]/[BuLi]	yield (%)	$M_{n,GPC}$[b] × 10^{-3}	$M_{w,GPC}/M_{n,GPC}$
1	*n*-BuLi		0.4	13.6	2.5
2	*tert*-BuLi		1.2	13.3	1.9
3	*n*-BuLi	1.0	17.3	4.7	3.1
4	*tert*-BuLi	1.0	14.9	3.8	2.2

[a] VC = 50 mL, BuLi solution ([*n*-BuLi] = 1.65 mol/L, [*tert*-BuLi] = 1.76 mol/L) = 5.0 mL. [b] Calibrated by polystyrene standard.

Thiol−Ene Reaction of PVCM. A thiol−ene reaction of PVCM was carried out for synthesizing the chain-end aminated PVC hydrochloride, and the procedure was as follows. To a solution of 2-(diethylamino)ethanethiol hydrochloride (DEAET·HCl; 2.291 g, 13.5 mmol) in 1,2-dichloroethane (DCE; 40 mL) which was degassed under a N_2 stream for 15 min prior to use, PVCM (500 mg, $M_{n,GPC}$ = 3400, vinyl-group functionality >0.9), which was synthesized with *n*-BuLi (ABr/BuLi = 1.0), and 2,2′-azobis(isobutyronitrile) (AIBN; 185 mg, 1.125 mmol) were added, and the mixture was brought to reflux at 90 °C under a N_2 stream. After 90 min, additional AIBN (185 mg, 1.125 mmol) in DCE (20 mL) was mixed in the solution, and reflux was continued for 90 min. The solution was then allowed to cool to room temperature and subsequently added to acidic methanol (0.5 wt % HCl in 200 mL) to precipitate the high-molecular-weight diethylamino PVC hydrochloride (PVC-DEA·HCl). The precipitate in the solution was filtered through Celite, and the solvent of the filtrate was evacuated by a high vacuum. The resulting solid was washed by deionized water to obtain the low-molecular-weight PVC-DEA·HCl. The high- and low-molecular-weight PVC-DEA·HCl had 347 and 80.4 mg yields, respectively.

MALDI-TOF-MS Analysis. For the MALDI-TOF-MS analysis, α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix was used. A cationizing agent was not used in this study. The sample (1 mg/mL) and the matrix solution (10 mg/mL) in tetrahydrofuran (THF) were spotted onto the MALDI sample target at 0.6 μL each and then dried at room temperature. The mass spectra were acquired using an AXIMA-CFR time-of-flight mass spectrometer (Shimadzu/Kratos, Manchester, UK) with a pulsed nitrogen laser (3 ns pulse width, 337 nm) in the reflectron positive ion mode. Protonated ions of CHCA, angiotensin I, were used for the mass calibration. All mass spectra were acquired by averaging 100 individual laser shots at the laser power of 20.05 mJ/cm^2.

Characterization of Polymers. The number-average molecular weight ($M_{n,GPC}$) and the weight-average molecular weight ($M_{w,GPC}$) of the polymer were determined by GPC using THF as the eluent at 40 °C after calibration by standard polystyrene. The PVC structure was determined from the ^{1}H NMR spectra of the polymer taken in THF-d_8 at 55 °C and the ^{13}C NMR spectra of the polymer taken in a mixed solvent of benzene-d_6/*o*-dichlorobenzene (3/7 v/v) at 120 °C with hexamethyldisiloxane (HMDS) as the internal standard by a Bruker AVANCE 300N NMR spectrometer.

RESULTS AND DISCUSSION

Polymerization of VC with BuLi in the Presence of ABr. The polymerization of VC with *n*- and *tert*-BuLi as the initiator and ABr as the end-functionalizer was examined. Table 1 shows the results of the VC polymerization with *n*-BuLi or *tert*-BuLi at −30 °C in the presence of ABr under a nearly bulk condition, in which the results of the polymerization in the absence of the bromide is also indicated to comparison. The polymerization of VC with BuLi in the presence of ABr proceeded to give a white polymer as well as in the absence of the bromide. ABr may act not only as an end-functionalizer but also as an accelerator because the product yield was higher than that obtained in the absence of the bromide. Although the reason for this acceleration by addition of ABr is not clear, this may be explained by the effect of a donor on the aggregation of alkyllithiums.[10] The molecular weight distribution of the polymer obtained in the presence of ABr was broad. This may be explained by heterogeneity of the polymerization system. The $M_{n,GPC}$ value of the polymer obtained using ABr was lower than that of the product obtained without the bromide, suggesting that PVC obtained in this reaction has a terminal vinyl group.

