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Controlled polymerization of vinyl chloride with *tert*-butyllithium

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Abstract

Polymerization of vinyl chloride (VC) with *tert*-butyllithum (*tert*-BuLi) was investigated from the point of controlled polymerization. The polymerization of VC proceeded at −30°C to give high polymers. The M_n of the polymers increased as a function of the reaction time and polymer yields, although the initiator efficiency was low. Linear dependence of the M_n of the polymer and polymer yields was observed, while M_w/M_n did not change significantly during the polymerization. The polydispersity (M_w/M_n) of the polymer was not narrow probably due to the heterogeneity of the reaction media. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Vinyl chloride; *tert*-butyllithium; Controlled polymerization

1. Introduction

Recently much effort has been focused on the controlled polymerization of many monomers with various kinds of polymerization mechanisms [1–5]. Living anionic polymerization is an excellent process for the controlled synthesis of polymers bearing well-defined structures [6]. The monomers applicable to this polymerization have been limited, and it is believed that the polymerization of vinyl chloride (VC) is difficult by deactivation reactions of anionic initiators and VC monomers.

However, Kolinsky et al. [7–10] reported that polymerization of VC with alkyllithiums proceeded to give high molecular weight polymers, but the structures of the polymers obtained were not characterized in detail. In a previous paper, we elucidated that the structure of the polymer obtained from the polymerization of VC with butyllithiums in *n*-hexane consisted of only regular head-to-tail units by using NMR spectroscopy [11]. However, the molecular weight of the polymer as a function of the reaction time and initiator concentration was not studied from the point of controlled polymerization.

Although Kolinsky et al. observed that the M_n of the polymers determined by viscometric measurement increased with reaction time, a study from the point of the controlled polymerization was not done [7]. In our previous paper, the polymerization in solution was also carried out at 40°C. We supposed that such a reaction temperature may cause side reactions. A lower reaction temperature may avoid the side reactions, leading to controlled polymerization. Therefore we investigated the polymerization behavior of VC with *tert*-butyllithium (*tert*-BuLi) by using gel permeation chromatography (GPC) to elucidate whether the controlled polymerization of VC is possible.

In this article, we report the capability of *tert*-BuLi to initiate controlled polymerization of VC. The structures of the polymers obtained with *tert*-BuLi are also discussed.

2. Experimental

2.1. Materials

VC was used after purification over calcium hydride. *tert*-BuLi diluted with pentane kindly supplied from Tosoh-Akuzo Co. was used without purification. Other reagents and solvents were used after purification by conventional methods.

2.2. Polymerization procedure

Polymerization was carried out in a sealed glass tube. The required amounts of reagents were charged in the glass tube by syringes through a rubber septum. VC stored over CaH_2 was introduced into the tube at −78°C by vacuum distillation. After polymerization, the contents of the tube were poured into a large amount of methanol to precipitate the polymer formed. Polymer yields were determined by gravimetry.

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Table 1
Polymerization of VC with *tert*-BuLi at −30°C ([VC] = 15.8 mol/l)

Entry	[*tert*-BuLi](mol/l)	Time (h)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	f^a (%)
1	0.165	50	40.3	2.7	2.4	9.3
2	0.033	75	27.8	9.7	2.5	8.9
3	0.168[b]	120	28.3	0.43	2.7	9.0

[a] Initiator efficiency (f) = $[\mathrm{VC}]_0 \times \text{yield} \times 62.5/([\textit{tert}\text{-BuLi}]_0 \times M_{n,\mathrm{observed}} \times 100)$.

[b] Polymerized in *n*-hexane, [VC] = 3.52 mol/l.

2.3. 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 tacticity of the polymers was determined from ^{13}C NMR spectra taken in the mixed solvent of benzene-d$_6$ and *o*-dichlorobenzene at 120°C with hexamethyldisiloxane (HMDS) as an internal standard on a JEOL α-400 NMR spectrometer. The reduction of PVC to the corresponding hydrocarbon polymer was carried out by the use of tri(*n*-butyl)tin hydride in the presence of AIBN [12,13].

3. Results and discussion

Since *tert*-BuLi was reported to be an effective initiator for the polymerization of VC [7,11], we used *tert*-BuLi as an initiator for this investigation. Table 1 shows the results of the polymerization of VC with *tert*-BuLi in nearly bulk at −30°C. The polymerization of VC has been initiated even at −30°C to give a high polymer as well as in *n*-hexane, although the polymerization rate was very slow. Kolinsky et al. pointed out that the polymer yield was 17.5% at the maximum because of solidification of the polymerization system [7,10]. There is no reason to indicate why the polymerization does not proceed after solidification. Actually, in our case the polymerization still proceeded after solidification of the system, and high polymer yields were obtained.

