Living Anionic Polymerization of 2-Vinylnaphthalene in THF in the Presence of Lithium Ion. Role of Monomer Purification

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Introduction. The complete absence of reactive electrophilic impurities is of critical importance in anionic vinyl polymerizations.[1] Deactivation by protonation or alkylation of polymer chain-end anions by impurities in the solvent or monomer, presence of labile functional groups in the monomer,[2,3] spontaneous hydride elimination,[4] or intramolecular reactions with penultimate pendent groups[5] are well documented. The use of suitable conditions and proper purification methods can eliminate many of these problems and allow living polymerizations in which the active chain ends survive long enough for polymerization, chain-end functionalization, and formation of block copolymers.[6−8] While the partial destruction of initiator by impurities prior to polymerization would not complicate the control of anionic polymerizations,[9] the deactivation of propagating anion by small amounts of impurities, not readily scavenged by conventional purification methods, does tend to interfere with polymerization control.

In our initial investigations[10] on the anionic polymerization of 2-vinylnaphthalene (2VN), we noticed a surprising tendency of this monomer to give broader molecular weight (MW) distributions and other complications that were not observed for the corresponding polymerizations of styrene,[8,11] styrene derivatives and similar vinyl aromatic monomers under otherwise identical conditions.[12,13] For instance, P2VN prepared by initiation with *t*-BuLi in THF at −78 °C had broader molecular weight distributions than expected for conventional living polymerizations. End-functionalization, for instance with chlorotrimethylsilane ((TMS)Cl), was not quantitative, especially at low anion concentrations.[10] Furthermore, there are no reports of systematic 2VN polymerization studies aimed at investigating its potential for living anionic polymerization. In most studies, the degree of control of molecular weight (MW) or MW distributions were not reported.[14−17]

Although we have found that the anionic polymerization of 2VN may give reasonably narrow MW distributions with some degree of MW control, our studies did not indicate that the polymerization of this monomer was living.[10] However, careful studies showed that an unconventional monomer purification plays a crucial role in achieving living 2VN polymerization. This paper demonstrates that the living polymerization of 2VN is not possible unless minute amounts of 2-acetylnaphthalene (2AN) in the 2VN are removed.

Experimental Section. Materials. THF was purified by distillation from Na/K−benzophenone followed by distillation from 1,4-dipotassio-1,1,4,4-tetraphenylbutane (DD-K_2). *tert*-Butyllithium (Aldrich, 1.7 M solution in pentane) after evaporation of pentane was sublimed in a vacuum at 60 °C, dissolved in hexane to needed concentrations, and stored in a freezer in ampules. 1,1,4,4,7,7,10,10-Octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene[18] (OMOHN) was recrystallized from methanol, dried in a vacuum, and dissolved in purified THF. Lithium OMOHN was prepared by stirring OMOHN in THF with lithium chunks for 15−20 min at 0 °C and used immediately. Chlorotrimethylsilane ((TMS)Cl, 1.0 M solution in THF, Aldrich) was twice distilled from CaH_2, distributed into and stored in ampules.

Method A. 2-Vinylnaphthalene (2VN, Aldrich, Alfa Aesar, 95%) was dissolved in THF and stirred under vacuum over CaH_2 overnight. Then THF was distilled off and 2VN was vacuum sublimed from CaH_2. This procedure was repeated once (experiments 1−6, Table 1).

Method B. 2VN (5 g) was dissolved in toluene (10 mL) and stirred under high vacuum over solid $LiAlH_4$ for 5 h at room temperature. Toluene was then distilled into a side flask, and the remaining 2VN was sublimed at 60 °C into this flask. This solution was now stirred over CaH_2, and after stirring (for about 5 h), toluene was distilled into the trap. To remove residual $LiAlH_4$, the monomer was sublimed from this CaH_2 into a collection flask. Purified THF (40 mL) was added into this flask from an ampule. The resulting monomer solution was distributed into ampules equipped with break seals.