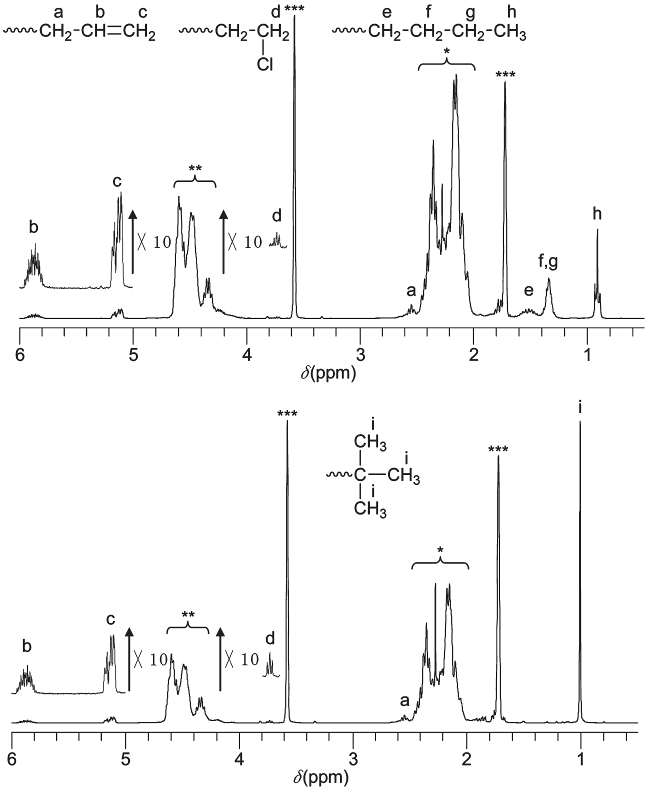

Figure 1. ^{1}H NMR spectra of the products obtained with *n*-BuLi (top, entry 3) and *tert*-BuLi (bottom, entry 4). *Assigned to the main-chain methylene proton of PVC. **Assigned to the main-chain methine proton of PVC. ***THF.

Structure of PVCM. To elucidate the structure of the products (entries 3 and 4), the ^{1}H NMR and H−H COSY spectra were measured at 55 °C in THF-d_8. The ^{1}H NMR spectra are shown in Figure 1, and the assignments of the polymer structure are indicated in the figure. The peaks based on the repeating units in PVC were observed at 1.8−2.6 ppm (methylene proton) and 4.0−4.8 ppm (methine proton), and the peaks identified as the structure derived from *n*-BuLi or *tert*-BuLi were also observed. The peaks estimated as protons of the terminal vinyl group were observed at 5.2 ppm ($-CH{=}CH_2$) and 5.8 ppm ($-CH{=}CH_2$). This was confirmed by the H−H COSY spectrum of the polymer as shown in Figure 2. From this figure, the allylic methylene proton ($-CH_2-CH{=}CH_2$, 2.5 ppm) is related to the chloro methine proton ($-CH_2-CHCl-$, 4.2 ppm) and is not related to the methylene proton ($-CH_2-CHCl-$). On the basis of these results, it is indicated that the PVCM shown in Figure 3 is synthesized by the polymerizations with BuLi in the presence of ABr. However, an undesirable termination reaction, such as proton or hydrogen abstraction, by the active species can be excluded as a very minor product in the VC polymerization with BuLi and ABr, since the small peak due to the terminal chloro

