The rapid, living, anionic polymerization of 2-vinylnaphthalene at ambient temperature: Characterization of an *n*-butyllithium/tetrahydrofuran system in 1,2,3,4-tetrahydronaphthalene

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ABSTRACT: We report the first well-controlled room temperature anionic polymerization of 2-vinylnaphthalene (2-VNP), using alkyllithium (RLi) initiators. The nucleophilicity and solubility of the RLi as well as that of the 2-vinylnaphthalenyllithium (VNPLi) and poly(2-vinylnaphthalenyl)lithium (PVNPLi) propagating species were found to be very important factors in this reaction. An initiator system composed of *n*-butyllithium (*n*-BuLi) with tetrahydrofuran (THF) in 1,2,3,4-tetrahydronaphthalene (THN) was determined to be the most effective of the various systems examined. The *n*-BuLi/THF complex initiates polymerization and the resulting VNPLi/THF and PVNPLi/THF complexes act as propagating species at room temperature. These species offer adequate nucleophilicity and stability without promoting side reactions. As a result, rapid anionic polymerization was achieved. Various poly(2-VNP) products with well-defined polymeric chain structures were synthesized by this process at room temperature. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41901.

INTRODUCTION

Anionic polymerization is a very important method of synthesizing hydrocarbon polymers. Precisely controlled anionic polymerization is a particularly useful means of generating homopolymers, copolymers, block copolymers, and ω-functionalized polymers having well-defined chain structures. A variety of monomers, such as styrene (St) derivatives, methacrylic acid derivatives, and diene monomers, have been polymerized using this method. Among the St derivatives, 2-vinylnaphthalene (2-VNP) is favored for the synthesis of naphthalene-containing polymers, since it tends to produce chain structures with excellent optical and electrical properties. Numerous studies have thus been devoted to the synthesis of poly(2-VNP) (PVNP) with well-defined chain structures via the anionic polymerization of 2-VNP.[1–12]

Recently, Nossarev *et al.* reported that the alkyllithium (RLi) and alkylpotassium (RK) initiated anionic polymerization of 2-VNP in tetrahydrofuran (THF) (or in a toluene/THF mixture) at −78°C appears to proceed via a living reaction process. This same study found that a key factor related to this phenomenon is the application of an unconventional method when purifying commercially available 2-VNP to remove 2-acetylnaphthalene, a reagent used during the synthesis of 2-VNP and an important impurity.[8–10] Even when using specially purified 2-VNP, however, the well-controlled anionic polymerization of this monomer at room temperature remains challenging due to a variety of factors, including side reactions,[7] a low rate of initiation reaction and low initiator efficiency, such that the initiator efficiency at room temperature is actually considerably lower than that at −78°C.[10] These significant obstacles have prevented the further study of potential applications of PVNP.

As we reported in previous papers, the type of RLi, the solvent and addition of a polar additive will all greatly affect the anionic polymerization of 1,3-cyclohexadiene (1,3-CHD; a diene monomer) and 4-diphenylaminostyrene (4-DAS; a St derivative) at ambient temperature.[13–20] These studies further demonstrated that the application of a suitable polymerization system resulted in the first-ever instance of well-controlled (i.e., living) anionic polymerization of 1,3-CHD and 4-DAS.[13–15,18] We therefore anticipated that identifying an appropriate polymerization system for 2-VNP would allow its well-controlled anionic polymerization at ambient temperature. For this reason, we carefully

examined the effects of the type of RLi, and the solvent as well as various polar additives on the room temperature anionic polymerization of 2-VNP.

In this paper, we report the first successful example of the room temperature living anionic polymerization of 2-VNP. We also describe in detail the characteristics of the *n*-butyllithium (*n*-BuLi)/THF system in 1,2,3,4-tetrahydronaphthalene (THN), which was used to accomplish the rapid polymerization.

EXPERIMENTAL

Materials

Cyclohexane ($\geq$99.5%), toluene ($\geq$99.8%), THN (99.0%), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, $\geq$99.5%), and THF ($\geq$99.9%) were refluxed over calcium hydride (CaH$_2$, 95%) and then distilled under dry argon. Methyltriphosphonium bromide (MPB, $\geq$98.0%) and 2-naphthaldehyde (NPA, 98.0%) were dried under reduced pressure. Other reagents were used as received unless otherwise stated. MPB was purchased from Tokyo Chemical. All other reagents were purchased from Sigma-Aldrich.

