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# Control of main chain structure and possibility of molecular weight control of polymer on polymerization of vinyl chloride with *tert*-butyllithium

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**Abstract**

The controlled polymerization of vinyl chloride (VC) with *tert*-butyllithium (*tert*-BuLi) was investigated. The polymerization of VC with *tert*-BuLi at − 30 °C proceeded to give a high molecular weight polymer in good yield. In the polymerization of VC − 30 to 0 °C under nearly bulk, the relationship between the $M_n$ of polymers and polymer yields gave a straight line passed through the origin, but the $M_w/M_n$ of PVC was not narrow. When $CH_2Cl_2$ was used as polymerization solvent, the $M_n$ of PVC increased with the polymer yield, and the $M_w/M_n$ of 1.25 was obtained. Structure analysis of the resulting polymers indicates that the main chain structure could be regulated in the polymerization of VC with *tert*-BuLi. Accordingly, a control of molecular weight of polymer and main chain structure is possible in the polymerization of VC with *tert*-BuLi.



*Keywords:* Vinyl chloride; *tert*-Butyllithium; Main chain control

## 1. Introduction

Living polymerizations are very fascinating polymerization mechanism from the viewpoint of polymer architecture, and have been investigated by many polymerization methods [1,2]. If such polymerization can be applied to the polymerization of vinyl chloride (VC), poly(vinyl chloride) (PVC) with well-defined structure will be synthesized, and give a useful information between the structure and thermal stability of PVC. However, even an anionic polymerization of VC has been believed to be difficult by deactivation of anionic initiators and VC monomers. Nevertheless, Kolinsky et al. [3–6] reported that polymerization of VC with alkyllithium (RLi) proceeded to give polymers, and that the molecular weight of PVC increased with reaction time, which was determined by viscosity measurement. However, they did not refer to the polymerization of VC with RLi from the viewpoint of molecular weight control of the polymer.

Moreover, as long as we synthesize PVC by radical polymerization, it is difficult to synthesize PVC without anomalous structures such as $C_2$, $C_4$ branches, long-branches, head-to-head bond, and internal olefin units [7]. However, an anionic polymerization of VC makes it possible to synthesize PVC without anomalous units.

Our previous preliminary reported results for polymerization of VC with butyllithium (BuLi) [8,9] suggest that simultaneous control of molecular weight of polymers and main chain structure will be possible in the polymerization of VC with *tert*-BuLi. In this article, we will describe such polymerization of VC with *tert*-BuLi in nearly bulk, *n*-heptane and $CH_2Cl_2$.

## 2. Experimental

### 2.1. Materials

VC was used after purification over calcium hydride. *n*-BuLi, *sec*-BuLi and *tert*-BuLi purchased from Kanto Chemical were used after dilution with polymerization solvents without purification. Other reagents and solvents were used after purification by conventional methods.

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### 2.2. Polymerization procedure

Polymerization was carried out in a sealed glass tube (∅18 mm × L150 mm). The required amounts of reagents were charged into the tube by syringes through rubber septum. In typical cases, 0.1–2 ml of *tert*-BuLi (1.64 mol/l) was charged, and if necessary 17 ml of $CH_2Cl_2$ was charged. VC (2–10 ml) was introduced into the tube at −78 °C by vacuum distillation. The polymerization was carried out for a given time at a constant temperature. After the polymerization, the contents of the tube were poured into a large amount of methanol to precipitate the polymer formed. The resulting polymers were dried under vacuum at room temperature for an overnight. Polymer yields were determined by gravimetry.

