Anionic Polymerization of *N*-Vinylcarbazole with Alkyllithium as an Initiator

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ABSTRACT: The anionic polymerization of *N*-vinylcarbazole (NVC) with alkyllithium (RLi) as an initiator was achieved for the first time. The yield of poly(*N*-vinylcarbazole) (PNVC) was considerably affected by the molar ratio of RLi to NVC. The polymerization temperature, type of solvent, additives, and type of initiator influenced the anionic polymerization of NVC. The highest yield was obtained with *tert*-butyllithium (*t*-BuLi) as an initiator, with a molar ratio of approximately $[t\text{-BuLi}]_0/[\text{NVC}]_0 = 0.1$. Aliphatic hydrocarbons with relatively low solubility for NVC and PNVC were considered to be appropriate solvents for the anionic polymerization of NVC. The ^{1}H NMR spectrum strongly supports the polymer chain structure of PNVC. The coordination of NVC nitrogen atoms to the lithium atoms of RLi presumably reduces the electron density of the vinyl group, and the anionic polymerization of NVC becomes possible.

Introduction

Anionic polymerization is a very important polymerization methods for the synthesis of polymers. A variety of monomers, such as diene monomers, styrene derivatives, and methacrylic acid derivatives have been polymerized using this method. The necessary condition for vinyl monomers to undergo anionic polymerization is the presence of vinyl groups with low electron density. Therefore, up until now it has been believed that monomers having vinyl groups with a high electron density cannot be polymerized using anionic polymerization except the case of vinyl ferrocene.[1] For instance, there has been no example of the anionic polymerization of *N*-vinylcarbazole (NVC), because of the presence of nitrogen atoms (a strong electron-donor) adjoining the vinyl group.[2−4]

We recently reexamined the possibility of anionic polymerization of NVC in order to develop a new polymerization method for *N*-vinyl monomers. With regard to anionic polymerization, the polymerization reactions and microstructure of the polymers are strongly affected by the complexing agents (such as amine and ether) used. For example, 1,3-cyclohexadiene, a typical cyclic diene monomer, can undergo living polymerization only with a specific molar ratio of alkyllithium (RLi) and amine as an initiator.[5−7]

Considering this aspect, NVC could be regarded as a monomer accompanied by an amine as a complexing agent within the same molecule. That is, both a polymerization site and a complexing agent site appear to coexist in this monomer. Consequently, it is expected that the molar ratio of RLi and amine (nitrogen atoms) is a key factor for the anionic polymerization of NVC (Scheme 1).

The anionic polymerization of NVC with RLi has been studied on the basis of the above concept. As a result, it was discovered that a specific molar ratio of RLi and NVC was a particularly active reaction system for the anionic polymerization of NVC. We report the first successful example of the anionic polymerization of NVC. The polymerization conditions and polymerization mechanism for the synthesis of poly(*N*-vinylcarbazole) (PNVC) are discussed in detail.

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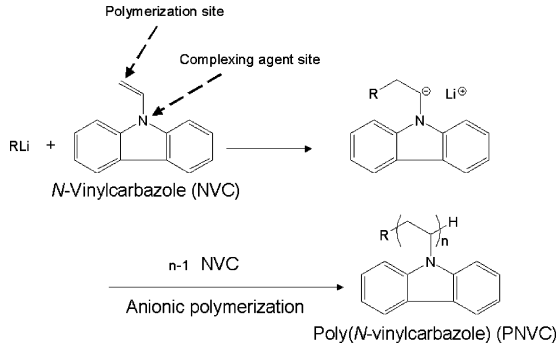
Scheme 1. Anionic Polymerization of *N*-Vinylcarbazole with RLi as an Initiator



Experimental Section

Materials. Cyclohexane (≥99.5%), methylcyclohexane (≥99%), normal hexane (*n*-hexane) (95%), toluene (≥99.8%), tetrahydrofuran (THF) (≥99.9%), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (≥99.5%) were refluxed over calcium hydride (CaH_2) (90−95%) and then distilled under an argon atmosphere. *N*-Vinylcarbazole (NVC) (98%) and *N*-ethylcarbazole (NEC) (97%) were recrystallized in cyclohexane and then dried under reduced pressure in dry argon. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (98%), lithium fluoride (LiF) (≥99.99%), lithium chloride (LiCl) (99.998%), lithium bromide (LiBr) (99.999%), and carbazole (95%) were dried under reduced pressure in dry argon. *sec*-Butyllithium (*s*-BuLi; 1.40 M in cyclohexane), *tert*-butyllithium (*t*-BuLi; 1.70 M in pentane), *n*-butyllithium (*n*-BuLi; 1.60 M in hexane), and methanol (MeOH) (≥99.9%) were used without further purification. All reagents were purchased from Aldrich.

Polymerization of NVC with Alkyllithium: Polymerization Method A. A well-dried 50 mL Schlenk tube was purged with dry argon, and polymerization solvent, such as cyclohexane (5.0 mL) was added at room temperature (ca. 25 °C) using a hypodermic syringe. Alkyllithium (RLi) was then supplied to this solution with a hypodermic syringe under a dry argon atmosphere. NVC (10.3 mL of a 0.5 M solution or 12.9 mL of a 0.4 M solution in polymerization solvent, 5.17 mmol) was added to this solution, and the reaction mixture was magnetically stirred under a dry argon atmosphere. After the polymerization, dry MeOH was added to the reaction mixture in an equimolar amount to the lithium (Li) atoms present in the reaction mixture, to terminate the reaction. The

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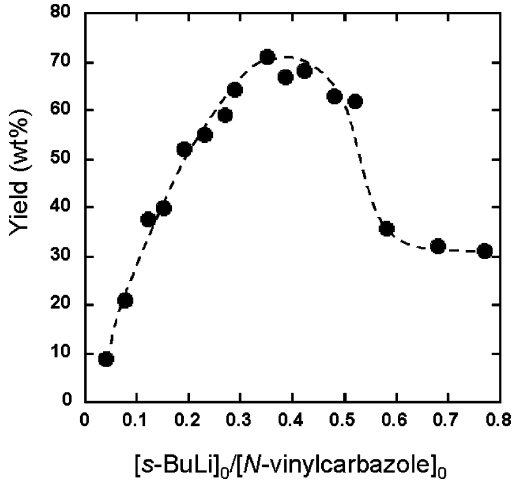


Figure 1. Relationship between the molar ratios of [*sec*-butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ and the yield (wt %) of poly(*N*-vinylcarbazole) from *N*-vinylcarbazole. Polymerization was performed under a dry argon atmosphere in cyclohexane at room temperature (ca. 25 °C) for 24 h. [*N*-Vinylcarbazole]/ [cyclohexane] = 1.00 g/15.3 mL.