The 2-VNP was synthesized via a standard Wittig reaction, so as to avoid the incorporation of 2-acetylnaphthalene as an impurity, and purified using silica gel column chromatography. Triphenylphosphonium methylide was prepared by mixing MPB (12.5 g, 35.0 mmol) and *n*-BuLi (35.0 mmol) at room temperature (*ca.* 25°C) in dry THF for 2 h under dry argon. A solution of NPA (5.47 g, 35.0 mmol) in THF was then added, and the reaction mixture was magnetically stirred under dry argon at room temperature for 24 h. The crude 2-VNP obtained was purified using silica gel column chromatography with 3/1 (v/v) *n*-hexane/dichloromethane and toluene as developing solvents at room temperature. Pure 2-VNP was obtained in 96% yield.

^{1}H NMR (δ, ppm): 7.90–7.66 (*m*, 4*H*), 7.66–7.50 (*m*, 1*H*), 7.50–7.30 (*m*, 2*H*), 6.94–6.70 (*dd*, 1*H*), 5.94–5.72 (*dd*, 1*H*), 5.38–5.20 (*dd*, 1*H*).[21]

Polymerization of 2-VNP

A well-dried 50-mL Schlenk tube was purged with dry argon and 5.0 mL of polymerization solvent (cyclohexane, toluene, or
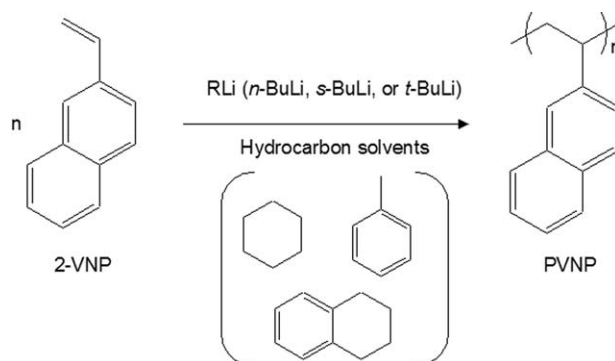
Scheme 1. Anionic polymerization of 2-vinylnaphthalene with alkyllithium species in hydrocarbon solvents.

THN) was added at room temperature (*ca.* 25°C) using a syringe. RLi (*n*-BuLi; 1.60 molL^{-1} in *n*-hexane, *s*-butyllithium (*s*-BuLi); 1.40 molL^{-1} in cyclohexane or *t*-butyllithium (*t*-BuLi); 1.70 molL^{-1} in pentane) was then supplied to this solution with a syringe under dry argon. If necessary, a polar additive (TMEDA or THF) was subsequently added under dry argon. After all reactants had been placed in the tube, the mixture was stirred for 10 min. A solution of 2-VNP (as a 0.648 molL^{-1} solution in the chosen polymerization solvent) was added to the tube and the combined reactants were magnetically stirred under dry argon at room temperature. After polymerization had proceeded for the desired length of time, the reaction was terminated by adding dry methanol (MeOH) to the reaction mixture in an amount equimolar to the quantity of lithium (Li) atoms present. The polymerization mixture was then poured into a large volume of MeOH to precipitate the polymer, which was subsequently separated by filtration. The product was dried under reduced pressure under dry argon at room temperature for 24 h, resulting in a white powder.

Measurements

The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI, M_w/M_n) were determined using gel permeation chromatography (GPC) instrumentation equipped with a differential refractive index

Table I. Anionic Polymerization of 2-VNP with RLi in Hydrocarbon Solvents at Room Temperature[a]

Polymer no.	Initiator	Solvent	(2-VNP)$_0$/(Li)$_0$	Yield (wt %)	M_n (gmol^{-1})	PDI
1	*n*-BuLi	Cyclohexane	13.0 : 1.00	53	3300	1.23
2	*s*-BuLi	Cyclohexane	13.0 : 1.00	70	2580	1.20
3	*t*-BuLi	Cyclohexane	13.0 : 1.00	62	2810	1.20
4	*n*-BuLi	Toluene	13.0 : 1.00	80	2420	1.18
5	*s*-BuLi	Toluene	13.0 : 1.00	74	2020	1.14
6	*t*-BuLi	Toluene	13.0 : 1.00	74	2510	1.20
7	*n*-BuLi	THN[b]	13.0 : 1.00	100	3170	1.28
8	*s*-BuLi	THN	13.0 : 1.00	77	1820	1.49
9	*t*-BuLi	THN	13.0 : 1.00	84	2410	1.59