### 2.3. Reduction of the polymers

PVC was converted to the corresponding hydrocarbon polymer with tri(*n*-butyl)tin hydride ($Bu_3SnH$) and AIBN in the mixed solvent of *p*-xylene and THF [10,11]. First PVC (0.25 g) was completely dissolved in the mixed solvent of *p*-xylene (20 ml) and THF (30 ml) at 50 °C, and then *p*-xylene solution (10 ml) of $Bu_3SnH$ (0.18 g) and AIBN (0.008 g) were added into the reaction system. After the reaction was carried out for an hour, *p*-xylene solution (25 ml) of $Bu_3SnH$ (0.68 g) and AIBN (0.09 g) were further added, and reacted for additional 3 h. After the reaction, the reaction mixtures were poured into a large amount of methanol to precipitate the reaction product. The methanol insoluble product was collected by filtration and washed well with an excess of methanol, dried under vacuum at 50 °C. The product was purified by re-precipitation from hot *p*-xylene into methanol.

### 2.4. Characterization of the polymers

The number-average molecular weight ($M_n$) and the weight-average molecular weight ($M_w$) of the polymer were determined by GPC using THF as an eluent at 38 °C calibrated as standard polystyrenes. The structures and tacticity of the polymers were determined from $^1H$ and $^{13}C$ NMR spectra taken in a mixed solvent of benzene-$d_6$ and *o*-dichlorobenzene (3/7 volume ratio) at 120 °C with hexamethyldisiloxane (HMDS) as an internal standard on a JEOL A-400 NMR spectrometer.

## 3. Results and discussion

### 3.1. Polymerization of VC with BuLi

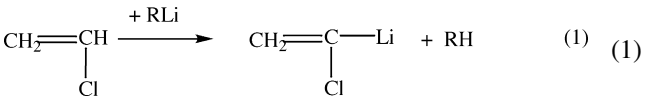
Table 1 shows the results of the polymerization of VC with three kinds of BuLi at −30 °C under the nearly bulk condition. Among the BuLi examined, *tert*-BuLi showed the highest activity for the polymerization of VC giving a high molecular-weight polymer in a good yield. On the other hand, *n*-BuLi and *sec*-BuLi are not effective for the polymerization of VC although the reason is not clear.

Table 1
Polymerization of VC with RLi at −30 °C

| RLi | [RLi] (mol/l) | Time (h) | Yield (%) | $M_n$ ($\times 10^{-4}$) | $M_w/M_n$ | $f$ (%)[a] |
|---|---|---|---|---|---|---|
| *t*-BuLi | 0.16 | 46 | 40.3 | 2.1 | 2.3 | 11.8 |
| *n*-BuLi | 0.16 | 45 | 4.1 | 5.3 | 2.5 | 0.5 |
| *sec*-BuLi | 0.16 | 48 | Trace | – | – | – |

[VC] = 15.8 mol/l, [RLi] = 0.16 mol/l.
[a] $f = \{[VC]_0 \times \text{Yield} \times 62.5/([RLi]_0 \times M_{n,observed})\} \times 100$.

Although *tert*-BuLi was found to be most effective initiator for the polymerization of VC, but initiator efficiency ($f$) calculated by the polymer yield and the observed molecular weight of PVC was considerable low as listed in Table 1. Since RLi is known to induce easily metallation reaction with VC [3], the low initiator efficiency might be attributed to that the most part of *tert*-BuLi charged was consumed by the metallation at the early stage of the polymerization, leading to the formation of inactive products for the polymerization as shown in Eqs. (1) and (2) [3]. However, some of *tert*-BuLi may propagate to give PVC.




(1)


(2)

To accelerate the polymerization of VC with *tert*-BuLi, the addition of base compounds such as THF and *N*,*N*,*N*′,*N*′-tetramethylethyenediamine (TMEDA) was examined, since these bases are known to accelerate the polymerization of vinyl monomers [2]. However, the polymerization did not proceed in the presence of a small amount of base compounds [8]. This may be attributed to enhancement of the reaction between *tert*-BuLi and VC.

Although the accurate mechanism is not clear, it seems that LiCl formed by the reaction of VC and RLi may stabilize the active site for the polymerization of VC as pointed out by Kolinsky and his coworkers [4].