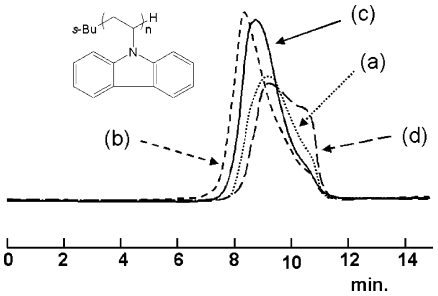


Figure 2. Gel permeation chromatography (GPC) traces of poly(*N*-vinylcarbazole) synthesized by anionic polymerization of *N*-vinylcarbazole with *s*-buthyllithium as an initiator. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by GPC using a UV detector calibrated with polystyrene standards. (a) [*sec*-butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ = 0.039, yield 9.0 wt %, M_n = 11 700, molecular weight distribution (M_w/M_n) = 4.85. (b)[*sec*-butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ = 0.12, yield 41 wt %, M_n = 20 700, M_w/M_n = 7.95. (c) [*sec*-butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ = 0.35, yield 71 wt %, M_n = 26 000, M_w/M_n = 5.12. (d) [*sec*-butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ = 0.68, yield 32 wt %, M_n = 6700, M_w/M_n = 4.70.

polymerization mixture was then poured into a large volume of MeOH to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure in a dry argon atmosphere at room temperature for 24 h, resulting in a white powdery polymer.

Polymerization of NVC with Alkyllithium: Polymerization Method B. NVC (1.00 g, 5.17 mmol) was placed into a well-dried 50 mL Schlenk tube at room temperature (ca. 25 °C). The Schlenk tube was then alternately evacuated and filled with dry argon several times, and was further dried under reduced pressure for 24 h. The polymerization solvent, for example cyclohexane (15.3 mL), was added using a hypodermic syringe at room temperature (ca. 25 °C). RLi was then supplied to this solution with a hypodermic syringe, and the reaction mixture was magnetically stirred under a dry argon atmosphere. Termination of the polymerization and separation of the polymers obtained were performed using procedures similar to those described above.

Measurements. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (M_w/M_n) were determined using gel permeation chromatography (GPC) equipment with a UV detector (Shimadzu SPD-6A) and a Shimadzu Shim-pack GPC-80 M column (the length of the column was 300 mm, the diameter of column was 8 mm, and the effective molecular weight range was 100−4000000) at 40 °C.

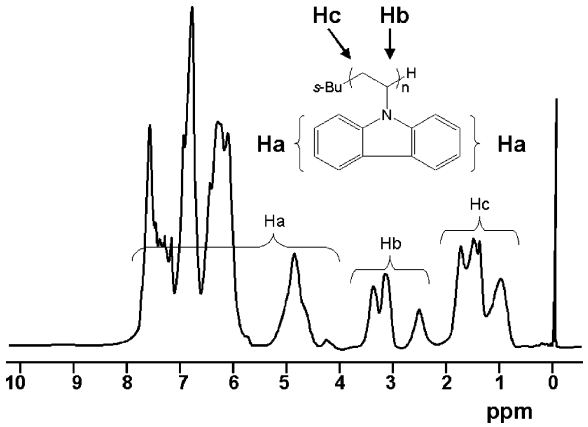


Figure 3. ^{1}H NMR spectrum of poly(*N*-vinylcarbazole) ([*sec*-butyllithium]$_0$/ [*N*-vinylcarbazole]$_0$ = 0.35, Number-average molecular weight (M_n) = 26 000, molecular weight distribution (M_w/M_n) = 5.12) in a 3.0 wt % solution of $CDCl_3$ at 50 °C. (Ha) Aromatic protons on the pendant carbazole groups: 4.0−8.2 ppm. (Hb) Methine protons in the main chain: 2.2−4.0 ppm. (Hc) Methylene protons in the main chain: 0.7−2.2 ppm.[8]

Table 1. Influence of Polymerization Temperature on the Anionic Polymerization of *N*-Vinylcarbazole (NVC)[a]

no.	initiator	temp (°C)	yield (wt %)	M_n[b]	M_w/M_n[c]
1	*s*-BuLi	room temp	66	22 100	6.01
2	*s*-BuLi	40	37	15 700	4.47
3	*s*-BuLi	60	29	13 700	6.39

[a] Polymerization was carried out in cyclohexane under a dry argon atmosphere for 24 h using the polymerization method B. [*s*-BuLi]$_0$/[NVC]$_0$ = 0.35/1.00. [NVC]/[cyclohexane] = 1.00 g/15.3 mL. [b] Number-average molecular weight. Estimated by gel permeation chromatography (GPC). [c] Molecular weight distribution. Estimated by GPC.

Table 2. Effect of Solvents on the Anionic Polymerization of *N*-Vinylcarbazole (NVC)[a]

no.	initiator	solvent	yield (wt %)	M_n[b]	M_w/M_n[c]
1	*s*-BuLi	cyclohexane	66	22 100	6.01
4	*s*-BuLi	methylcyclohexane	58	24 800	5.65
5	*s*-BuLi	toluene	22	12 200	2.82
6	*s*-BuLi	THF	0		

[a] Polymerization was carried out under a dry argon atmosphere at room temperature for 24 h using the polymerization method B. [*s*-BuLi]$_0$/[NVC]$_0$ = 0.35/1.00. [NVC]/[solvent] = 1.00 g/15.3 mL. [b] Number-average molecular weight. Estimated by gel permeation chromatography (GPC). [c] Molecular weight distribution. Estimated by GPC.