[a] Polymerization of 2-VNP with RLi was carried out in hydrocarbon solvents (10.0 mL) under dry argon at room temperature for 3 h. Solvent/RLi = 10.0 mL : 0.25 mmol.
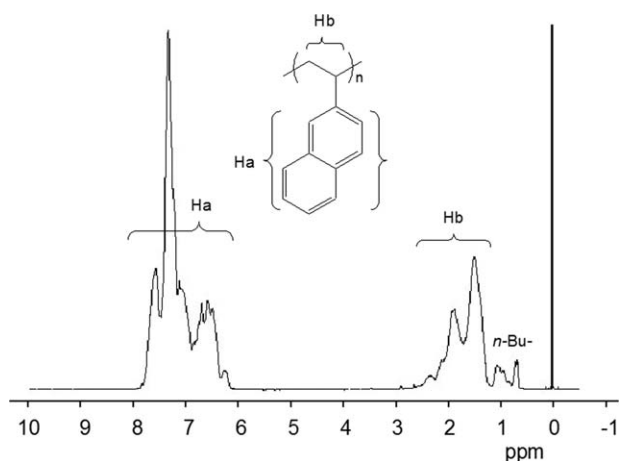[b] 1,2,3,4-Tetrahydronaphthalene (THN).

Figure 1. ^{1}H NMR spectrum of poly(2-vinylnaphthalene) obtained using *n*-butyllithium in 1,2,3,4-tetrahydronaphthalene ($M_n = 3170$, PDI = 1.28). Spectrum acquired from a 3.0 wt % solution in CDCl$_3$ at 50°C.

(RI) detector (Shimadzu RID-6A), a UV detector (Shimadzu SPD-6A), and a Shimadzu Shim-pack GPC-80M column (length: 300 mm; diameter: 8 mm; effective molecular weight range of 100–4,000,000) at 40°C. THF was used as the eluent at a flow rate of 1.0 mLmin^{-1}. A molecular weight calibration curve was obtained using polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) spectra of the polymers were acquired in deuterated chloroform (CDCl$_3$) at 400 MHz using a Jeol JNM-ECX 400 spectrometer.

RESULTS AND DISCUSSION

Anionic Polymerization of 2-VNP with RLi in Hydrocarbon Solvents at Room Temperature

In order to obtain basic information concerning the polymerization reaction, the anionic polymerization of 2-VNP was performed for 3 h in three different hydrocarbon solvents (cyclohexane, toluene, or THN) using three types of RLi (*n*-BuLi, *s*-BuLi, or *t*-BuLi) at room temperature (Scheme 1). The results obtained are summarized in Table I.

In cyclohexane (a typical aliphatic hydrocarbon solvent), the addition of RLi to the 2-VNP solution resulted in a gradual change in the color of the solution to dark red, indicating the formation of the 2-VNP anion. After 3 h of reaction, PVNP yields were obtained in the order of *s*-BuLi (70 wt %) > *t*-BuLi (62 wt %) > *n*-BuLi (53 wt %) and PDI values were in the range of 1.20–1.23 (Table I, entries 1–3). These low yields and

high PDI values indicate relatively slow initiation and propagation reaction rates during the room temperature anionic polymerization in cyclohexane, due to insufficient nucleophilicity of the RLi and poly(2-vinylnaphthalenyl)lithium (PVNPLi) species.

When toluene (a typical aromatic hydrocarbon solvent) was employed, the color of the 2-VNP solution immediately changed to dark red when either *n*- or *s*-BuLi were added, while the change was more gradual when *t*-BuLi was used. Compared to the results with cyclohexane, higher yields of PVNP were obtained, in the order of *n*-BuLi (80 wt %) > *s*- and *t*-BuLi (74 wt %). In addition, *n*-and *s*-BuLi resulted in lower PDI values (1.18 and 1.14), although *t*-BuLi produced a somewhat higher PDI of 1.20 (Table I, entries 4–6). The initiation reaction therefore appears to be considerably faster when using either *n*- or *s*-BuLi in toluene at room temperature.

THN is a hydrocarbon solvent with both aliphatic and aromatic moieties. In reaction solutions using THN as the solvent, the addition of the RLi species resulted in a gradual color change to dark red, again indicating the formation of the 2-VNP anion. Interestingly, when *n*-BuLi was used as an initiator, the yield of PVNP was 100%, although the PDI value was higher than in previous trials, at 1.28 (Table I, entry 7). The use of *s*-BuLi and *t*-BuLi gave 77 and 84 wt % yields of PVNP, with PDI values of 1.49 and 1.59 (Table I, entries 8 and 9). THN therefore appears to be the most effective hydrocarbon solvent for the anionic polymerization of 2-VNP at room temperature.