Table 2
Polymerization of VC with *tert*-BuLi at −30 °C

| [*tert*-BuLi] (mol/l) | Time (h) | Yield (%) | $M_n$ ($\times 10^{-4}$) | $M_w/M_n$ |
|---|---|---|---|---|
| 0.165 | 46 | 40.3 | 2.1 | 2.3 |
| 0.033 | 72 | 22.6 | 8.1 | 2.8 |
| 0.168[a] | 120 | 28.3 | 0.5 | 2.7 |

[VC] = 15.8 mol/l.
[a] Polymerized in *n*-hexane under condition of [VC] = 3.52 mol/l.

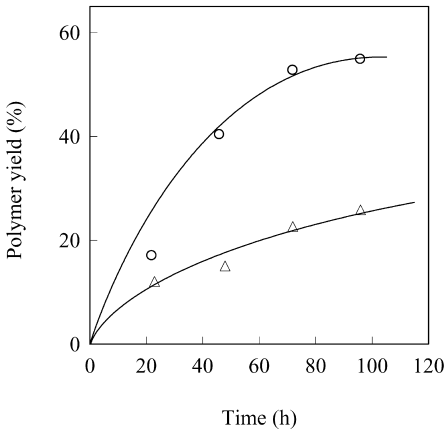



Fig. 1. Polymerization of VC with *tert*-BuLi at −30 °C; [VC] = 15.8 mol/l, [*tert*-BuLi] = 0.165 mol/l (○) and 0.033 mol/l (△).

### 3.2. Polymerization of VC with tert-BuLi

Since *tert*-BuLi showed the highest activity for the polymerization of VC among BuLi's examined, the polymerization of VC with *tert*-BuLi was further investigated. The results of polymerization of VC with *tert*-BuLi in nearly bulk at −30 °C are shown in Table 2, in which the results of that in *n*-hexane are also indicated to comparison. When the polymerization was carried out under nearly bulk, the molecular weight of polymer was higher than that obtained in *n*-hexane, although polymerization was slow even in nearly bulk condition.

Although Kolinsky and his coworkers reported that the polymer yield did not exceeded 17.5% by solidification of the polymerization system [3,6], the polymerization of VC proceeded even after solidification to afford high molecular weight polymers in good yields.

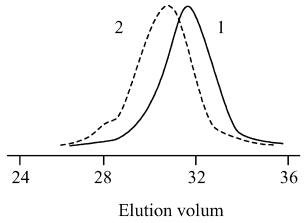



Fig. 4. GPC elution curves for PVC obtained with *tert*-BuLi at −30 °C (1) for 24 h and (2) 96 h; [VC] = 15.8 mol/l, [*tert*-BuLi] = 0.165 mol/l.

To elucidate the possibility for control of molecular weight of the polymers in polymerization of VC with *tert*-BuLi, a kinetic study of the polymerization was performed. The kinetic curves for the polymerization of VC with *tert*-BuLi at −30 °C are shown in Fig. 1. The polymer yields and the $M_n$ of the polymers increased as a function of reaction time, suggesting that molecular weight control of PVC will be possible. To clarify further this point, the first-order plot ($\ln[VC]_0/[VC]_t$ vs. polymerization time) for the polymerization with the *tert*-BuLi at −30 °C was done, and the results are shown in Fig. 2. Linear relationship between $\ln[VC]_0/[VC]_t$ and polymerization time was observed, indicating that the concentration of the active ends kept constant during polymerization reaction. Moreover, the $M_n$ of the polymers was plotted against polymer yields, and the results are shown in Fig. 3. The relationships between the polymer yields and the $M_n$s of the polymers gave a straight line passed through the origin. The polydispersities of the polymers kept almost constant during the polymerization, although they were not narrow. The typical GPC elution curves are shown in Fig. 4, from which the curves shifted to