THF was used as the eluent, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene standards. ^{1}H NMR spectra of the polymers were measured in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) at 500 MHz using a JEOL JNM LA-500 spectrometer.

Results and Discussion

Discovery of the Anionic Polymerization of NVC. To reveal the possibility for anionic polymerization of NVC, anionic polymerization of NVC was attempted using various molar ratios of *s*-BuLi (a typical alkyllithium) and NVC in cyclohexane at room temperature (ca. 25 °C) for 24 h, according to polymerization method A. The results obtained from these polymerizations are shown as Figure 1.

The anionic polymerization of NVC was very difficult when the molar ratio of [*s*-BuLi]$_0$/[NVC]$_0$ was lower than 0.04, and only a few reaction products were observed in the reaction system. Subsequently, a large amount of *s*-BuLi was used to ascertain the possibility of the anionic polymerization of NVC. As a result, it was found that the color of the reaction system

Table 3. Effect of Polar Additives on the Anionic Polymerization of *N*-Vinylcarbazole (NVC)[a]

no.	initiator (mmol)	additive (mmol)	yield (wt %)	M_n[b]	M_w/M_n[c]
1	*s*-BuLi (1.80)	none	66	22 100	6.01
7	*s*-BuLi (1.80)	TMEDA[d](1.80)	2.8	4 300	1.86
8	*s*-BuLi (1.80)	DABCO[e] (1.80)	24	18 000	3.79
9	*s*-BuLi (1.80)	NEC[f] (1.80)	59	22 600	6.72
10	*s*-BuLi (1.80)	NEC (0.90)	63	25 800	5.80

[a] Polymerization was carried out in cyclohexane under a dry argon atmosphere at room temeprature for 24 h using the polymerization method B. $[s\text{-BuLi}]_0/[NVC]_0 = 0.35/1.00$. [NVC]/[solvent] = 1.00 g/15.3 mL. [b] Number-average molecular weight. Estimated by gel permeation chromatography (GPC). [c] Molecular weigth distribution. Estimated by GPC. [d] *N,N,N′,N′*-Tetramethylethylenediaine. [e] 1,4-Diazabicyclo[2.2.2]octane.[f] *N*-Ethylcarbazole.

Table 4. Anionic Polymerization of *N*-Vinylcarbazole (NVC) with Several Kinds of Alkyllithiums[a]

no.	initiator	temp (°C)	yield (wt %)	M_n[b]	M_w/M_n[c]
1	*s*-BuLi	room temp	66	22 100	6.01
11	*t*-BuLi	room temp	59	17 300	4.68
12	*n*-BuLi	room temp	40	16 700	10.2

[a] Polymerization was carried out in cyclohexane under a dry argon atmosphere for 24 h using the polymerization method B. $[BuLi]_0/[NVC]_0 = 0.35/1.00$. [NVC]/[cyclohexane] = 1.00 g/15.3mL. [b] Number-average molecular weight. Estimated by gel permeation chromatography (GPC). [c] Molecular weight distribution. Estimated by GPC.

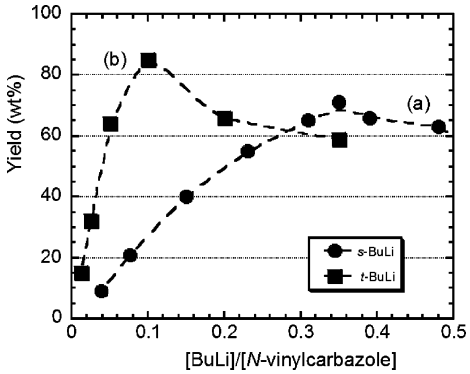


Figure 4. Relationship between the molar ratios of $[\text{butyllithium}]_0/[N\text{-vinylcarbazole}]_0$ ((a) $[\textit{sec}\text{-butyllithium}]_0/[N\text{-vinylcarbazole}]_0$; (b) $[\textit{tert}\text{-butyllithium}]_0/[N\text{-vinylcarbazole}]_0$) and the yield (wt %) of poly(*N*-vinylcarbazole) from *N*-vinylcarbazole. Polymerization was performed under a dry argon atmosphere in an aliphatic hydrocarbon solvent ((a) cyclohexane; (b) *n*-hexane) at room temperature (ca. 25 °C) for 24 h, according to polymerization method A. [*N*-Vinylcarbazole]/ [cyclohexane] = 1.00 g/15.3 mL.

Table 5. Anionic Polymerization of *N*-Vinylcarbazole (NVC) with *t*-BuLi[a]

no.	initiator	solvent	yield (wt %)	M_n[b]	M_w/M_n[c]
13	*t*-BuLi	cyclohexane	79	20 200	5.88
14	*t*-BuLi	*n*-hexane	85	16 400	3.99

[a] Polymerization was carried out under a dry argon atmosphere at room temperature for 24 h using the polymerization method A. $[t\text{-BuLi}]_0/[NVC]_0 = 0.10/1.00$. [NVC]/[solvent] = 1.00 g/15.3mL. [b] Number-average molecular weight. Estimated by gel permeation chromatography (GPC). [c] Molecular weight distribution. Estimated by GPC.

solution changed to yellow and became opaque. Finally, the anionic polymerization of NVC became possible for the first time when the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ was higher than 0.04.

As shown in Figure 1, the yield of PNVC was increased with increasing molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$. The highest yield of PNVC was obtained with a $[s\text{-BuLi}]_0/[NVC]_0$ molar ratio of approximately 0.38. Under this polymerization condition, the

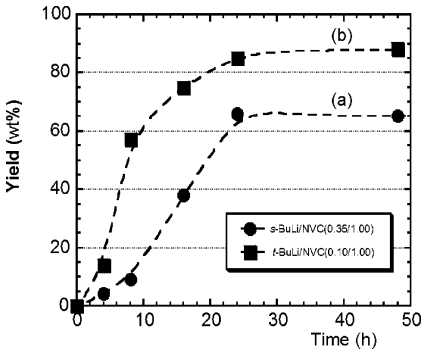


Figure 5. Time−yield relationship for the anionic polymerization of *N*-vinylcarbazole with butyllithium as an initiator ((a) *sec*-butyllithium; (b) *tert*-buthyllithium). Polymerization was performed under a dry argon atmosphere in an aliphatic hydrocarbon solvent ((a) cyclohexane; (b) *n*-hexane) at room temperature (ca. 25 °C). $[\textit{sec}\text{-butyllithium}]_0/[N\text{-vinylcarbazole}]_0 = 0.35/1.00$. $[\textit{tert}\text{-butyllithium}]_0/[N\text{-vinylcarbazole}]_0 = 0.10/1.00$. [*N*-Vinylcarbazole]/[solvent] = 1.00 g/15.3 mL.