The results in Table I demonstrate that the anionic polymerization of 2-VNP at room temperature is greatly affected by both the solvent and the RLi initiator. The combination of toluene and *n*-(or *s*-)BuLi resulted in high initiation reaction rates, while THN gave the highest rate of propagation. The combination of *n*-BuLi and THN (Table I, entry 7) was particular effective, producing a 100% yield, which suggests that no side reactions occurred during the polymerization. We therefore anticipated that this system had the potential to allow the well-controlled anionic polymerization of 2-VNP at ambient temperature.

Figure 1 shows a typical ^{1}H NMR spectrum for PVNP synthesized with *n*-BuLi in THN (Table I, entry 7). The peaks from 6.0 to 8.0 ppm (Ha) are assigned to aromatic protons on the naphthyl groups in the polymer while the peaks from 1.2 to 2.6 ppm (Hb and Hd) are assigned to methine and methylene protons, respectively. The peaks from 0.6 to 1.2 ppm are attributed to methyl and methylene protons in the butyl residues resulting from the *n*-BuLi.

Table II. Effects of Toluene/THN Ratio on the Anionic Polymerization of 2-VNP[a]

Polymer no	Initiator	Solvent (vol./vol.)	(2-VNP)$_O$/(Li)$_O$	Reaction time (h)	Yield (wt %)	M_n (gmol^{-1})	PDI
4	*n*-BuLi	Toluene/THN (=10 : 0)	13.0 : 1.00	3	80	2420	1.18
10	*n*-BuLi	Toluene/THN (=5 : 5)	13.0 : 1.00	3	97	2750	1.25
11	*n*-BuLi	Toluene/THN (=2 : 8)	13.0 : 1.00	3	100	2940	1.27
7	*n*-BuLi	Toluene/THN (=0 : 10)	13.0 : 1.00	3	100	3170	1.28
12	*n*-BuLi	Toluene/THN (=10 : 0)	13.0 : 1.00	24	92	2920	1.22

[a] Polymerization of 2-VNP with RLi was carried out in hydrocarbon solvents (10.0 mL) under dry argon at room temperature. Solvent/RLi = 10.0 mL : 0.25 mmol.

Table III. Effects of Polar Additives on the Anionic Polymerization of 2-VNP[a]

Polymer no	Initiator system (Li:additive)[b]	Solvent	$(2\text{-VNP})_O/(\text{Li})_O$	Yield (wt %)	M_n (gmol^{-1})	PDI
13	n-BuLi/TMEDA (1.00 : 1.25)	Cyclohexane	13.0 : 1.00	56[c]	1690	1.15
14	n-BuLi/THF (1.00 : 1.25)	Cyclohexane	13.0 : 1.00	57[c]	1660	1.15
15	n-BuLi/TMEDA (1.00 : 1.25)	Toluene	13.0 : 1.00	87	1680	1.19
16	n-BuLi/THF (1.00 : 1.25)	Toluene	13.0 : 1.00	87	1700	1.19
17	n-BuLi/TMEDA (1.00 : 1.25)	THN	13.0 : 1.00	97	2900	1.17
18	n-BuLi/THF (1.00 : 1.25)	THN	13.0 : 1.00	100	2020	1.15

[a] Polymerization of 2-VNP with RLI was carried out in hydrocarbon solvents (10.0 mL) under dry argon room temperature for 3 h. Solvent/RLi = 10.0 mL : 0.25 mmol.
[b] mol./mol.
[c] Polymerization system was heterogeneous.

Effects of Toluene/THN Ratios on the Anionic Polymerization of 2-VNP

During the anionic polymerization of 2-VNP with RLi at room temperature (Table I), toluene appeared to be more effective than cyclohexane in accelerating the initiation reaction due to improved nucleophilicity of the RLi species. Meanwhile, THN seemed to accelerate the propagation reaction due to improved nucleophilicity of the PVNPLi. The next logical step in the investigation was thus to assess the effectiveness of a toluene/THN mixed solvent, by following the anionic polymerization of 2-VNP with n-BuLi in the mixed solvent (toluene/THN = 10 : 0, 5 : 5, 2 : 8, or 0 : 10 (vol./vol.)) at room temperature for 3 h. As a reference, the same polymerization was performed in toluene at room temperature for 24 h. The results obtained are displayed in Table II.