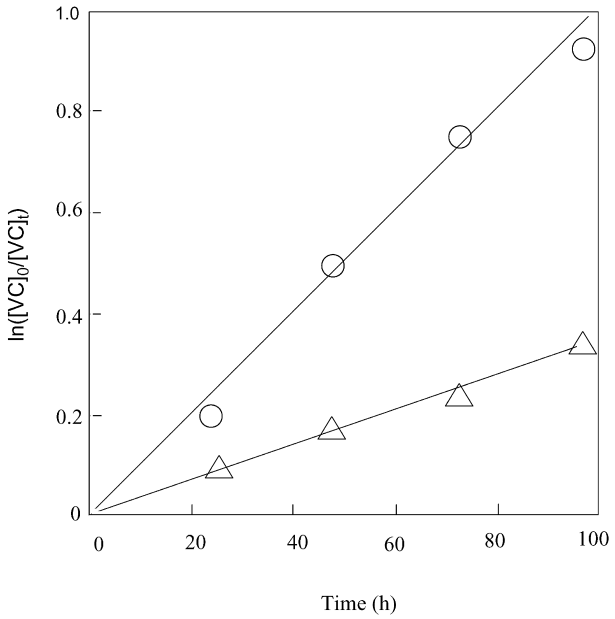



Fig. 2. First order plot for the polymerization of VC with *tert*-BuLi at −30 °C; [VC] = 15.8 mol/l, [*tert*-BuLi] = 0.165 mol/l (○) and 0.033 mol/l (△).

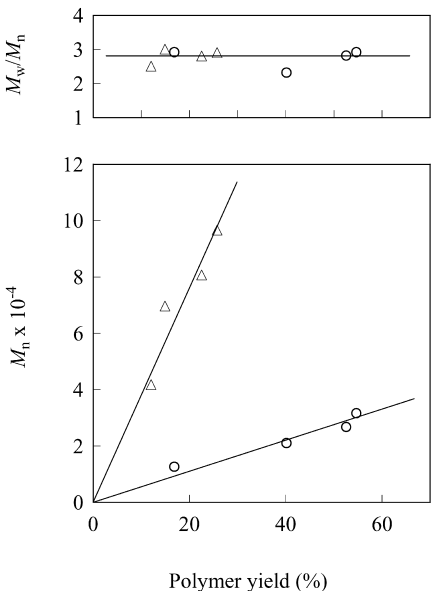



Fig. 3. Relationships of $M_n$ and $M_w/M_n$ upon the polymer yields in the polymerization of VC with the *tert*-BuLi at −30 °C; [VC] = 15.8 mol/l, [*tert*-BuLi] = 0.165 mol/l (○) and 0.033 mol/l (△).

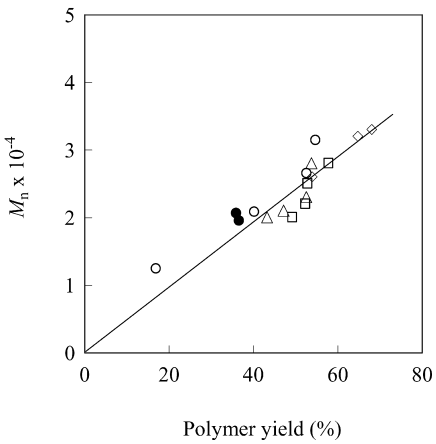



Fig. 5. Relationships of $M_n$ and $M_w/M_n$ upon the polymer yields in the polymerization of VC with the *tert*-BuLi at −30 °C (○), −18 °C (◇), −10 °C (□), 0 °C (△) and 20 °C (●): [VC] = 15.8 mol/l, [*tert*-BuLi] = 0.165 mol/l.

the higher molecular weight side with reaction time. Namely, the kinetic study suggests that the control of molecular weight of PVC is possible.

The effect of polymerization temperature on the polymerization of VC with *tert*-BuLi was examined. As shown in Fig. 5, the relationships between polymer yields and the $M_n$ of polymers gave a straight line passed through the origin regardless of polymerization temperatures, suggesting that the amount of active site for the polymerization is not different at the reaction temperature examined. This may reflect a difference in the activation energy for the deactivation reaction and initiation.