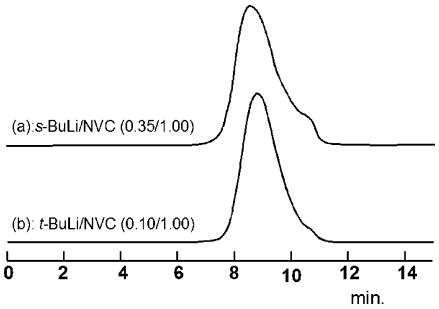


Figure 6. Gel permeation chromatography (GPC) traces of poly(*N*-vinylcarbazole) synthesized by anionic polymerization of *N*-vinylcarbazole with butyllithium as an initiator ((a) *sec*-butyllithium; (b) *tert*-butyllithium). Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by GPC using a UV detector calibrated with polystyrene standards. Polymerization was performed under a dry argon atmosphere in an aliphatic hydrocarbon solvent ((a) cyclohexane; (b) *n*-hexane) at room temperature (ca. 25 °C) for 24 h, according to polymerization method A. $[\textit{sec}\text{-butyllithium}]_0/[N\text{-vinylcarbazole}]_0 = 0.35/1.00$. $[\textit{tert}\text{-butyllithium}]_0/[N\text{-vinylcarbazole}]_0 = 0.10/1.00$. [*N*-Vinylcarbazole]/[solvent] = 1.00 g/15.3 mL.

color of poly(*N*-vinylcarbazolyl)lithium (PNVCLi) was an opaque yellow, as described above. After some time, the reaction system gradually became heterogeneous and white colored compounds appeared. The relationship between the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ and the yield of PNVC was not a simple one. When the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ was higher than 0.4, the yield of PNVC was decreased; however, the yield of PNVC became steady at 30 wt % yield when the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ was higher than 0.6.

Figure 2 shows the results of gel permeation chromatography (GPC) analyses for each of the polymers obtained. When the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ is lower than 0.05 (Figure 2a), the GPC profile shows a single broad peak. When the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ was from 0.05 to 0.2, the GPC profile displayed a single monomodal peak (Figure 2b). When the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ is between 0.2 and 0.55, the GPC profile shows a single rounded peak (Figure 2c). On the other hand, when the molar ratio of $[s\text{-BuLi}]_0/[NVC]_0$ is over 0.55, the GPC profile displays a broad bimodal peak (Figure 2d).

From the results obtained, it is clear that the yield of PNVC is considerably affected by the molar ratio of *s*-BuLi and NVC in the anionic polymerization of NVC. In addition, the initiation reaction for NVC with *s*-BuLi appears to be slow for the anionic polymerization. On the other hand, the propagation reaction appears to be relatively fast; however, some side reactions, such

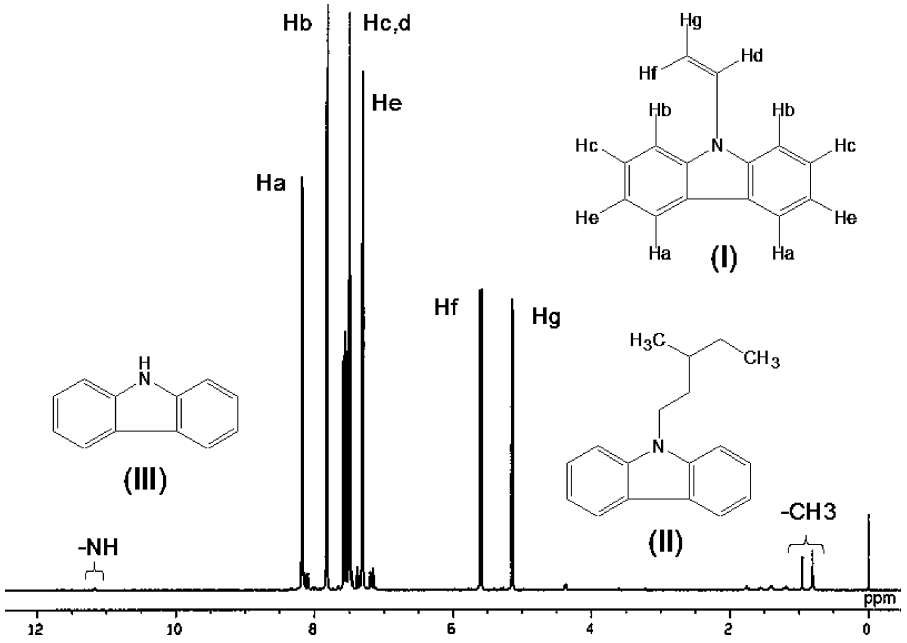


Figure 7. Typical ^{1}H NMR spectrum of the MeOH soluble compounds (a mixture of unreacted *N*-vinylcarbazole and byproducts) in the polymerization mixture of *s*-BuLi/NVC system. ^{1}H NMR spectra were measured in a 3.0 wt % solution of deuterated dimethyl sulfoxide (DMSO-d_6) at 50 °C. Polymerization was performed under a dry argon atmosphere in cyclohexane at room temperature (ca. 25 °C) for 24 h. [*sec*-butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ = 0.35/1.00. [*N*-Vinylcarbazole]/[cyclohexane] = 1.00 g/15.3 mL. Key: (I): *N*-vinylcarbazole; (II) butyl adduct of *N*-vinylcarbazole; (III) carbazole.

as transfer and termination reactions, seemed to occur under these polymerization conditions.