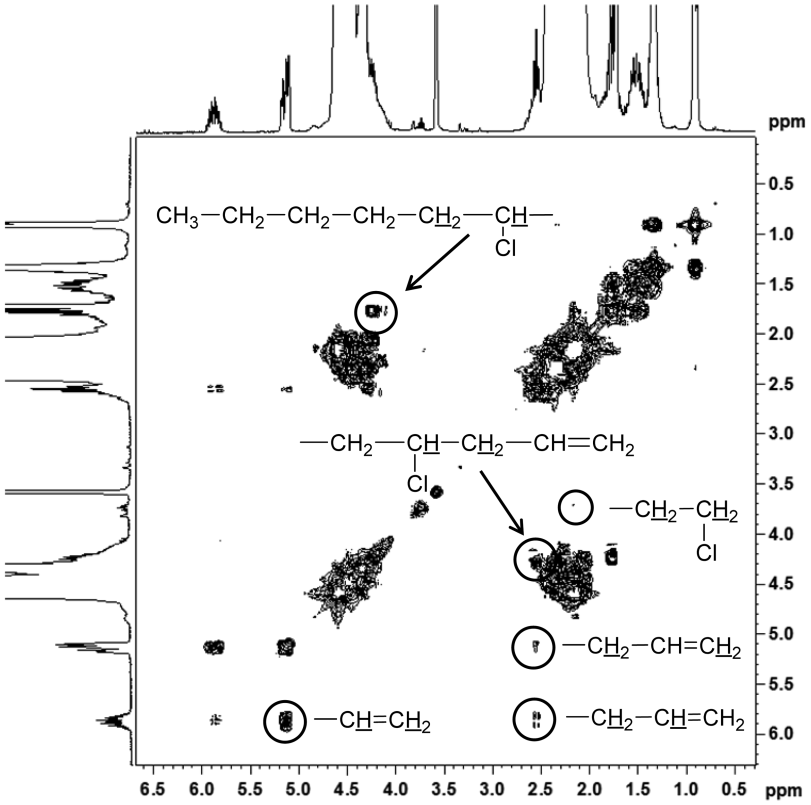

Figure 2. H−H COSY spectrum of PVCM obtained with *n*-BuLi (entry 3).

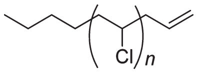

Figure 3. Structure of PVCM estimated by the NMR spectra.

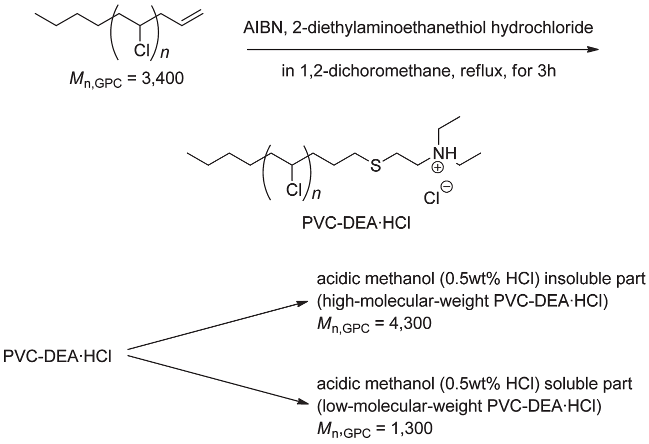

Figure 4. Thiol−ene reaction of PVCM with DEAET·HCl and the fractionation of PVC-DEA·HCl by the solubility in acidic methanol.

methylene proton ($-\mathrm{CH_2}-CH_2\mathrm{Cl}$, 3.7 ppm) was observed in the ^{1}H NMR spectrum.

After the chain-end group was clarified, the functionalities of the vinul group (f_1, f_2) were calculated by eqs 1−3 {a_{methine}: the peak area of methine proton of PVC main chain (1H); a_{vinyl}: the peak area of methylene proton of vinyl group (2H); $a_{-\mathrm{CH_2Cl}}$: the peak area of methylene proton of the terminal chloro structure (2H)}. The f_1 value of PVCM obtained using *n*-BuLi or *tert*-BuLi was 0.96 or 0.86, and the f_2 value of the macromonomers was 0.91 or 0.87, respectively. It is clear that the PVCM, which has a greater than 0.9 terminal functionality, can be synthesized by the polymerization of VC with *n*-BuLi and ABr.

$$M_{\mathrm{n,\,NMR}} = 57 + 62.5 \times \frac{a_{\mathrm{methine}} \times 2}{a_{\mathrm{vinyl}}} + 41 \tag{1}$$

$$f_1 = \frac{M_{\mathrm{n,\,GPC}}}{M_{\mathrm{n,\,NMR}}} \tag{2}$$

$$f_2 = \frac{a_{\mathrm{vinyl}}}{a_{\mathrm{vinyl}} + a_{-\mathrm{CH_2Cl}}} \tag{3}$$

For a radical mechanism, a chain transfer reaction to the monomer or the polymer should occur, leading to the formation of defect structures. If the polymerization of VC proceeds by an anionic mechanism, defect structures, such as a branch structure, may be induced by the addition reaction of active species or unreacted BuLi to the PVC main chain. However, no such information about such structures was observed based on the ^{1}H NMR spectra of the polymers.

