Chapter 3

Living Anionic Polymerization of 2-Vinylnaphthalene in Tetrahydrofuran

3.1 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] is 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.

Although the well-controlled anionic polymerization of 2-isopropenylnaphthalene (2IPN) has been reported,[10] this has not been the case for the corresponding polymerization of 2-vinylnaphthalene (2VN). Our preliminary studies indicated that the anionic polymerization in THF of 2VN purified by up to three sublimations from CaH_2 under high vacuum is neither living, nor well controlled and

gives rise to low MW P2VN (M_n<5000) with broadened molecular weight distributions.[11] 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.[12-15] A more careful investigation carried out in our laboratory showed that the 2VN contains traces of 2-acetylnaphthalene and that treating the monomer with $LiAlH_4$ in toluene quantitatively removes this impurity. Thus, t-BuLi and lithium naphthalide initiated polymerizations of the purified 2VN gave good agreement of calculated and experimental MW's, and polymerization resumption experiments showed quantitative initiation of additional 2VN without any precursor SEC traces.

However the lithium naphthalide initiated polymerization of purified 2VN in THF at –78 °C, although conforming to living polymerizations, still gave rather wide MW distributions compared to other polymerizations of this type. In contrast to this, potassium naphthalide initiated polymerizations of this carefully purified 2VN in THF at –78 °C are consistent with being both living and well controlled. Thus, under these conditions, it is possible to prepare P2VN of very high molecular weight (as high as 90,000) or narrow polydispersities (PDI as low as 1.06). Also, the demonstrated block-copolymerization with other vinyl monomers and resumption of homopolymerization experiments show excellent persistence of the chain ends under the above conditions.

3.2 Experimental

Polymerizations were run in high vacuum in THF at –78 ºC in flamed glassware using Teflon valves and break-seal techniques as reported elsewhere.[16] A *t*-BuLi solution in hexane (2×10^{-6} moles, 5 mL, exp. # 97, Table 3.2) 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} moles) was rapidly added to this *t*-BuLi solution and stirred at –78 °C. After stirring for 10 min, the polymerization was terminated with degassed methanol (0.3 mL).

The dilithium or dipotassium salts of poly(2-vinylnaphthalene) (P2VN-$Li_2(K_2)$) were prepared via electron-transfer from the lithium or potassium salts of naphthalene or OMOHN to 2VN or by 2VN initiation with AMS-K_2 in THF/toluene mixtures (98/2 v/v) at –78 °C. After stirring for 10-30 min, 15 mL of this P2VN-K_2 solution was transferred into another flask and a THF solution of 1,4-bis(bromomethyl)benzene (DBX) (7mL, 1.4×10^{-2} M, 1×10^{-4} moles) was added into it drop-wise until the solution decolorized. The remaining 7 mL of the P2VN-$Li_2(K_2)$ solution was terminated with degassed methanol. The polymers were recovered in quantitative yields by precipitation upon addition of methanol (150 mL) and dried in vacuum at 50 °C for 2 days.

3.3 Polymerizations in the Presence of Lithium Ion. Role of Monomer Purification.

The monomer from commercial sources is a brownish solid[15] which contains protic impurities such as methanol that vigorously react with CaH_2. The monomer we purchased also contained 20-25 percent of polymer as indicated by SEC. Purification of 2VN for anionic polymerizations has most commonly involved recrystallization from methanol and/or repeated vacuum distillation or sublimation.[12-15,17] There is, however, a report by Takano *et. al.* in which 2VN was purified by a more rigorous but experimentally complicated procedure.[18] 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 3.1). 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 3.1 a).

In order to elucidate the origins of MWD broadening, we terminated these *t*-BuLi initiated polymerizations with chlorotrimethylsilane (TMSCl). 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 3.1 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 3.1, exp. # 8-10). 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 percent molar impurities. At very high monomer to initiator ratios (Table 3.1, exp. # 98) no polymer was formed.

Proton NMR of conventionally purified 2VN (sublimed twice from CaH_2) (Figure 3.2 a) clearly shows a small peak at 2.67 ppm that does not correspond to the reported NMR spectrum of 2VN.[19] This resonance remains even after 3 consecutive 2VN sublimations in vacuum from CaH_2. We attribute this peak to 2-acetylnaphthalene (2AN), which is an intermediate in the commercial 2VN synthesis.[20] 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 towards nucleophilic species, deactivating P2VN anions either by proton transfer (pK_a is about 23)[21] or by nucleophilic attack of the P2VN anion on the carbonyl group. Integration of this peak (2.67 ppm) relative to the 2VN resonances indicates the presence of approximately one mole percent of the impurity, consistent with the results of our end-functionalization studies (Table 3.1). The carbon-13 NMR spectrum of the same 2VN sample corroborates the presence of 2AN by the clearly seen resonances at 192.4 (Figure 3.3

b) and 25.4 ppm (Figure 3.3 c), which are attributed to carbonyl and methyl carbons, respectively. The peaks seen at 26.2 and 68.0 ppm come from tetrahydrofuran[22] which remains in trace quantities after solvent evaporation.