### 3.3. Polymerization of VC with tert-BuLi in $CH_2Cl_2$

The $M_w/M_n$ of the polymer was not narrow in the polymerization of VC with *tert*-BuLi in nearly bulk and in *n*-heptane. Since PVC is known to be insoluble in VC monomer [12], the heterogeneity of the system might be responsible for such a broad $M_w/M_n$ of the PVC. If this is correct, PVC with narrow $M_w/M_n$ will be synthesized. We examined the polymerization of VC in $CH_2Cl_2$ for this purpose, and the results are shown in Table 3. In the early stage of polymerization of VC with *tert*-BuLi, the polymer bearing the $M_n$ of $1.9 \times 10^3$ and the $M_w/M_n$ of 1.25 was obtained. The $M_w/M_n$ became somewhat broader as the polymerization proceeded, but it was still narrow as compared with those obtained in nearly bulk or *n*-hexane.

Table 3
Polymerization of VC with *tert*-BuLi in $CH_2Cl_2$

| Time (h) | Yield (%) | $M_n$ ( $\times 10^{-3}$) | $M_w/M_n$ |
|---|---|---|---|
| 1.5 | 4.6 | 1.9 | 1.25 |
| 3 | 10.3 | 2.4 | 1.37 |
| 12 | 24.6 | 3.0 | 1.47 |
| 53 | 38.1 | 3.7 | 1.62 |

[VC] = 1.76 mol/l, [*tert*-BuLi] = $8.2 \times 10^{-2}$ mol/l.

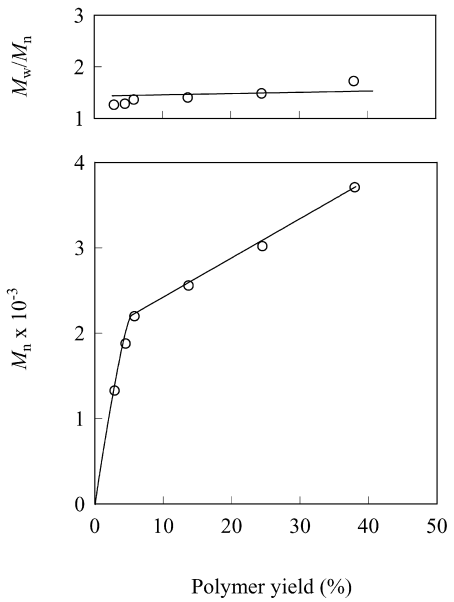



Fig. 7. Relationships of $M_n$ and $M_w/M_n$ upon the polymer yields in the polymerization of VC with *tert*-BuLi in $CH_2Cl_2$ at −30 °C; [VC] = 1.76 mol/l, [*tert*-BuLi] = $8.2 \times 10^{-2}$ mol/l.

Moreover, the GPC elution curves are shown in Fig. 6. The elution curves shifted to the higher molecular weight side with reaction time. Thus, the control of molecular weight of PVC in the polymerization of VC with *tert*-BuLi in $CH_2Cl_2$ may be possible under restricted conditions.

To elucidate a possibility of a controlled polymerization of VC with *tert*-BuLi in $CH_2Cl_2$, the kinetic study was performed. Since the polymer yields and the $M_n$s of polymers increased with the reaction time, the relationships between $M_n$s of PVC and polymer yields were plotted. The results are shown in Fig. 7. Although the $M_n$ of PVC increased with reaction time, the curve can be divided two lines depending on the $M_n$ of PVC. In the range of the $M_n$ of PVC up to $2 \times 10^3$, the relationships between the $M_n$ of PVC and polymer yield gave a straight line passed through the origin. In addition, the $M_w/M_n$ of PVC kept narrow in this

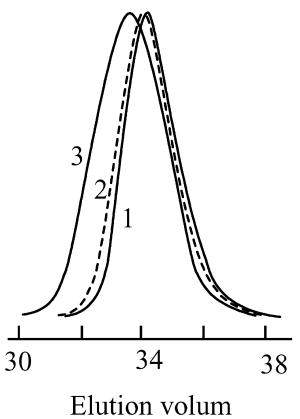



Fig. 6. GPC elution curves for the PVC obtained with tert-BuLi in $CH_2Cl_2$; (1) 1.5 h, (2) 3 h and (3) 12 h. For polymerization conditions, see foot note of Table 3.