As listed in Table 1, the initiator efficiency was as low as about 9%. Since alkyllithiums are known to be efficient metallation agents with VC as shown in Eq. (1), the low initiator efficiency may be attributed to the fact that *tert*-BuLi was consumed for the most part in the metallation reaction in the early stage of the polymerization to give lithium acetylide and lithium chloride which are inactive

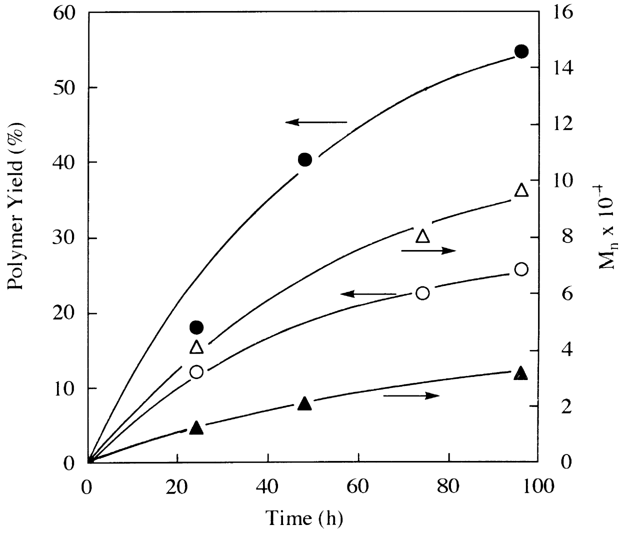


Fig. 1. Polymerization of VC with *tert*-BuLi at −30°C; [VC] = 15.8 mol/L, [*tert*-BuLi] = 0.165 mol/L (●, ▲) and 0.033 mol/L (○, △).

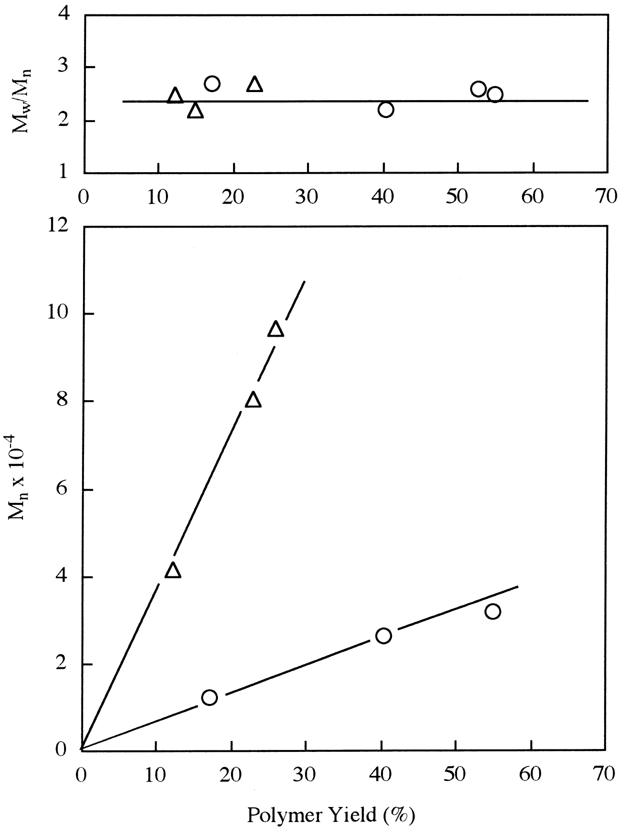


Fig. 2. Relationships of M_n and M_w/M_n upon the polymer yields in the polymerization of VC with *tert*-BuLi at −30°C; [VC] = 15.8 mol/L, [*tert*-BuLi] = 0.165 mol/L(○) and 0.033 mol/L (△).

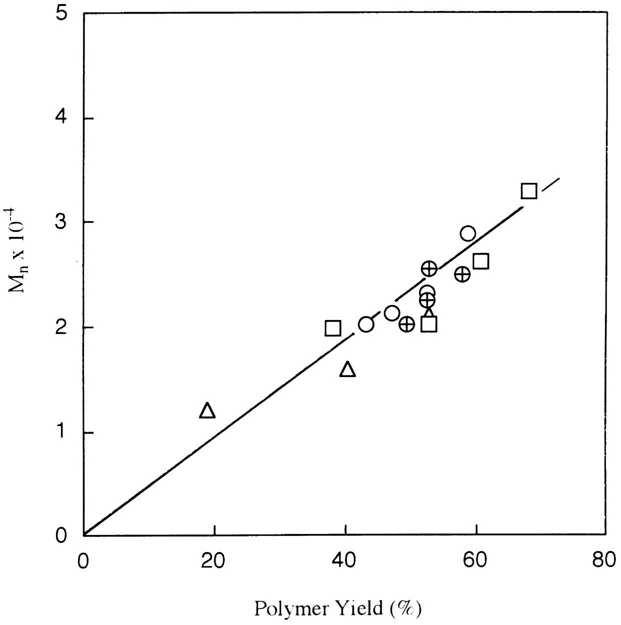
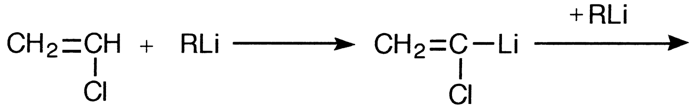