The use of reagents that are effective for the purification of styrene, such as dibutylmagnesium, 9-potassio-9-methylfluorene 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 vacuum at 60 °C, the ^{1}H NMR spectrum shows no traces of 2-acetylnaphthalene (Figure 3.2 b). 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.[12] High MW P2VN (M_n about

100,000) forms with very narrow MW distributions (as low as 1.03) (Figure 3.1 b, Table 3.2). 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 hr at –78 °C, the MWD narrowed from 1.30 to about 1.10 (Table 3.2, exp. # 88, 89). 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.[23] SEC analysis reveals the absence of the P2VN precursor (Figure 3.4), 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 hr) 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.

3.4 Potassium Ion Mediated Living Anionic Polymerization of 2-Vinylnaphthalene

The lithium naphthalide initiated anionic polymerizations of 2VN in THF at –78 °C are not well-controlled giving wider polydispersities (Table 3.3). The 2VN

polymerization initiated with potassium naphthalide is better controlled, showing features characteristic of both controlled and living polymerizations. Thus, in the presence of potassium naphthalide, initiation/polymerization occurs rapidly and gives rise to P2VN with narrower polydispersities (D = 1.12-1.15) compared to the Li-Naph initiated polymerizations (Table 3.3). There are also visual differences between the Li and K ion mediated radical anion 2VN initiations. Thus, upon addition of 2VN to a Li-Naph in THF/toluene (98/2 v/v) at –78 °C, the color first changes to a dark brown over a period of 1-2 minutes and then to dark green that differs slightly from that of Li-Naph. The corresponding changes for the case of K-Naph are complete in 15-20 sec. These color changes would appear to indicate the presence of transient intermediates, either monomer radical anion or other anionic intermediates. Although the lifetime of 2VN radical anions is not expected to be long considering the rapid dimerization of the related styrene radical anions into the 1,1,4,4-substituted dianions under these conditions,[9,24] it may be sufficient for the observation of the 2VN radical anions.

The use of the potassium radical anion of 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene[25] (K-OMOHN) generally gives P2VN with even narrower polydispersities compared to P2VN initiated with K-Naph (Table 3.3).

The MW distributions of the polymerizations initiated with simple anionic initiators are consistently narrower than seen with the radical anions. Thus, the use of AMS-K_2 or t-BuLi as initiators gives polymers with narrower polydispersities than

with the radical anion initiators (Table 3.3, # 4, 30, 31). These differences may indicate that one or more steps in the radical anion mediated initiation process are slow on the polymerization time scale.[9] This would be consistent with the OMOHN radical anion initiated polymerizations giving narrower MW distributions compared to those initiated with naphthalide radical anions. OMOHN, having a lower electron affinity on account of the four electron donating alkyl groups, is expected to be a better electron donor toward 2VN. Thus, the electron-transfer to 2VN from K-OMOHN is expected to occur faster than with K-Naph.

The formation of narrower MWD P2VN with the carbanion initiators (t-BuLi and AMS-K_2) is consistent with the electron transfer to monomer being the rate limiting initiation step rather than the well known radical anion dimerization[24] or the subsequent addition of monomer to the 1,4-bis(2'-naphthyl)butane dianion. The narrower MWD's for P2VN polymers obtained with K-Naph compared to Li-Naph indicate that rate of electron transfer compared to the subsequent initiation/polymerization steps is faster in the presence of the K ion. This is further corroborated with the runs where Cs-Naph was used as an initiator (Table 3.3, # 106, 107). Similar to polystyryl anion in THF, the propagation in the presence of cesium is expected to be slower than with lithium or potassium.[26] This will lead to relatively faster initiation compared to the subsequent propagation and, thus, narrower distributions.