Polymerizations. Polymerizations were run in high vacuum in THF at −78 °C in flamed glassware using Teflon valves and break-seal techniques as reported elsewhere.[19] A *t* -BuLi solution in hexane (2×10^{-6} mol, 5 mL, experiment 2, Table 2) was poured into the polymerization flask, and 4−4.5 mL of hexane was evaporated into the trap. THF (15 mL) was then distilled into the polymerization flask kept at −78 °C. The chilled 2VN solution in THF (0.3 g in 5 mL, 1.9×10^{-3} mol) was rapidly added to this *t*-BuLi solution and stirred at −78 °C. After the mixture was stirred for 10 min, the polymerization was terminated with degassed methanol (0.3 mL). The polymers were recovered in quantitative yields by precipitation upon addition of methanol (150 mL) and dried in a vacuum at 40 °C for 2 days.

Characterization. Size exclusion chromatography (SEC) was carried out at room temperature with THF as the carrier solvent at a flow rate of 1 mL/min using Waters model 510 pump, a model 410 differential refractometer and two "Ultrastyragel" 500 and 10^4 Å columns calibrated with polystyrene standards (Polysciences). All polymers were analyzed by SEC *prior* to precipitation. Proton and carbon-13 NMR data were acquired on a Bruker AM-250 FT instrument operating at 250 and 62.9 MHz, respectively, in $CDCl_3$. The spectra were acquired in sealed tubes in order to avoid water contamination.

Results and Discussion. Poly(2-vinylnaphthalene) (P2VN) has received attention, especially in modeling energy transfer in complex systems.[20,21] There are reports describing radical, cationic and anionic polymerization techniques to prepare P2VN and P2VN block copolymers.[16,22,23] While most of these reports involved

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Table 1. Effect of the Monomer Impurity Concentrations on P2VN–Li End-Functionalization[a]

			P2VN–TMSCl					
no.	[*t*-BuLi], mM	[2VN], mM	$M_n^{calcd} \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	TMS,[b] %	[impurity,] mM	mol % impurities in monomer
1	10.8	35.0	0.50	0.68	1.39	95	0.54	1.5
2	10.8	56.0	0.80	0.91	1.25	90	1.08	1.9
3	7.9	85.7	1.67	1.40	1.16	86	1.11	1.3
4	3.8	85.7	3.47	3.48	1.18	60	1.52	1.8
5	1.4	92.3	10.2	5.66	2.00	20	1.12	1.2
				10.7[c]	1.16			
6	0.5	100	31.0					

[a] 2VN was sublimed from CaH_2 2 times. Sublimed *t*-BuLi was used as initiator. Conditions: one time addition of 2VN/THF and stirring for 30–60 min at −78 °C. SEC characterization: RI detector and PS standards. [b] TMS group incorporation, as determined by integration of *t*-Bu and TMS peaks in ^1H NMR for precipitated and dried polymers. [c] SEC trace of the unfractionated polymer without low MW tailing.

Table 2. Resumption Polymerizations in THF at −78 °C with Purified 2VN[a]

		P2VN–MeOH				P2VN-*b*-P2VN-MeOH			
no.	[I],[b] mM	[M], mM	t_1, min	$M_n \times 10^{-3}$	PDI	[M], mM	t_2, min	$M_n \times 10^{-3}$	PDI
1	1.0	30	5	3.40	1.10				
2	0.1	95	10	110	1.03				
3	1.6	35	10	4.80	1.30	70	10	31.5	1.11
4	1.0	40	60	9.50	1.30	70	10	31.7	1.10

[a] Polymerizations of the first 2VN portion in THF at −78 °C carried out for t_1 minutes, after which a portion was protonated; to the remaining polymer anion a second aliquot was added rapidly dropwise and stirred for additional time t_2. Conversion of 2VN is quantitative. [b] Initiator used: *t*-BuLi used as received (experiment 1), sublimed *t*-BuLi (experiment 2), and Li–OMOHN (experiments 3 and 4).

the synthesis of P2VN by radical polymerizations, there is a smaller number of papers dealing with anionic polymerization of this interesting monomer. The reasons for this include difficulties controlling the polymerization of this monomer, tedious purifications that include typically one or more sublimations and the occurrence of an inadvertent thermal polymerization at ambient temperatures.