When the polymerization was performed in the mixed solvent over 3 h, the yield of PVNP increased from 80 to 100% with increases in the proportion of THN, while the PDI narrowed from 1.28 to 1.18 with increases in the proportion of toluene (Table II, entries 4, 10, 11, and 7). These results demonstrate that improvements in initiation and propagation reactions seemed to be mutually exclusive when using the toluene/THN mixed solvent system. In the case of the anionic polymerization

of 2-VNP with n-BuLi in toluene alone (Table II, entry 12), the yield of PVNP remained below 92 wt %, even though the polymerization was carried out for 24 h. It was therefore necessary to take further steps to improve the initiation and propagation reactions during 2-VNP polymerization.

Effects of Polar Additives on the Anionic Polymerization of 2-VNP

Polar additives, such as amines and ethers, are regarded as useful complexing agents for both RLi and polymer-lithium (PLi) species during anionic polymerization with RLi in hydrocarbon solvents. This complexation enhances the nucleophilicity of the reactive species, and thus, polar agents can significantly affect both the progress of the polymerization reaction and the microstructure of the resulting polymer. As an example, TMEDA (a typical amine-based complexing agent) dramatically reduces side reactions, increases rates of initiation and propagation reactions and enhances initiation efficiency during the anionic polymerization of 1,3-CHD with n-BuLi in cyclohexane. This complexation agent was responsible for the first successful example of the living anionic polymerization of 1,3-CHD.[13–15] TMEDA has also been found to greatly modify the anionic polymerization of 4-DAS. The benzyllithium (BzLi)/TMEDA system in toluene, which is prepared from a combination of t-BuLi and TMEDA in toluene, was demonstrated to effectively control side reactions, improve initiation and propagation rates and increase initiation efficiency, leading to the first successful example of the living anionic polymerization of 4-DAS.[18]

Based on the above studies, we anticipated that the presence of polar additives would have a pronounced effect on the anionic polymerization of 2-VNP with RLi in hydrocarbon solvents, similar to the effects observed with 1,3-CHD and 4-DAS. In order to confirm this, the anionic polymerization of 2-VNP using the n-BuLi/TMEDA (or THF) system was carried out at room temperature for 3 h in three different hydrocarbon solvents (i.e., cyclohexane, toluene, and THN). The results obtained are summarized in Table III.

When using the n-BuLi/TMEDA (or THF) system in cyclohexane, the polymerization system gradually became heterogeneous (Table III, entries 13 and 14). Although the PVNP yield remained around 60 wt % due to the low solubility of
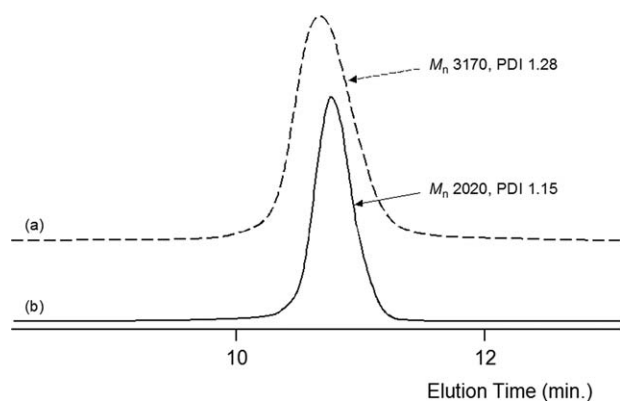

Figure 2. GPC traces of poly(2-vinylnaphthalene) obtained using n-butyllithium in 1,2,3,4-tetrahydronaphthalene (a: M_n = 3170, PDI = 1.28) and an n-butyllithium/tetrahydrofuran (1.00/1.25) system in 1,2,3,4-tetrahydronaphthalene (b: M_n = 2020, PDI = 1.15). M_n and PDI were obtained by GPC calibrated using polystyrene standards.

Table IV. Optimization of the Li/THF Ratio[a]

Polymer no	Initiator system (Li:additive)[b]	Solvent	$(2\text{-VNP})_O/(\text{Li})_O$	Yield (wt %)	M_n (gmol^{-1})	PDI
7	n-BuLi/THF (1.00 : 0.00)	THN	13.0 : 1.00	100	3170	1.28
18	n-BuLi/THF (1.00 : 1.25)	THN	13.0 : 1.00	100	2020	1.15
19	n-BuLi/THF (1.00 : 4.00)	THN	13.0 : 1.00	86	2960	1.31
20	n-BuLi/THF (1.00 : 8.00)	THN	13.0 : 1.00	27	1810	1.88

[a] Polymerization of 2-VNP with RLi was carried out in hydrocarbon solvents (10.0 mL) under dry argon at room temperature for 3 h. Solvent/ RLi = 10.0 mL : 0.25 mmol.
[b] mol./mol.