The complex nature of the initiation process and the absence of detailed kinetic studies make it difficult to resolve this issue conclusively. Side reactions, for instance the nucleophilic attack of the oligomeric P2VN chain end anions on the

penultimate 2-naphthyl groups, are possible. In such a case, the anions formed would be capable of further monomer initiation and this would obviously complicate the analysis. Such intermediate "complexes" have been suggested for the Na ion mediated polymerization of 2VN in THF at ambient temperatures.[12] More recently, intramolecular addition of chain end anions to pendent naphthalene groups have been postulated for the alkyllithium initiated polymerization of 2-isopropenylnaphthalene in THF at elevated temperatures.[5] However, given the above narrow MW distributions of P2VN observed for the t-BuLi and AMS-K_2 initiated polymerizations, the occurrence of complexes or intramolecular side reactions does not seem likely at the low temperatures employed here (see below).

Further indication for better control of the 2VN polymerization in the presence of K ion comes from restart polymerization experiments. As seen from Table 3.4, upon addition of a second portion of 2-vinylnaphthalene to the P2VN-K_2 stored for periods up to one hour at –78 °C, the polymerization proceeds to give narrow distribution higher molecular weight P2VN with complete absence of the P2VN precursor (Figure 3.5).

Although, the storage of longer than one hour was not tested, it would appear that the persistence of P2VN-K_2 anion is sufficient to allow convenient end-functionalization and block copolymerizations.

3.4.1 Formation of Block Copolymers

Addition of a recently reported new vinyl monomer, 9,9-dimethyl-2-vinylfluorene (DMVF),[27] quantitatively gives narrow distribution higher MW

PDMVF-*b*-P2VN-*b*-PDMVF block-copolymers (Table 3.4) with the expected statistical narrowing of polydispersity.[23] As judged by the rapid color change from dark green to the dark red characteristic of the poly(9,9-dimethyl-2-vinylfluorenyl) anion, the initiation by the P2VN dianion of DMVF is fast and quantitative. SEC analysis of the block copolymers shows a narrowing of the MW distribution upon polymerization of the second block and no indication of any residual P2VN anion precursor (Figure 3.6). These observations confirm significant stability of the P2VN anion in the presence of potassium ion under the above conditions.

The proton NMR of the PDMVF-*b*-P2VN-*b*-PDMVF copolymer shows clearly the presence of the 9,9-dimethylfluorenyl protons of the PDMVF block (Figure 3.7, b). Due to the high PDMVF content, the block copolymer NMR closely resembles the reported PDMVF spectrum.[27]

The initiation of 2VN by the highly basic poly(α-methylstyryl) dianion (PAMS-K_2) is fast as observed by the rapid color change. This is not surprising given the high basicity and nucleophilicity of the PAMS anion.[21] The formation of P2VN-*b*-PAMS-*b*-P2VN block copolymers with slightly narrower distribution is consistent with the living and controlled character of the 2VN polymerizations reported above (Table 3.4, # 95, Figure 3.8 a).

However, upon addition of AMS to a P2VN-K_2 solution at –78 °C, over about 15 min a *gradual* color change was observed from dark green to dark red, indicating a relatively slow crossover initiation to the PAMS anion. This is not surprising given the higher basicity of the PAMS anion compared to that of P2VN

and the generally lower reactivity of AMS associated with the greater steric hindrance in reactions of this monomer.[1]

The formation of the PAMS-*b*-P2VN-*b*-PAMS block copolymer, surprisingly, proceeded in a controlled manner as indicated by the relatively narrow MW distribution of this block copolymer (Table 3.4). Thus, at least in this case, there is no indication of deactivation by "backbiting" of the highly basic PAMS anion onto the pendent 2VN groups of the P2VN block. An "intramolecular complex" was proposed for the addition of styrene[12] or α-methylstyrene[28] to poly(1-vinylnaphthalene) and poly(2-vinylnaphthalene) anions or addition of the P2IPN anion to a penultimate pendent naphthalene in the presence of Na ion at ambient temperatures in THF.[5] The formation of a "complex" (i.e. formation of a molecular entity not involving covalent bonds) for instance through the physical interaction between chain end ion pair and penultimate naphthyl groups does not seem likely in our case. Thus, the relatively narrow molecular weight distribution of the PAMS-*b*-P2VN-*b*-PAMS copolymer is probably due to the fact that the AMS homopolymerization is very slow. Thus, at an AMS anion concentration of approximately 3×10^{-3} M only eight percent of the AMS is converted after more than one hour (Table 3.4, # 94) from which an AMS homopolymerization rate constant on the order of about 7×10^{-3} L/(mole sec) is estimated. This value is comparable to a previously reported value of 12×10^{-3} L/(mole sec) at a slightly higher temperature (–59 °C).[29] A slow AMS initiation/propagation is consistent with the observed shift towards a symmetrical narrow distribution higher MW SEC curve without a clear

indication of residual P2VN precursor (Figure 3.8 b). In this case, no statistical narrowing of the MW distribution is observed most likely due to the relatively small increase in the degree of polymerization. Proton NMR shows the expected resonances due to the respective blocks (Figure 3.7 c). Thus, the resonances of alpha methyl group of PAMS block at 0.0-1.3 ppm are visible with a prominent resonance at about 0.4 ppm due to the heterotactic triad that is quite typical for PAMS formed in the presence of potassium ion.[30,31]