Table 4
Elemental analysis of PVC obtained with *tert*-BuLi at −30 °C

| Element | Observed value | Calculated value |
|---|---|---|
| C (%) | 38.8 | 38.6 |
| H (%) | 4.93 | 4.87 |

$M_n = 3.1 \times 10^4$.

period, which can be explained by that the PVC with molecular weight less than $2 \times 10^3$ was dissolved in $CH_2Cl_2$. On the other hand, the values of $M_w/M_n$ of PVC slightly increased after the system became heterogeneity. Namely, the heterogeneity of the polymerization system plays a role for determining the $M_w/M_n$ of the polymer.

### 3.4. Structure of PVC

The polymerization of VC with *tert*-BuLi will be possible to regulate the polymer structure. To check this point, the structure of the PVC obtained with *tert*-BuLi was analyzed by elemental analysis and NMR spectroscopy. Table 4 shows the elemental analysis of the polymers prepared from the polymerization of VC with *tert*-BuLi. The carbon and hydrogen contents of the polymer were in a good agreement with the calculated values for assuming that polymer consists of repeating $-CH_2-CH(Cl)-$ unit.

The $^1$H NMR spectra of the PVC obtained with the *tert*-BuLi at −30 °C are shown in Fig. 8. Although no peaks based on the internal double bonds in the main chains were observed [13], it is difficult to elucidate the presence of the short and long branches in the main chain by the $^1$H and $^{13}$C NMR spectra of PVC from a viewpoint of fine separation of the signals [14], and branching structure of PVC was identified by $^{13}$C NMR spectra of product after reduction of PVC with *n*-$Bu_3SnH$ [10,11]. Thus, the PVC was converted to the corresponding hydrocarbone polymer by *n*-$Bu_3SnH$ in the presence of AIBN to elucidate the branching structures.

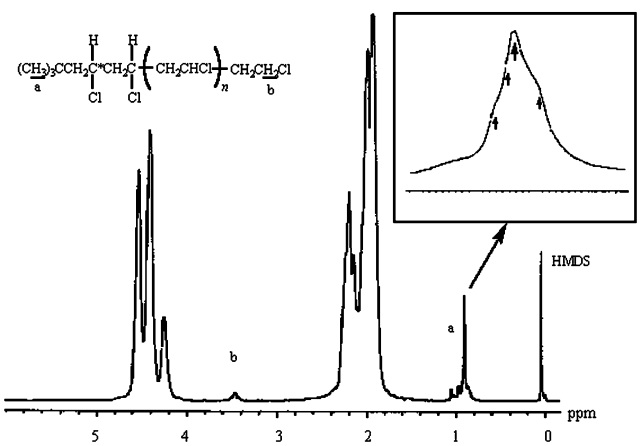



Fig. 8. $^1$H NMR spectra of the PVC obtained with the *tert*-BuLi at −30 °C. Measured in the solvent of benzene-$d_6$ and *o*-dichlorobenzene (30/70 vol%) at 120 °C.

The $^{13}$C NMR spectra of the reaction product are shown in Fig. 9. The peaks due to methylene carbon at 55–58 ppm and methyne carbon at 45–48 ppm due to the PVC disappeared completely, and new main peak due to methylene carbon appeared at 29.6 ppm in addition to very small peaks due to chain end of the product. The spectrum was same as the polymer obtained from polymerization of ethylene with *tert*-BuLi complexed with *tert*-diamines such as TMEDA [15]. No peaks based on branches presented in the PVC obtained with *tert*-BuLi were observed in the reaction product.