A MALDI-TOF-MS analysis is one of the useful methods to define the structure of polymers. However, the measurement of the mass spectrum of PVC has not been successful, which may be due to no ionizing functionality of the polymer. If ionizing group can be introduced into the chain end of PVC, the mass spectrum may be observed. For this purpose, DEAET·HCl was selected to introduce the diethylamino group ionized by hydrochloride at the chain end using the thiol−ene reaction as shown in Figure 4.

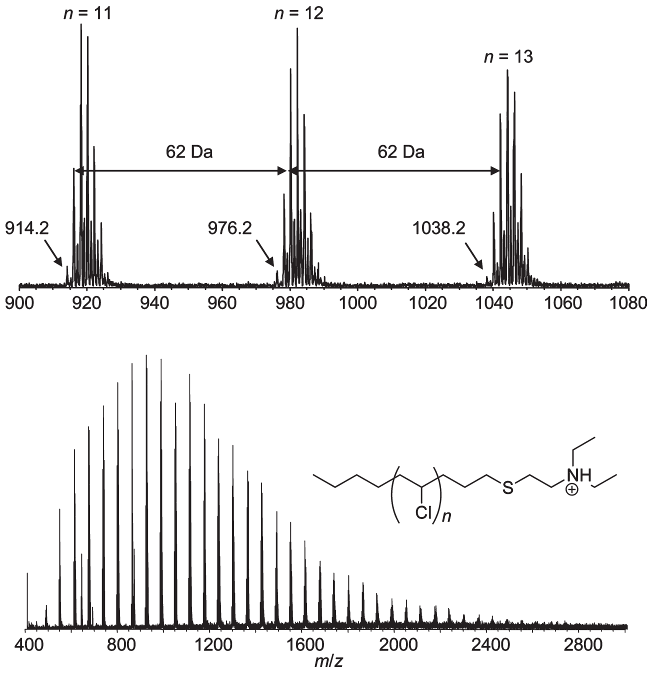

Figure 5. MALDI-TOF mass spectrum of the low-molecular-weight PVC-DEA·HCl obtained with *n*-BuLi.

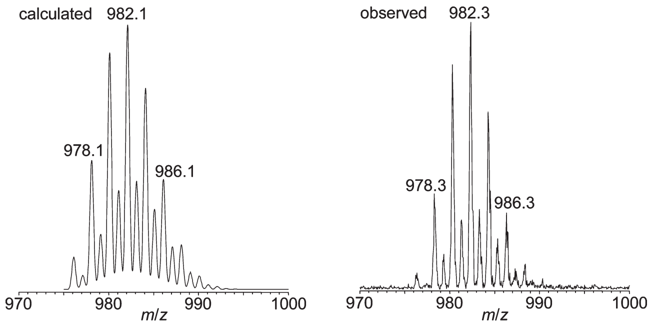

Figure 6. Theoretical and experimental isotope distribution of MALDI-TOF mass spectrum of PVC-DEA·H$^+$ obtained with *n*-BuLi in the area between *m/z* 970 and 1000 ($n = 12$, $C_{37}H_{66}Cl_{12}S_1N_1$).

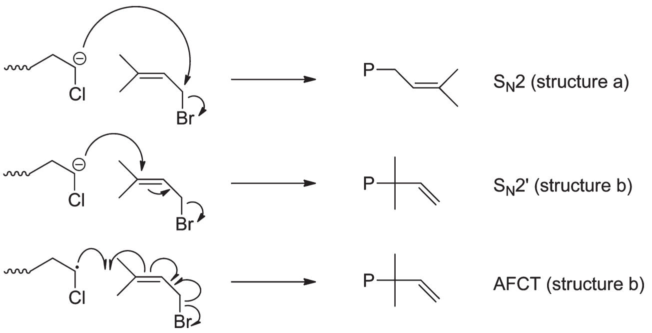

Figure 7. Possible synthesis mechanisms of PVCM.