3.4.2 End-functionalization Reactions

Although not strictly required for living polymerizations, the ease and degree of end-functionalization is of interest as an additional useful criterion for the "degree of livingness" of polymerizations, as it reflects the shelf-life of the P2VN anions under the reaction conditions.[26,32] Such reactions are also required for the synthesis of stars and macrocyclic vinylaromatic polymers.[33-37] Thus, a few coupling reactions, resembling step polymerizations, of P2VN-K_2 with 1,4-DBX were carried out at relatively high concentrations (>10^{-3} M). SEC analysis of the polymer products of this step polymerization show that the apparent peak MW (M_p) is increased roughly 20-fold compared to that of the corresponding protonated precursor dianion, indicating high efficiency of coupling (Table 3.5).

The high degree of end-functionalization is again consistent with the persistence, and high reactivity and chemoselectivity of the P2VN anion at these conditions. Thus, side reactions such as proton transfer and/or halogen exchange or elimination reactions not leading to the coupled products appear to be absent. It would thus appear that the living polymerization of 2VN is suitable for the synthesis

of P2VN block copolymers as well as homopolymer architectures, such as stars and macrocyclic P2VN.

3.5 References

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Table 3.1. Effect of the monomer impurity concentrations on P2VN-Li end-functionalization[a]

#	[*t*-BuLi] mM	[2VN] mM	P2VN-TMSCl					
			M_n^{calc} ´10^{-3}	M_n ´10^{-3}	M_w/M_n	TMS[b] %	[impurity] mM	mol. % impurities in monomer
7	10.8	35.0	0.50	0.68	1.39	95	0.54	1.5
11	10.8	56.0	0.80	0.91	1.25	90	1.08	1.9
10	7.9	85.7	1.67	1.40	1.16	86	1.11	1.3
9	3.8	85.7	3.47	3.48	1.18	60	1.52	1.8
8	1.4	92.3	10.2	5.66	2.00	20	1.12	1.2
				10.7[c]	1.16			
98	0.5	100	31.0	-	-	-	~ 1.5	

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 ºC. SEC characterization: RI detector and PS standards. b) TMS-group incorporation, as determined by integration of *t*-Bu and TMS peaks in ^{1}H NMR for precipitated and dried polymers. c) SEC trace of the unfractionated polymer without low MW tailing.

Table 3.2. Resumption polymerizations in THF at –78 °C with purified 2VN[a]

#	[I][b] mM	P2VN-MeOH				P2VN-*b*-P2VN-MeOH			
		[M] mM	t_1 min	M_n ´10^{-3}	PDI	[M] mM	t_2 min	M_n ´10^{-3}	PDI
72	1.0	30	5	3.40	1.10				
97	0.1	95	10	110	1.03				
88	1.6	35	10	4.80	1.30	70	10	31.5	1.11
89	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 drop-wise and stirred for additional time t_2. Conversion of 2VN is quantitative. b) Initiator used: *t*-BuLi used as received (exp. # 72), sublimed *t*-BuLi (exp. # 97). Li-OMOHN (exp. # 88, 89).

Table 3.3. Radical anion initiated polymerizations of 2-vinylnaphthalene in THF at –78 °C[a]

#	Initiator I	[I] mM	[2VN] mM	DP_n (calc.)	P2VN-MeOH	
					M_n	PDI
76	Li-Naph	6.5	55	17	2300	1.40
89	Li-OMOHN	–	44	–	9500	1.30
4	K-Naph	6.1	91	30	3900	1.15
30	K-OMOHN	2.6	62	48	5600	1.10
82[b]	K-OMOHN	–	90	–	88,000	1.15
31	AMS-K_2	2.0	65	65	7600	1.07
106	Cs-Naph	4.3	125	58	6170	1.08
107	Cs-Naph	5.0	80	32	3360	1.10

a) SEC characterization using RI detector and polystyrene standards. b) Calculated initiator concentration 0.4 mM, but some initiator deactivation occurred prior to polymerization.