In addition, the initiation end and terminal end of the PVC obtained with *tert*-BuLi at −30 °C were identified by the $^1$H NMR spectrum as shown in Fig. 8. The peak due to the methyl proton of the *tert*-butyl group at the initiation chain end appeared at 0.90 ppm as four splitting lines, reflecting the different configurations of the proximal VC units, which is consistent with the reported results [13]. The signal due to the methylene protons of the –CH(Cl)H end group introduced into the terminal chain end were also observed at 3.4–3.5 ppm [16]. The integral intensity ratios of the initiation chain end and the terminal chain end were determined to be 9:2. On the basis of these results, it is clear that the main chain structure can be regulated in the polymerization of VC with *tert*-BuLi at −30 °C.

### 3.5. Tacticity of PVC

Triad tacticity of the PVC obtained from the polymerization of VC with *tert*-BuLi at −30 °C was determined by $^{13}$C NMR spectra of the polymers [17]. The tacticity of polymers determined from the area of splitting peaks of the methine carbon in the chain are listed in Table 5. The tacticity of the PVC obtained with *tert*-BuLi in nearly bulk at −30 °C was a little different from that obtained with the radical polymerization [18]. When the polymerization was carried out in $CH_2Cl_2$ at −30 °C, the content of syndiotactic triad (rr) of the polymer increased as compared with that obtained in bulk, suggesting that homogeneous system may be favor for producing syndiotactic polymer. However, it is not clear now the relationships between tacticity of the polymers and the molecular weight control of the polymer.

Table 5
Tacticity of PVC obtained with *tert*-BuLi at −30 °C

| Initiator | Solvent | Triad tacticity | | |
|---|---|---|---|---|
| | | mm | mr | rr |
| *tert*-BuLi | –[a] | 18 | 46 | 36 |
| *tert*-BuLi | *n*-Hexane[b] | 17 | 49 | 34 |
| *tert*-BuLi | $CH_2Cl_2$[c] | 10 | 46 | 44 |
| AIBN | Toluene | 12 | 49 | 39 |

[a] [*tert*-BuLi] = $1.65 \times 10^{-1}$ mol/l, [VC] = 15.8 mol/l.
[b] [*tert*-BuLi] = $1.68 \times 10^{-1}$ mol/l, [VC] = 3.52 mol/l.
[c] [*tert*-BuLi] = $8.2 \times 10^{-2}$ mol/l, [VC] = 1.76 mol/l.

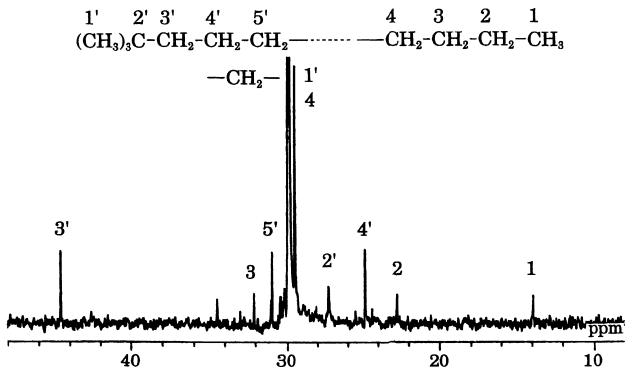



Fig. 9. $^{13}C$ NMR spectra of product after reduction of PVC with *n*-$Bu_3SnH$ in the presence of AIBN. Measured in a mixed solvent of benzene-$d_6$ and *o*-dichlorobenzene (30/70 vol%) at 120 °C.

## 4. Conclusion

The polymerization of VC with *tert*-BuLi under nearly bulk gave a high molecular weight polymer in good yield. The relationships between the $M_n$ of the polymers and the polymer yields gave a straight line, and the line passed through the original point. It is evident that the chain end of the polymer remains active. In the early stage of polymerization of VC with *tert*-BuLi in $CH_2Cl_2$, the polymer bearing the $M_n$ of $1.9 \times 10^3$ and the value of $M_w/M_n$ of 1.25 was obtained. The polymerization of VC with *tert*-BuLi also gave the PVC with well-defined structure. Accordingly, *tert*-BuLi may be promoted the polymerization of VC under mild conditions to give a high molecular weight polymer with well-defined structure.

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