Figure 3 shows a typical ^{1}H NMR spectrum of PNVC synthesized by the anionic polymerization method. The spectrum obtained was similar to the ^{1}H NMR spectrum for PNVC polymerized by radical or cationic polymerization.[8] The ratio of Ha/Hb/Hc was 8/1/2. This proton ratio strongly supports the polymer chain structure shown for PNVC in Figure 3.

Influence of Polymerization Temperature on the Anionic Polymerization of NVC. From the perspective of basic polymer chemistry, it is very important for new polymerization reactions to reveal the optimum polymerization conditions. Therefore, the effect of polymerization temperature on the anionic polymerization of NVC with *s*-BuLi ([*s*-BuLi]$_0$/[NVC]$_0$ = 0.35/1.00) as an initiator was examined. The polymerization was performed in cyclohexane under a dry argon atmosphere for 24 h using polymerization method B. The results obtained are summarized in Table 1.

PNVC polymerized at 40 °C showed the narrowest M_w/M_n range than at other temperatures. However, the M_n and the yield of PNVC decreased with increasing polymerization temperature. Consequently, the rate of the initiation reaction seems to be increased in a high-temperature atmosphere. At the same time, side reactions (i.e., transfer and decomposition reactions) also seem to be increased under high-temperature conditions.

For the anionic polymerization of NVC, both the rate of initiation reaction and the control of side reactions are thought to be very important factors in obtaining high yield and a narrow M_w/M_n range for PNVC. From the results obtained, a relatively low polymerization temperature is considered to be appropriate for the anionic polymerization of NVC.

Effect of Solvents on the Anionic Polymerization of NVC. It is well-known that anionic polymerization of conventional monomers, such as butadiene (Bd), isoprene (Ip), styrene (St), and methyl methacrylate (MMA), are strongly affected by the types of solvents used. Consequently, it was expected that the polymerization solvent would be an important factor for the anionic polymerization of NVC.

To reveal the effect of solvents, anionic polymerization of NVC with *s*-BuLi ([*s*-BuLi]$_0$/[NVC]$_0$ = 0.35/1.00) was performed in several different solvents at room temperature under a dry argon atmosphere for 24 h, using polymerization method B. The polymerization results are summarized in Table 2.

As expected, the anionic polymerization of NVC with *s*-BuLi as an initiator is significantly affected by the type of solvents used. Among three types of solvents, aliphatic hydrocarbon solvents, such as cyclohexane and methylcyclohexane, gave good results with high yield. Although a relatively narrow M_w/M_n range was observed, use of an aromatic hydrocarbon solvent, such as toluene, considerably impedes the anionic polymerization of NVC. Therefore, side reactions seem to be accelerated in an aromatic hydrocarbon solvent.

When an ether such as THF was used as a solvent, the color of the polymerization mixture changed to red, and no PNVC was obtained as for the previous study.[3] THF, a strong complexing agent for *s*-BuLi, appears to cause unfavorable side reactions, such as transfer and decomposition reactions by the polarization of C−Li bonds in organolithium compounds.

The order of solubility for NVC and PNVC in the following solvents is THF > toluene > methylcyclohexane > cyclohexane. Therefore, it is concluded that the yield of PNVC is decreased with increasing solubility of the NVC and PNVC reaction system. In this polymerization system, aliphatic hydrocarbons with relatively low solubility for NVC and PNVC are considered to be appropriate solvents for the anionic polymerization of NVC. In an aliphatic solvent, the propagation reaction of the polymer chain seems to be the dominant reaction.

Effect of Polar Additives on the Anionic Polymerization of NVC. In the case of anionic polymerization, polar additives such as amine and ether are regarded as strong complexing agents for organolithium compounds. In general, these complexing agents strongly affect the polymerization reactions and microstructure of the polymers.[5−7]

The effect of polar additives was examined to obtain basic information for the anionic polymerization of NVC. The polymerization of NVC with *s*-BuLi ([*s*-BuLi]$_0$/[NVC]$_0$ = 0.35/