The thiol–ene reaction of PVCM with DEAET·HCl proceeded to give PVC-DEA·HCl. By extraction with acidic methanol, the product can be divided into the high- and low-molecular-weight PVC-DEA·HCl. The conversion of PVCM to PVC-DEA·HCl was nearly 90%, which was determined by the NMR spectroscopy, independent of the molecular weight of the polymer.

Since PVC-DEA·HCl was synthesized, the MALDI-TOF-MS measurement was conducted. Although a fine mass spectrum of the high-molecular-weight PVC-DEA·HCl was not observed due to the low signal-to-noise (S/N) ratio, a well-defined mass spectrum was obtained using the low-molecular-weight PVC-DEA·HCl with a good S/N ratio as shown in Figure 5. The MALDI mass spectrum of PVC-DEA·HCl obtained with *n*-BuLi in the absence of any ionizers exhibited only one series of ions repeating at the interval of 62 Da (which was repeating VC unit), and the peaks appeared from *m/z* 500 to 2500. They are the ions eliminated Cl$^-$ from PVC-DEA·HCl with the polymerization degree *n* of 4–36, $[57 + 62n + 41 + 169 - \mathrm{Cl}]^+$. For the MALDI-TOF-MS analysis of PVC-DEA·HCl obtained with *tert*-BuLi, a similar spectrum was also observed as shown in Figure S1.

Figure 6 and Figure S2 show the enlarged spectrum in the area between *m/z* 970 and 1000 ($n = 12$), indicating the isotope distribution, and the isotope distribution calculated from PVC-DEA·H$^+$ is also indicated for comparison. The distribution well agrees with calculated one. It is revealed that PVCM obtained with *n*- and *tert*-BuLi in the presence of ABr has a well-defined structure. To the best of the authors' knowledge, this is probably the first mass spectrum of PVC.

Polymerization Mechanism of VC with BuLi. An anionic or radical mechanism, such as $\mathrm{S_N2}$, $\mathrm{S_N2'}$, or the addition–fragmentation chain transfer (AFCT) type, should be considered in the termination reaction of the VC polymerization with BuLi and ABr. Actually, the vinyl-terminated PVC macromonomer was also obtained by the polymerization of VC with BPO/DMA as a radical initiator in the presence of ABr, though the polymer yield was very low as shown in Table S1 and Figure S3. Although the terminal structure of the PVCM is not changed regardless of the termination mechanism, the mechanism will be distinguished in the case of the allyl bromide derivative with an asymmetric structure as shown in Figure 7. The polymerization of VC with *n*-BuLi in the presence of 1-bromo-3-methyl-2-butene (BMB) instead of ABr was examined, and the ^{1}H NMR spectrum of the product is shown in Figure 8. The ^{1}H NMR spectrum of the products obtained by the polymerization of VC with BPO/DMA as a radical initiator in the presence of BMB is included for comparison. Figure 9 shows the H–H COSY spectrum of the product obtained by the polymerization of VC with *n*-BuLi in the presence of BMB. Although the peaks were observed in the double-bond region of the ^{1}H NMR spectrum for the product obtained by the polymerization with *n*-BuLi in the presence of BMB, such peaks were not observed in the other spectrum. The molar ratio (structure a/b in Figure 7) was estimated to be 3.92, which was calculated from the peak areas at 5.1, 5.2, and 5.9 ppm in Figure 8 (left). Taking the terminal structure into consideration, the polymerization of VC with BuLi may be explained by an anionic mechanism rather than a radical mechanism.

Effect of ABr on Polymerization. The acceleration effect of ABr was observed on the polymerization of VC with BuLi as already described. For the anionic polymerization of vinyl monomers with alkyllithium, the acceleration effect of donor reagents, such as ethers or amines, was observed by changing the aggregation state of the alkyllithium.[11] However, the effect of an alkyl bromide, such as ABr, on the polymerization activity was not investigated. Thus, the effect of the ABr/BuLi molar ratio on the polymerization of VC was examined, and the results are listed in