Fig. 3. Relationships of M_n and M_w/M_n upon the polymer yields in the polymerization of VC with *tert*-BuLi at −30°C (△), −18°C (□), −10°C (⊕) and 0°C (○):[VC] = 15.8 mol/L, [*tert*-BuLi] = 0.165 mol/L.

for the polymerization [7]



$$\mathrm{CH_2{=}\underset{\underset{\displaystyle Cl}{|}}{C}H} + \mathrm{RLi} \longrightarrow \mathrm{CH_2{=}\underset{\underset{\displaystyle Cl}{|}}{C}{-}Li} \xrightarrow{+\mathrm{RLi}} \mathrm{CLi{\equiv}CLi} + \mathrm{LiCl} + \mathrm{RH} \qquad (1)$$

To elucidate the polymerization behavior, we carried out a kinetic study of the polymerization of VC with *tert*-BuLi. Fig. 1 shows kinetic curves for the polymerization of VC with different *tert*-BuLi concentrations at −30°C. The polymer yields and M_n of the polymers increased with reaction time. Since the M_n of the polymers increased with time, the M_n of the polymers was plotted against polymer yield as depicted in Fig. 2. The linear dependence between the polymer yields and the M_n of the polymers observed is evidence that the chain end of the polymer remains active.

However, the polydispersity of the polymer was not narrow, and this cannot be disregarded while drawing conclusions. Since PVC is almost insoluble in VC, the heterogeneity of the reaction media might be partly responsible for such a broad polydispersity observed. To clarify this point, we are now investigating the polymerization of VC in CH_2Cl_2 that can dissolve relatively low molecular PVC. As a preliminary result, the polymer with a M_n of 2.6×10^3 and polydispersity of 1.30 was obtained from the polymerization of VC in CH_2Cl_2. Thus, the heterogeneity of the system plays a role in determining the polydispersity of the resulting PVC. The M_n of the polymers is inversely proportional to the *tert*-BuLi concentration. Namely, the M_n of the polymer could be controlled by the initial concentration of the *tert*-BuLi.

The effect of polymerization temperature on the polymerization of VC with the *tert*-BuLi was examined. Fig. 3 shows the relationships between the polymer yields and the M_n of the polymers. It is noteworthy to point out that the relationships between polymer yields and M_n of the polymers lay on a straight line passing through the original point regardless of the polymerization temperatures, suggesting that the initiator efficiency of the *tert*-BuLi is independent within the reaction temperatures examined.

In the controlled polymerization, the polymer with a well-defined structure can be synthesized. To check this point, the structure of the polymer was analyzed by elemental analysis and NMR spectroscopy. From an elemental analysis of the resulting polymer, the C and H contents of the polymer (C: 38.6%, H: 4.92%) were in good agreement with the calculated values (C: 38.4%, H: 4.84%) for assuming that the polymer consisted of $–CH_2–CHCl–$ units. In the ^1H NMR spectra of the PVC obtained with the *tert*-BuLi at −30°C, no peaks based on the internal double bonds in the main chains were observed [14]. In addition, the resonance due to the methyl protons of the *tert*-butyl group at the initiating chain end was observed at 0.90 ppm as four split lines, reflecting the different configurations of the proximal VC units, which is consistent with the reported results [16]. The methylene protons of the $–CH_2Cl$ group introduced into the terminal chain end were also observed at 3.4–3.5 ppm [17]. The ^{13}C NMR spectra of the corresponding hydrocarbon polymer derived from the PVC reduced by n-Bu_3SnH in the presence of AIBN [12,13] coincided with that of the polymers obtained from the polymerization of ethylene with the *tert*-BuLi complexed with *tert*-diamines such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine [14]. These findings indicate that the *tert*-BuLi initiated the polymerization of VC and the polymerization was terminated by adding the methanol, and the main chain of the polymer consisted of only regular head-to-tail units. Accordingly, the PVC with a well-defined structure could be synthesized from the polymerization of VC with *tert*-BuLi in nearly bulk at −30°C.

The tacticity of the PVC obtained from the polymerization of VC with *tert*-BuLi at −30°C was estimated from the area of each split peak of methine carbon by the ^{13}C NMR spectra of the polymers [15]. The tacticity of the PVC thus determined was: mm = 18%, mr = 46%, rr = 36%, respectively. These values are not so different from those obtained with the conventional radical polymerization reported (mm = 12%, mr = 49% and rr = 39%) [15].

In conclusion, *tert*-BuLi has been shown to promote the controlled polymerization of VC under mild polymerization conditions to give a polymer with a well-defined structure.

A detailed study is now underway, and will be reported in a forthcoming paper.

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