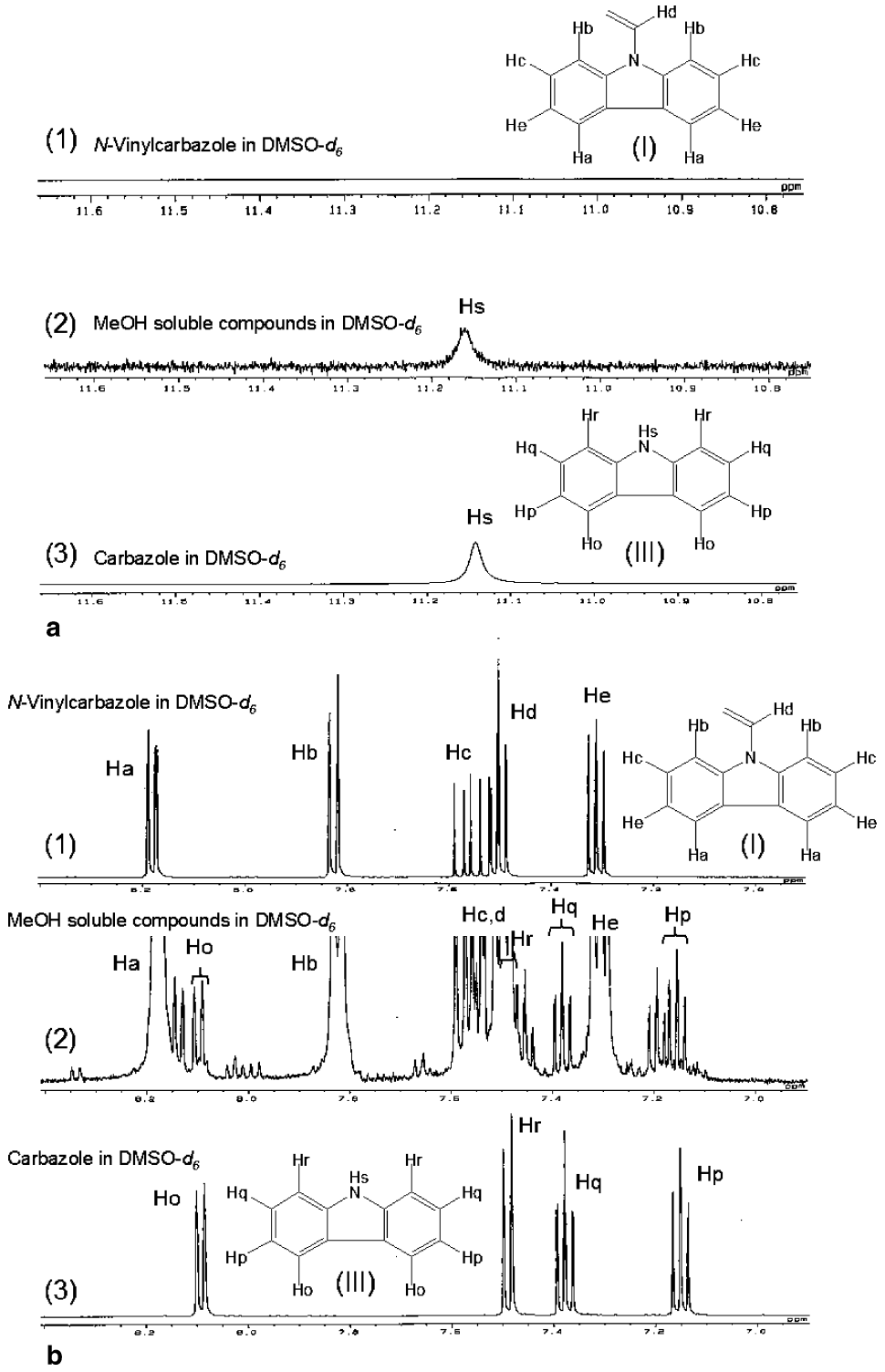


Figure 8. ^{1}H NMR spectra of (1) *N*-vinylcarbazole, (2) MeOH soluble compounds (a mixture of unreacted *N*-vinylcarbazole and byproducts) in the polymerization mixture of *s*-BuLi/NVC system, and (3) carbazole. ^{1}H NMR spectra were measured in a 3.0 wt % solution of deuterated dimethyl sulfoxide (DMSO-d_6) at 50 °C. Polymerization was performed under a dry argon atmosphere in cyclohexane at room temperature (ca. 25 °C) for 24 h. [*sec*-Butyllithium]$_0$/[*N*-vinylcarbazole]$_0$ = 0.35/1.00. [*N*-Vinylcarbazole]/[cyclohexane] = 1.00 g/15.3 mL. Key: (I) *N*-vinylcarbazole; (III) carbazole.

1.00) was performed in cyclohexane with several different additives at room temperature under a dry argon atmosphere for 24 h, using polymerization method B. The results are displayed in Table 3.

When *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (a typically strong complexing agent) was used as an additive, a low yield of PNVC with a low M_n and narrow M_w/M_n range was observed. During the polymerization, the color of the reaction mixture was changed from dark brown to red. Therefore, the initiation and side reactions seem to be accelerated by the addition of TMEDA to the reaction system. The addition of 1,4-Diazabicyclo[2.2.2]octane (DABCO) to the polymerization system considerably impeded the anionic polymerization of NVC. In contrast, *N*-ethylcarbazole (NEC) was found to be almost inert as an additive for the anionic polymerization of NVC.

Table 6. Effect of Additives on the Anionic Polymerization of *N*-Vinylcarbazole (NVC) with *t*-BuLi[a]

no.	$[t\text{-BuLi}]_0/[\text{NVC}]_0$ (mmol)	additive (mmol)	yield (%)	M_n[b]	M_w/M_n[c]
14	0.517/5.17	none	85	16 400	3.99
15	0.517/5.17	LiF (2.59)	75	22 100	5.57
16	0.517/5.17	LiCl (2.59)	77	19 600	6.49
17	0.517/5.17	LiBr (2.59)	69	16 800	7.77
18	0.517/5.17	NEC[d] (0.517)	72	24 500	5.17
19	0.129/5.17	none	42	32 200	9.41
20	0.129/5.17	LiF (0.645)	50	31 600	7.48
21	0.129/5.17	LiCl (0.645)	53	30 000	7.50
22	0.129/5.17	LiBr (0.645)	28	19 900	10.9
23	0.129/5.17	NEC (0.517)	38	22 000	10.5

[a] Polymerization was carried out in *n*-hexane under a dry argon atmosphere at room temperature for 24 h using the polymerization method A. [NVC]/[*n*-hexane] = 1.00 g/15.3 mL. [b] Number-average molecular weight. Estimated by gel permeation chromatography (GPC). [c] Molecular weight distribution. Estimated by GPC. [d] *N*-Ethylcarbazole.

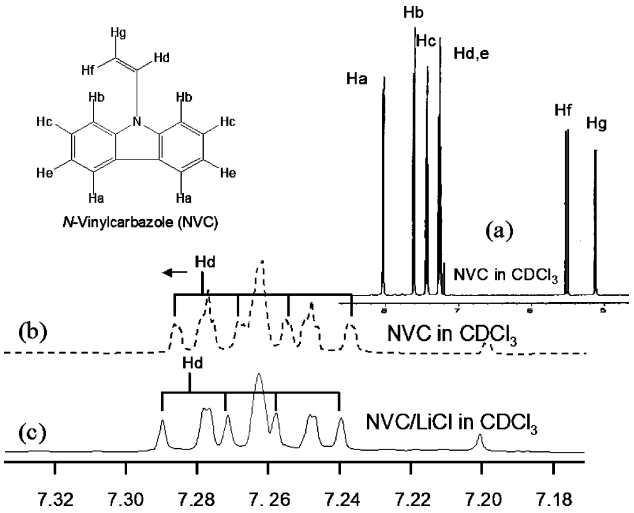


Figure 9. ^{1}H NMR spectra of *N*-vinylcarbazole (a and b) and a mixture of *N*-vinylcarbazole/ lithium chloride (LiCl) (c). ^{1}H NMR spectra were measured in a 3.0 wt % solution of deuterated chloroform ($CDCl_3$) at 50 °C. [*N*-Vinylcarbazole]/[LiCl] = 1/5.