the (P)VNPLi/TMEDA (or THF) complex in cyclohexane, both polymeric products exhibited low values of PDI (1.15). The application of TMEDA or THF thus seems to improve both the initiation efficiency and initiation reaction rate, although the poor solubility of the reactive complex in cyclohexane is thought to retard the propagation reaction. When toluene was used in place of cyclohexane, the M_n of both PVNP products was approximately 1700, while the yield in both cases was 87 wt % and the PDI was 1.19 (Table III, entries 15 and 16). These results indicate that both the initiator efficiency and the propagation rate are somewhat improved in toluene (Table I, entry 4). When THN was employed as the solvent, essentially quantitative yields of PVNP (97 and 100 wt %) were obtained, along with low PDI values (1.17 and 1.15) (Table III, entries 17 and 18). It is particularly of interest that the M_n of the PVNP obtained by the anionic polymerization of 2-VNP with the n-BuLi/ THF system in THN (Table III, entry 18) was very close to the theoretical value calculated from the molar ratio of n-BuLi and 2-VNP ($154 \times 13 + 57 + 1 = 2060$).

Figure 2 shows the GPC traces obtained for polymer no. 7 in Table I (Figure 2a) and polymer no. 18 in Table III (Figure 2b). These chromatograms demonstrate that the polymer obtained from the anionic polymerization of 2-VNP with n-BuLi alone in THN has a value of M_n greater than the theoretical value and exhibits a rather broad GPC peak, indicating low initiator efficiency and a slow initiation reaction rate (Figure 2a). In contrast, the polymer obtained using the n-BuLi/THF (1.00/1.25) system in THN shows a sharp unimodal peak which may be attributed to high initiator efficiency and a high rate of initiation reaction (Figure 2b). These data show that the coordination of THF to n-BuLi considerably enhances the nucleophilicity of the n-BuLi, leading to improved initiation efficiency and an increased initiation rate without side reactions. In addition, the nucleophilicity of (P)VNPLi is enhanced by its coordination with THF and this appears to accelerate the propagation reaction rate while again avoiding side reactions. The n-BuLi/THF system in THN therefore represents an attractive means of obtained the well-controlled anionic polymerization of 2-VNP at room temperature.
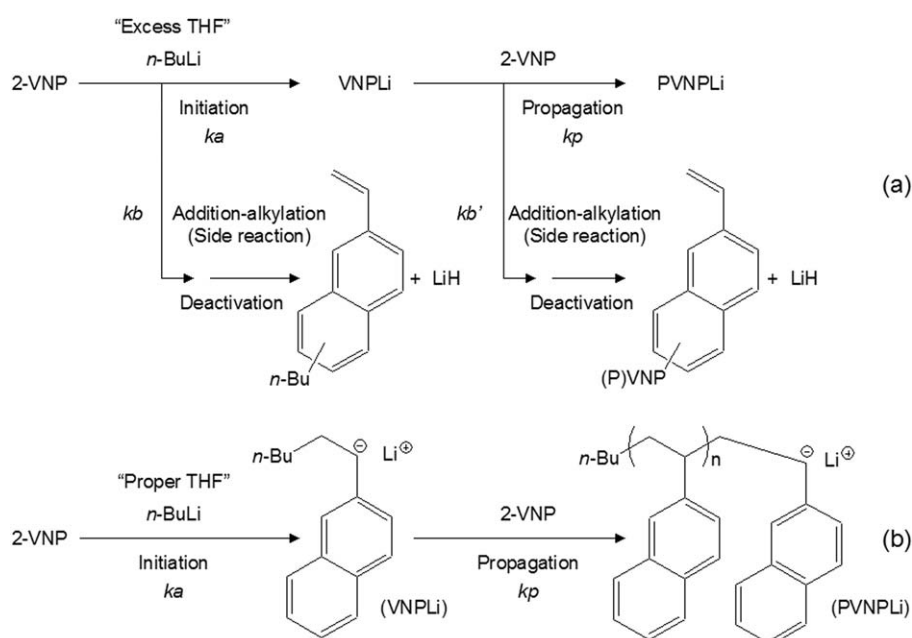
Scheme 2. Uncontrolled (a) and well-controlled anionic polymerization of 2-vinylnaphthalene with an n-butyllithium/tetrahydrofuran system in 1,2,3,4-tetrahydronaphthalene.
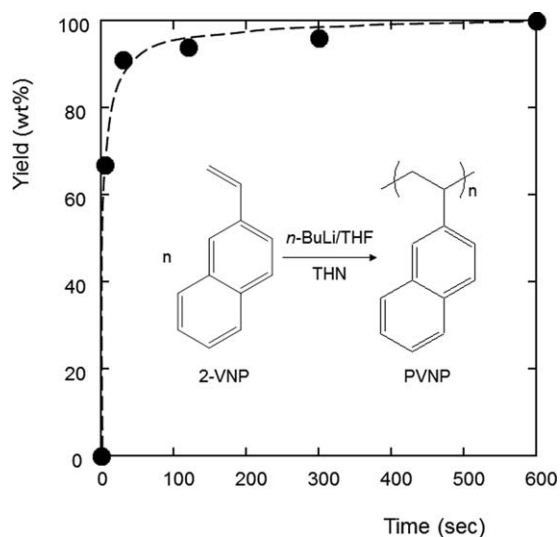
Figure 3. Time–conversion relationship during the anionic polymerization of 2-vinylnaphthalene with an *n*-butyllithium/tetrahydrofuran (1.00/1.25) system in 1,2,3,4-tetrahydronaphthalene. Polymerization was performed under dry argon at room temperature (*ca.* 25°C). (2-vinylnaphthalene)$_0$/(*n*-butyllithium)$_0$ = 26.0. 2-vinylnaphthalene/1,2,3,4-tetrahydronaphthalene = 1.00 g/10.0 mL.
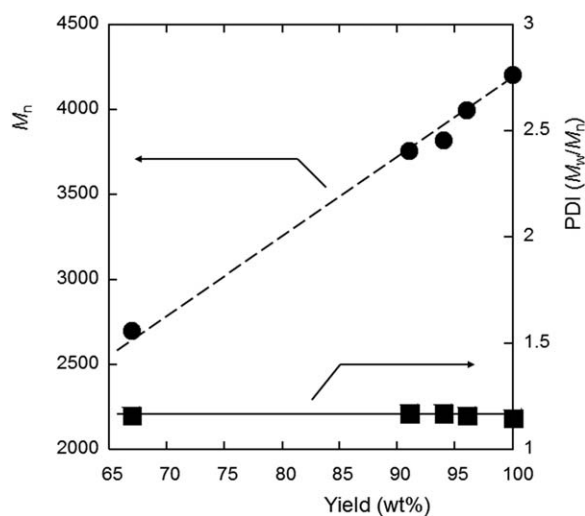