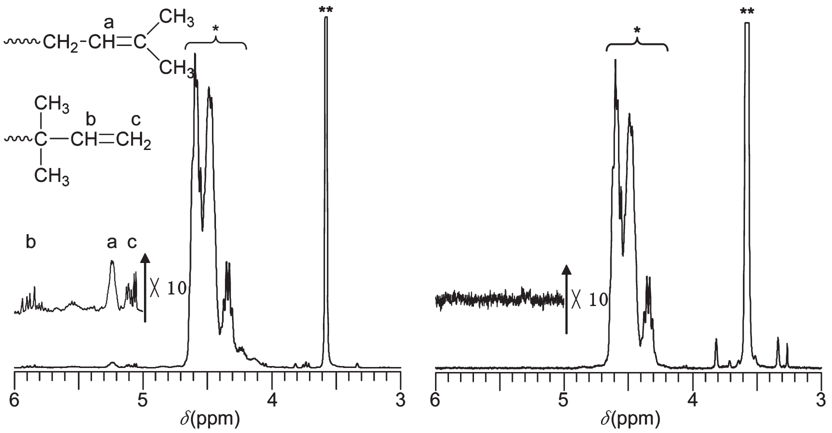

Figure 8. ^{1}H NMR spectrum of the products obtained with *n*-BuLi (left) and BPO/DMA (right) in the presence of BMB. ^{a}Polymerized at −30 °C. *Assigned to the main-chain methine proton of PVC. **THF.

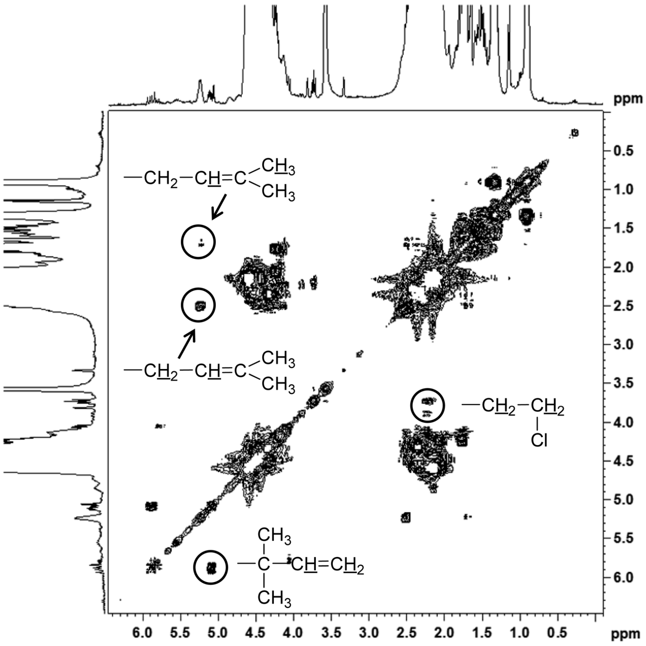

Figure 9. H−H COSY spectrum of PVC obtained with *n*-BuLi in the presence of BMB.

Table 2. The yield and the molecular weight of PVCM decreased with an increase in the ABr/BuLi molar ratio, suggesting that ABr is able to react with the active species. Although the influence of ABr on the aggregation state was unclear, the solubility of PVC in THF decreased with the increasing molar ratio. Since the solubility of polymers is strongly affected by their stereoregularity, PVC with a poor THF solubility may have a high stereoregularity.

Table 2. Effect of ABr/BuLi Molar Ratio on Polymerization of VC with BuLi[a]

entry	initiator	[ABr]/[BuLi]	yield (%)	$M_{n,NMR} \times 10^{-3}$	tacticity[c] (%) rr	mr	mm
(1)	*n*-BuLi		0.4	13.6[b]	39	46	15
(3)	*n*-BuLi	1.0	17.3	4.9	39	49	12
5	*n*-BuLi	3.0	4.1	2.2	43	46	11
6	*n*-BuLi	5.0	1.9	1.7	47	43	10
7	*n*-BuLi	10	0.4	1.2	61	34	5
(2)	*tert*-BuLi		1.2	13.3[b]	39	45	16
(4)	*tert*-BuLi	1.0	14.9	4.6	43	47	10
8	*tert*-BuLi	3.0	2.6	2.0	49	41	10
9	*tert*-BuLi	5.0	0.7	1.6	56	36	7
10	*tert*-BuLi	10	0.3	1.1	81	14	5

[a] VC = 50 mL, BuLi solution (*n*-BuLi: 1.65 mol/L; *tert*-BuLi: 1.76 mol/L) = 5.0 mL. [b] Measured by GPC analysis. [c] Measured by ^{13}C NMR spectroscopy.