For this anionic polymerization, strong complexing agents, such as TMEDA, DABCO, and THF (Table 2), are thought to cause side reactions. Coordination of a strong complexing agent to the Li atom in an organolithium compound (e.g., RLi, PNVCLi) causes the C−Li bond to become strongly polarized, and unfavorable side reactions (i.e., transfer and decomposition reactions) are significantly increased. With respect to the anionic polymerization of NVC, the coordination of nitrogen atoms in carbazole groups to the Li atom in organolithium compounds seems to be the one and only appropriate reaction system.

Therefore, for this polymerization system, it is considered that the yield of PNVC is decreased with increasing polarity of the reaction system. For the anionic polymerization of NVC with RLi as an initiator, the existence of polar additives in the reaction mixture is concluded to be an inappropriate reaction condition.

Anionic Polymerization of NVC with Several Types of Alkyllithium. In anionic polymerization, the initiation reaction is an important reaction process, and usually the type of initiator used strongly affects the rate of reaction. The anionic polymerization of NVC was carried out in cyclohexane with several types of RLi ($[\text{RLi}]_0/[\text{NVC}]_0 = 0.35/1.00$) at room temperature under a dry argon atmosphere for 24 h, using polymerization method B. The results are presented in Table 4.

It is clear from Table 4, that for the anionic polymerization of NVC, different types of initiator strongly affect the yield and M_w/M_n of PNVC. The yield of PNVC was in the order *of* *s*-BuLi > *t*-BuLi > *n*-BuLi in this polymerization condition. On the other hand, *t*-BuLi gave the narrowest M_w/M_n range for PNVC than the other initiators. PNVC initiated by *n*-BuLi showed a very broad M_w/M_n range. Therefore, the rate of the initiation reaction is considered to be on the order of *t*-BuLi > *s*-BuLi > *n*-BuLi.

Each of the results is considered unusual, because the molecular weight of polymers obtained showed considerably higher than that of estimated from the molar ratio of Li and the monomer. Therefore, in the anionic polymerization of NVC with RLi as an initiator, only a small portion of the RLi can produce active PNVCLi to obtain a high molecular weight PNVC.

Subsequently, anionic polymerization of NVC was attempted using various molar rtios of *t*-BuLi and NVC in *n*-hexane at room temperature (ca. 25 °C) for 24 h, according to polymerization method A. The results obtained from these polymerizations are shown in Figure 4. Compared with anionic polymerization of NVC with *s*-BuLi as an initiator, the appropriate molar ratio of $[t\text{-BuLi}]_0/[\text{NVC}]_0$ showed considerably lower than that of $[s\text{-BuLi}]_0/[\text{NVC}]_0$. The highest yield of PNVC was obtained with a $[t\text{-BuLi}]_0/[\text{NVC}]_0$ molar ratio of approximately 0.10. Therefore, *t*-BuLi seems to have a higher efficiency for the initiation and propagation reactions of NVC than that of *s*-BuLi.

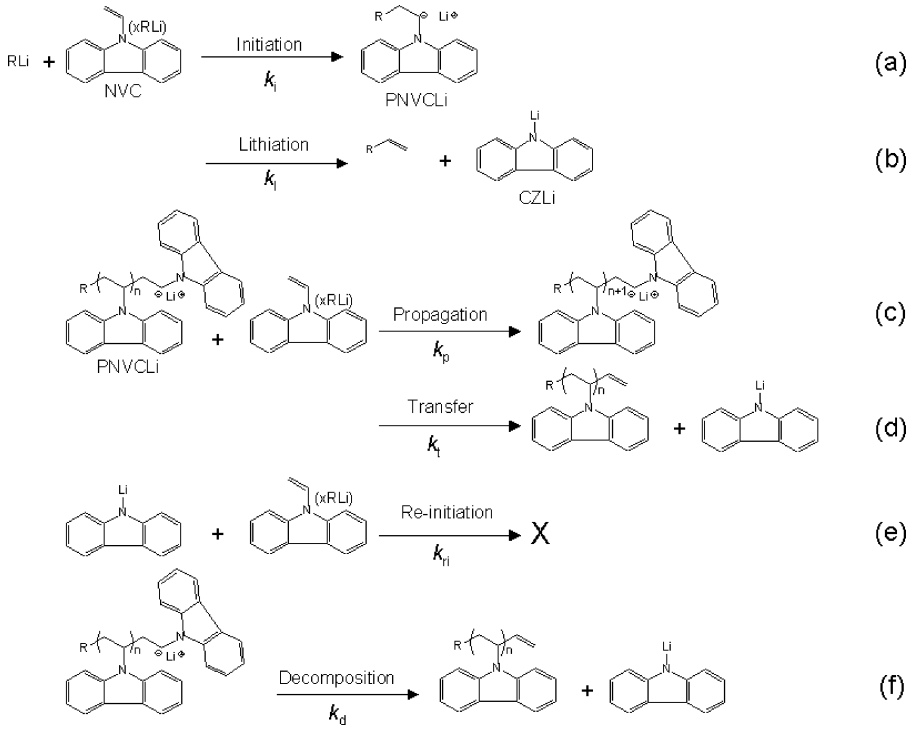
Effect of solvents on the anionic polymerization of NVC with *t*-BuLi as an initiator is shown in Table 5. The results obtained showed that *n*-hexane is a suitable solvent for this polymerization system to obtain high yield and narrow M_w/M_n of PNVC.

Figure 5 shows the relationship between the polymerization time and the yield of PNVC. Compared with *s*-BuLi/NVC system, the rate of the polymerization of *t*-BuLi/NVC system is considerably fast. Therefore, the complexation of *t*-BuLi and NVC can be considered more suitable condition to reduce electron density of the vinyl group in NVC than that of *s*-BuLi and NVC. The GPC profiles of PNVC obtained by anionic polymerization of NVC with *s*-BuLi and *t*-BuLi are shown in Figure 6 (part a, $[s\text{-BuLi}]_0/[\text{NVC}]_0 = 0.35/1.00$; part b, $[t\text{-BuLi}]_0/[\text{NVC}]_0 = 0.10/1.00$). The shoulder peak around 11 min was decreased in the case of *t*-BuLi/NVC system compared to *s*-BuLi/NVC system. That is, the unfavorable side reactions (e.g., transfer and decomposition reactions) fairly reduce in the *t*-BuLi/NVC system.