Figure 4. M_n and PDI as functions of conversion during the polymerization of 2-vinylnaphthalene with an *n*-butyllithium/tetrahydrofuran (1.00/1.25) system in 1,2,3,4-tetrahydronaphthalene at room temperature. (2-vinylnaphthalene)$_0$/(*n*-butyllithium)$_0$ = 26.0. M_n and PDI were obtained by GPC calibrated using polystyrene standards.

Optimization of the Li/THF Ratio for Well-Controlled Polymerization

From the results in Tables I and III, the coordination of THF to *n*-BuLi and (P)VNPLi is evidently a very important factor in the well-controlled anionic polymerization of 2-VNP in THN. We therefore expected that the Li/THF molar ratio would also strongly affect the polymerization reaction. To examine the effect of the Li/THF ratio on the polymerization reaction, 2-VNP was polymerized in THN with the *n*-BuLi/THF system as the initiator, applying various Li/THF ratios. The results obtained are summarized in Table IV.

As described previously, in the case of the anionic polymerization of 2-VNP with *n*-BuLi alone, the M_n of the PVNP obtained was considerably larger than the theoretical value and the PDI value of the polymer was elevated (Table IV, entry 7). When an optimal amount of THF is used, based on the quantity of *n*-BuLi (and PVNPLi), (Scheme 2a, Li/THF = 1.00 : 1.25), PVNP with a low PDI (1.15) is obtained in 100 wt % yield (Table IV, entry 18). Conversely, an excess of THF leads to excess nucleophilicity and results in an uncontrolled polymerization reaction; at Li/THF values of 1.00 : 4.00 and 1.00 : 8.00 (Table IV, entries 19 and 20), the yields of PVNP were reduced to 86 and 27 wt %, while the PDI values were increased to 1.31 and 1.88.

Eppley *et al.* reported that the addition–alkylation reaction of naphthalene is promoted by *t*-BuLi in hydrocarbon solvents.[22] The results in Table IV (entries 19 and 20) lead us to believe that a similar addition–alkylation reaction can occur as a side reaction during the 2-VNP polymerization when an excess of THF is used and that these side reactions inhibit initiation and propagation (Scheme 2a).