The monomer from commercial sources is a brownish solid[17] which contains protic impurities such as methanol that vigorously react with CaH_2. The monomer we purchased also contained 20–25% of polymer as indicated by SEC.[24] Purification of 2VN for anionic polymerizations has most commonly involved recrystallization from methanol and/or repeated vacuum distillation or sublimation.[14–17,25] There is, however, a report by Takano et al. in which 2VN was purified by a more rigorous but experimentally complicated procedure.[26] In this case, some deactivation of poly(4-vinylphenyl)-dimethylvinylsilane anion was reported to have occurred in the formation of poly(4-vinylphenyl)dimethylvinylsilane-*b*-P2VN block copolymers upon addition of 2VN, and this was attributed to the presence of impurities in 2VN.

We started our studies with 2VN purified by 2 consecutive vacuum sublimations from CaH_2. Polymerizations in THF were initiated using sublimed *t*-BuLi. In this case, we were able to prepare only low MW polymers (M_n < 4000) with acceptable but not very narrow MW distributions (Table 1).

However, in all our attempts to prepare high MW polymers, we observed broad MW distributions (MWD's) with pronounced tailing on the SEC curves (Figure 1a).

To elucidate the origins of MWD broadening, we terminated these *t*-BuLi initiated polymerizations with chlorotrimethylsilane ((TMS)Cl). The TMS group allows convenient observation of its signal in the ^1H NMR spectra, which, along with the well-resolved *t*-Bu initiator signal, should allow calculation of the degree of end-functionalization, and thus, the degree of polymer chain-end deactivation. Table 1 shows that the degree of TMS end-functionalization strongly depends on the monomer-to-initiator molar ratios. Thus, TMS end-functionalization decreases considerably (to 20%) with decreasing initiator concentration at constant 2VN concentration (Table 1, experiments 3–5). This suggests that the monomer contains significant fractions of impurities that are not removed by vacuum distillation or sublimation from CaH_2. From the degree of TMS incorporation, the monomer contains about 1.5% molar impurities. At very high monomer-to-initiator ratios (Table 1, experiment 6) no polymer was formed.

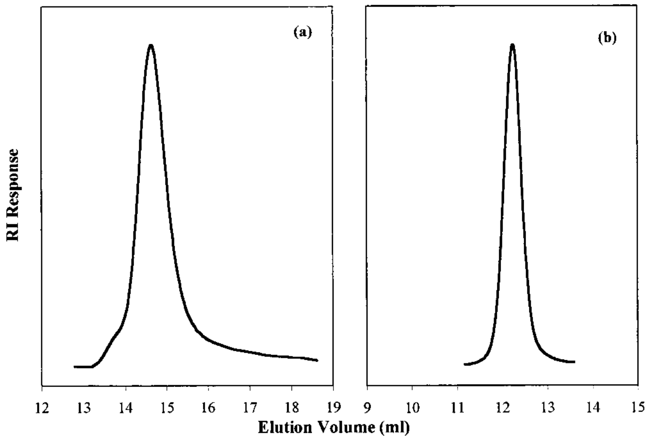

Figure 1. SEC curves of poly(2-vinylnaphthalene) prepared using sublimed *t*-BuLi and monomer purified (a) by two sublimations from CaH_2 (Table 1, experiment 5) and (b) by sublimation from $LiAlH_4$ followed by sublimation from CaH_2 (Table 2, experiment 2).

Proton NMR of conventionally purified 2VN (sublimed twice from CaH_2) clearly shows a small peak at 2.67 ppm that does not correspond to the reported NMR spectrum of 2VN.[27] This resonance remains even after three consecutive 2VN sublimations in a vacuum from CaH_2. We attribute this peak to 2-acetylnaphthalene (2AN), which is an intermediate in the commercial 2VN synthesis.[28] This compound is present in commercial 2VN due to incomplete hydrogenation and is not completely removed upon 2VN sublimation or distillation. This impurity should be highly reactive toward nucleophilic species, deactivating P2VN anions either by proton transfer (pK_a is about 23)[29] or by nucleophilic attack of the P2VN anion on the carbonyl group. Integration of this peak (2.67 ppm) relative to the 2VN