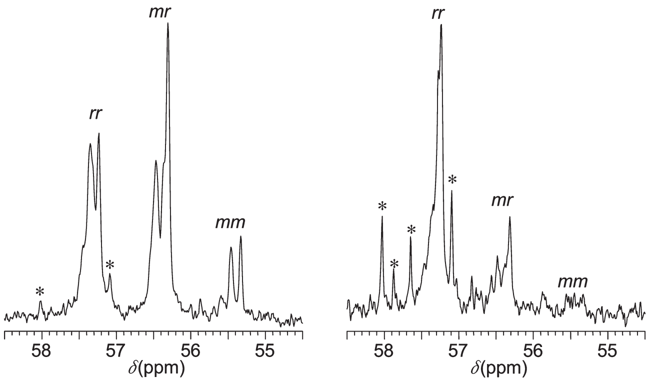

Figure 10. Methine carbon region of the ^{13}C NMR spectra of PVC obtained with *tert*-BuLi in the presence of ABr (left: [ABr]/[BuLi] = 1.0, entry 4; right: [ABr]/[BuLi] = 10, entry 10). *Assigned to the carbon near the end of the polymer chain.

Stereoregularity of PVC. The synthesis of the stereoregular PVC is an interesting theme, as it has not yet been synthesized. Thus, the stereoregularity of PVC obtained with BuLi in the presence of ABr was investigated. A typical ^{13}C NMR spectrum of PVC is shown in Figure 10 and Figure S4, from which it is clear that the polymer showed a rich triad syndiotactic (*rr*) content. Thus, the stereoregularity of PVC obtained in this study was also examined, and the results are listed in Table 2. Interestingly, the *rr* content of PVCM was enhanced by increasing the ABr/BuLi molar ratio. Among them, the PVCM obtained with *tert*-BuLi (ABr/BuLi = 10) was the most syndiotactic rich polymer. It was reported that lithium *tert*-butoxide affected the stereoregularity of polystyrene in the polymerization of styrene with BuLi in *n*-hexane.[12,13] Their authors described that the alkoxide, in an associated form with the growing polystyryl ion, could present enough steric hindrance to induce steeroregular placement of incoming monomer units. Although we assume that LiBr in the vicinity of active species affect the stereoregularity of PVC in the VC polymerization, the reason for increasing the stereoregularity is still obscure.

Although the radical polymerization of VC in the urea canal complexes or in the presence of aldehydes was reported as the method for the synthesis of a highly stereoregular PVC, the stereoregularity of the polymer was estimated only by a qualitative analysis, such as the X-ray diffraction pattern, IR, or solid-state NMR spectrum.[14−16] Since atactic PVC even has a crystallinity,[17] the information on such analysis is unclear about the stereoregularity of the polymer. As far as we know, this is the first example for synthesizing the highly syndiotactic PVC (*rr* > 80%) which is supported by the solution-state NMR spectrum.

CONCLUSION

The polymerization of VC with BuLi in the presence of ABr was investigated. The structure of the PVCM obtained with BuLi in the presence of ABr was estimated by ^{1}H NMR spectroscopy. The detailed structure was determined by the MALDI-TOF-MS analysis of the PVCM derivative. The polymerization of VC with *n*-BuLi in the presence of BMB instead of ABr was examined. Taking the terminal structure into consideration, the polymerization of VC with BuLi may be explained by an anionic mechanism rather than a radical mechanism. The syndiotactic rich PVC was found to be synthesized by the polymerization of VC with BuLi in the presence of ABr. Especially, the PVCM obtained with *tert*-BuLi (ABr/BuLi = 10) was the most syndiotactic polymer. In this article, the first mass spectrum of PVC with a well-defined structure was obtained, and a highly syndiotactic PVC (*rr* > 80%) was synthesized.

ASSOCIATED CONTENT

Supporting Information. MALDI-TOF-MS of PVC-DEA·HCl obtained with *tert*-BuLi, the ^{1}H NMR spectrum of the product with BPO/DMA in the presence of ABr, the ^{13}C NMR spectrum of PVC obtained with *n*-BuLi in the presence of ABr, and HSQC spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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