Polymerization Mechanism for the Anionic Polymerization of NVC. Although the vinyl group in NVC has a high electron density, the anionic polymerization of NVC did proceed. This is because the coordination of NVC nitrogen atoms to the lithium atoms of RLi causes a decrease in the electron density of the vinyl group in NVC, and the anionic polymerization of NVC becomes possible.

As described above, the initiation reaction and side reactions seem to be very important in the anionic polymerization of NVC using RLi as an initiator. To reveal the detail of this anionic polymerization, the MeOH soluble compounds in the polymerization mixture were examined by ^{1}H NMR analysis. After the polymerization, the polymerization mixture was poured into a large volume of MeOH to precipitate the polymer, which was then separated by filtration. The MeOH solution was then collected, and evaporation was carried out under reduced pressure at room temperature for 24 h, resulting in a yellow powdery compound. Subsequently, ^{1}H NMR measurements of those MeOH soluble compounds were performed in DMSO-d_6. Each ^{1}H NMR spectrum obtained was almost similar to the

Scheme 2. Polymerization Mechanism of *N*-Vinylcarbazole with RLi



^{1}H NMR spectrum of NVC, exclusive of those small signals from $-CH_3$ groups as a residue of *s*-(*t*-)BuLi, −NH groups, and other byproducts.

Figure 7 shows a typical ^{1}H NMR spectrum of the MeOH soluble compounds obtained from the *s*-BuLi/NVC system. The yellow powdery compound appeared to be NVC (I) containing a trace amount of butyl adduct of NVC (II) and carbazole (III). The existence of carbazole (III) as a byproduct of polymerization was confirmed by comparing ^{1}H NMR spectra of NVC (I), carbazole (III), and the yellow powdery compound (Figure 8, parts a and b).

Therefore, only a small amount of *s*-(*t*-)BuLi act as an initiator, and the remaining *s*-(*t*-)BuLi seems to act as a complexing agent to reduce the electron density of the vinyl group in NVC.

Table 6 shows the effect of additives on the anionic polymerization of NVC with *t*-BuLi. For $[t\text{-BuLi}]_0/[\text{NVC}]_0 = 0.517/5.17(0.10/1.00)$ system, the existence of additives showed not so good effects. On the other hand, in the case of $[t\text{-BuLi}]_0/[\text{NVC}]_0 = 0.129/5.17(0.025/1.00)$ system, the polymerization was improved by adding LiF or LiCl. From the results of ^{1}H NMR analysis, it was detected that the complexation of NVC with LiCl (or LiF) reduced the electron density of the vinyl group in NVC. The olefinic protons in the α-position from the nitrogen (Hd) of NVC were shifted downfield (lower field, higher ppm) (Figure 9). Therefore, the reduction of electron density of the vinyl group seems to be a key reaction for the anionic polymerization of NVC. Especially, an appropriate amount of *t*-BuLi to NVC such as No. 14 in Table 6 is considered to act effectively as a complexing agent and accelerate the anionic polymerization of NVC.

A polymerization mechanism for the anionic polymerization of NVC is proposed in Scheme 2. This anionic polymerization is expected to consist of 6 reactions; that is, (a) initiation, (b) lithiation, (c) propagation, (d) transfer, (e) reinitiation and (f) decomposition reactions.

Considering the anionic polymerization of NVC shown in Scheme 2, the initiation reaction (eq a) seems to be slow, due to the high electron density of the vinyl groups. Consequently, the M_w/M_n range of PNVC is not so narrow compared with the anionic polymerization of conventional monomers such as butadiene (Bd), isoprene (Ip), and styrene (St) (Figures 2 and 6; Tables 1−6). Therefore, the initiation reaction and lithiation reaction (eq b) are thought to be competitive reactions at the first stage of polymerization. The transferred compound is expected to be carbazolyllithium (CZLi). In addition, the propagation reaction (eq c) and transfer reaction (i.e., lithiation, eq d) seem to be competitive reactions. For that reason, the rate of polymerization appears to be slow in the initial stage of the polymerization (Figure 5). The transfer reaction (eq d) is the lithiation reaction to nitrogen atoms on the carbazole groups of NVC.[3] That is, it is a chain transfer reaction to the monomer and deactivation of PNVCLi.

The reinitiation reaction given by eq e is thought not to occur, because carbazole remains in the polymerization mixture (Figures 7 and 8). In contrast, the decomposition reaction (eq f) is thought to be possible as one of the deactivation (termination) reactions.[3]

Therefore, when a small amount of RLi is used, the anionic polymerization of NVC is very difficult due to side reactions such as lithiation, transfer, and decomposition. In contrast, when a sufficient amount of RLi is used for the anionic polymerization of NVC, a small amount of RLi act as an initiator, and the remaining RLi act as a complexing agent to reduce the electron density of the vinyl group in NVC. As a result, the anionic polymerization seems to become possible (Figures 1, 4, and 5, Scheme 2).

Conclusion

The anionic polymerization of NVC with RLi as an initiator was achieved for the first time. The yield of PNVC was considerably affected by the molar ratio of RLi and NVC. In addition, the polymerization temperature, type of solvent, additives, and type of initiator used influence the anionic polymerization of NVC. The highest yield was obtained with *t*-BuLi as an initiator, with a molar ratio of approximately

$[t\text{-BuLi}]_0/[\text{NVC}]_0 = 0.1$. Aliphatic hydrocarbons with relatively low solubility for NVC and PNVC are considered to be appropriate solvents for the anionic polymerization of NVC. The PNVC obtained has a high molecular weight, and the ^{1}H NMR spectroscopic measurements strongly support the polymer chain structure of PNVC.

A small amount of RLi act as an initiator, and the remaining RLi act as a complexing agent to reduce the electron density of the vinyl group in NVC. As a result, the anionic polymerization seems to become possible.

References and Notes

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