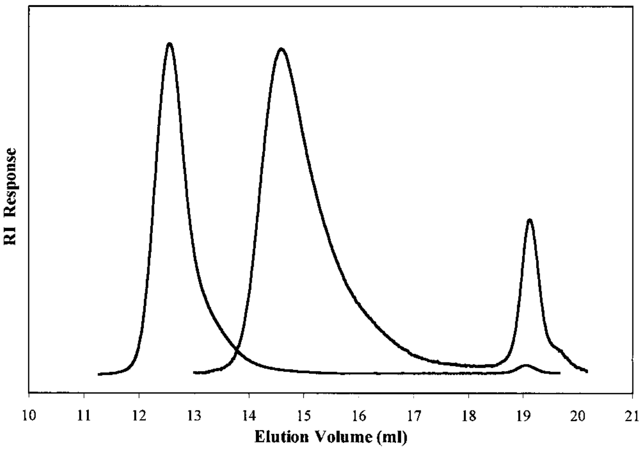

Figure 2. SEC curves of poly(2-vinylnaphthalene) from experiment 3 (Table 2): (a) P2VN precursor and (b) P2VN after addition of the second 2VN portion after 1 h of storage at −78 °C (peak at 19 mL corresponds to OMOHN).

resonances indicates the presence of approximately 1 mol % of the impurity, consistent with the results of our end-functionalization studies (Table 1). The carbon-13 NMR spectrum of the same 2VN sample corroborates the presence of 2AN by the clearly seen resonances at 192.4 and 25.4 ppm, which are attributed to carbonyl and methyl carbons, respectively.

The use of reagents that are effective for the purification of styrene, such as dibutylmagnesium, 9-potassio-9-methylfluorenyl or $LiAlH_4$ in polar solvents, such as THF, is not possible, as this leads to quantitative 2VN polymerization at room temperature or upon sublimation at elevated temperatures. However, we found that treatment of 2VN with $LiAlH_4$ in toluene effectively and completely removes the traces of 2AN. Thus, when commercial 2VN (4−5 g) was dissolved in 5−10 mL of toluene, stirred for 5 h at room temperature over the insoluble $LiAlH_4$ and then filtered or sublimed in a vacuum at 60 °C, the ^1H NMR spectrum shows no traces of 2-acetylnaphthalene. A final sublimation (from CaH_2) ensures removal of residual $LiAlH_4$, which can initiate 2VN polymerization upon dissolution in THF. Thus, an inadvertent initiation of 2VN with $LiAlH_4$ upon substitution of toluene with THF was observed giving very high MW P2VN ($M_n = 850\,000$) with a relatively narrow MW distribution (PDI = 1.12) and confirming the high purity of the monomer.

Polymerizations carried out with 2VN purified in this way are now both living and well-controlled.[9] Thus, initiation of 2VN with *t*-BuLi in THF at −78 °C is instantaneous, and monomer conversions are quantitative in all cases where the polymerization times are longer than several seconds.[14] High MW P2VN (M_n about 100 000) forms with very narrow MW distributions (as low as 1.03) (Figure 1b, Table 2). Also, the calculated and SEC molecular weights are similar.

The absence of terminating impurities in 2VN is also indicated by polymerization resumption experiments. Thus, upon introducing additional 2VN to P2VN dianion initiated with Li−OMOHN and stirred for 1 h at −78 °C, the MWD narrowed from 1.30 to about 1.10 (Table 2, experiments 3 and 4). The first block had rather broad polydispersity ($D = 1.30$), attributed tentatively to slow initiation and fast propagation[8] in these electron-transfer-initiated polymerizations. However, the MWD after further addition of 2VN showed the expected statistical narrowing.[30] SEC analysis reveals the absence of the P2VN precursor (Figure 2), confirming that the polymerization did not terminate spontaneously and that 2VN contained no terminating impurities. These results indicate that the 2VN polymerizations are living.

The polymerization resumption experiments also indicate that the shelf life of the P2VN anion in THF at −78 °C (more than 1 h) is long enough to conveniently perform post-polymerization reactions. Thus, formation of block copolymers and synthesis of other architecturally interesting structures of P2VN, such as stars and rings, should be possible. These studies are in progress.

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