Consequently, we conclude that an amount of THF equimolar to or slightly greater than the quantity of *n*-BuLi (and (P)VNPLi) in THN generates an appropriate level of nucleophilicity during the 2-VNP polymerization and that the resulting complexes are excellent initiating and propagating species for the well-controlled polymerization of 2-VNP (Scheme 2b).

Characteristics of the Anionic Polymerization of 2-VNP with the *n*-BuLi/THF (1.00/1.25) System in THN

The results in Tables I–IV indicate that only the *n*-BuLi/THF (1.00/1.25) system in THN is capable of producing the well-controlled (i.e., living) anionic polymerization of 2-VNP at room temperature. In order to further characterize this polymerization reaction, detailed studies were carried out, using a (2-VNP)$_0$/(*n*-BuLi)$_0$ ratio of 26.0 : 1.00.

Table V. Synthesis of Various PVNP by Rapid Anionic Polymerization[a]

Polymer no	Initiator system (Li:additive)[b]	Solvent	(2-VNP)$_0$ /(Li)$_0$	Reaction time (h)	Yield (wt %)	M_n (g.mol^{-1})	PDI
21	*n*-BuLi/THF (1.00 : 1.25)	THN	26.0 : 1.00	0.5	100	4660	1.15
22	*n*-BuLi/THF (1.00 : 1.25)	THN	52.0 : 1.00	0.5	100	8340	1.16
23	*n*-BuLi/THF (1.00 : 1.25)	THN	78.0 : 1.00	0.5	98	12860	1.13
24	*n*-BuLi/THF (1.00 : 1.25)	THN	104.0 : 1.00	0.5	94	16650	1.12

[a] Polymerization was carried out in THN (10.0 mL) under dry argon at room temperature.
[b] mol./mol.

During the polymerization of 2-VNP with the *n*-BuLi/THF (1.00/1.25) system in THN, the reaction solution was observed to undergo two color transitions. In the first transition, the THN solution of *n*-BuLi in the Schlenk tube took on a deep yellow coloration when THF was added, indicating the formation of an *n*-BuLi/THF complex. Subsequently, the color of the THN solution changed from deep yellow to dark red when 2-VNP was added, demonstrating the formation of the (P)VNPLi/THF complex. Surprisingly, the polymerization rate associated with this reaction system was extremely fast. As shown in Figure 3, 2-VNP to PVNP yields of 67, 91, 94, 96, and 100 wt % were evident after 10, 30, 120, 300, and 600 sec of reaction time. The M_n of the resulting polymer also increased linearly with yield while retaining a narrow PDI range (Figure 4). This reaction therefore appears to progress at a high rate, and thus, we have termed it a rapid anionic polymerization.

Subsequently, various PVNPs were synthesized using this rapid anionic polymerization process. As shown in Table V, the M_n values of the resulting polymers increase with increases in the $(2\text{-VNP})_0/(\text{Li})_0$ ratios, again exhibiting well-controlled anionic polymerization. In all cases, the polymer is obtained in almost quantitative yield (96–100 wt %) and with a narrow PDI range (1.12–1.16). In addition, all polymerization reactions were complete within 0.5 h.

Hence, we believe that we have demonstrated the first successful example of the living, anionic polymerization of 2-VNP at room temperature.

CONCLUSIONS

The anionic polymerization of 2-VNP with various RLi species in different hydrocarbon solvents at room temperature was examined in detail. The polymerization reaction was greatly affected by both the solvent type and the RLi. In initial trials, the use of toluene with *n*-(or *s*-)BuLi gave the highest initiation rate, while the use of THN produced the highest propagation rate. The combination of *n*-BuLi and THN generated 100% yields with no apparent side reactions during the polymerization. The nucleophilicity and solubility of the RLi, VNPLi, and PVNPLi were determined to be very important factors during anionic 2-VNP polymerization at room temperature, and this polymerization was remarkably improved by the optimization of solvents and polar additives. An *n*-BuLi/THF complex in THN was found to represent an excellent initiator system for the anionic polymerization of 2-VNP at room temperature, since the VNPLi/THF and PVNPLi/THF complexes, as propagating species, had sufficient nucleophilicity and lacked the ability to promote side reactions. As a result, the anionic polymerization of 2-VNP with the *n*-BuLi/THF (1.00/1.25)

system in THN allowed what we refer to as rapid anionic polymerization. Various PVNP products with well-controlled and defined polymeric chain structure were synthesized using this process. To the best of our knowledge, this is the first-ever report of the successful living anionic polymerization of 2-VNP at room temperature.

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