Table 3.4. Restart and block-copolymerization involving P2VN-K_2[a]

#	[I][b] mM	P(M1)					P(M2)-b-P(M1)-*b*-P(M2)				
		M1	[M1] mM	t_1 min	M_n ´10^{-3}	PDI	M2	[M2] mM	t_2 min	M_n ´10^{-3}	PDI
87	3.1	2VN	26	60	1.55	1.14	2VN	100	10	14.5	1.06
91	4.0	2VN	34	10	2.04	1.13	DMVF	85	15	9.50	1.07
94	5.4	2VN	48	15	3.00	1.14	AMS	200	70	4.17[c]	1.13
95	18	AMS	150	180	1.75[d]	1.09	2VN	250	5	11.4	1.07

a) Polymerizations of 2VN (M1) in THF at –78 °C for t_1 minutes; then 1/4 to 1/2 of the P2VN-K_2 solution is transferred into a side flask and monomer (M2) is added, stirred for time t_2 and terminated with methanol. b) Initiator: K-OMOHN (# 87, 91), K-Naph (# 94, 95). c) Conversion of AMS (gravimetrically) is 8%. *d*. Conversion of AMS (gravimetrically) is 50%.

Table 3.5. Coupling reactions of P2VN-K_2 and DBX in THF at –78 °C[a]

#	[I] mM	t_p[b] min	P2VN-MeOH			P2VN-DBX		
			M_n	PDI	M_p	M_n	PDI	M_p[c]
80	3.2	5	6000	1.12	7000	11700	5.22	112000
81	2.2	60	5600	1.12	6500	11500	3.86	82200

a) DBX is added into excess of P2VN-K_2/THF until color faded. K-Naph is used as initiator. SEC analysis using RI detector and polystyrene standards. b) Polymerization time. c) Apparent molecular weight of the polycondensation product formed by reaction of P2VN-K_2 with DBX.

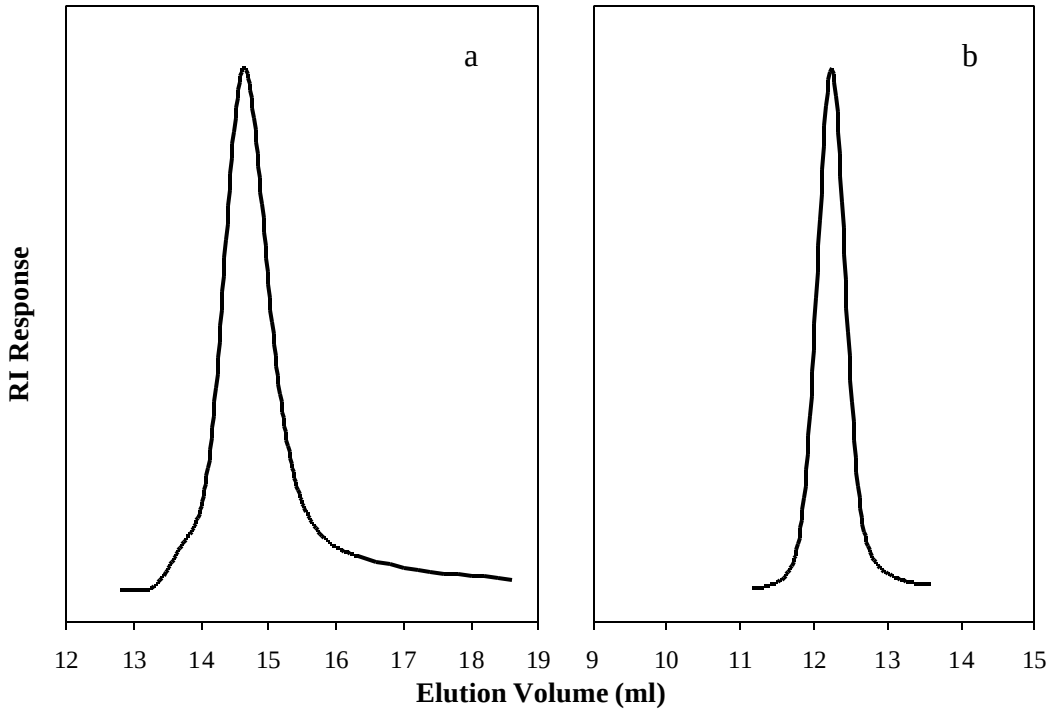

Figure 3.1. SEC curves of poly(2-vinylnaphthalene) prepared using sublimed *t*-BuLi and monomer purified a) by 2 sublimations from CaH_2 (Table 3.1, exp. # 8) and b) by sublimation from $LiAlH_4$ followed by sublimation from CaH_2 (Table 3.2, exp. # 97).

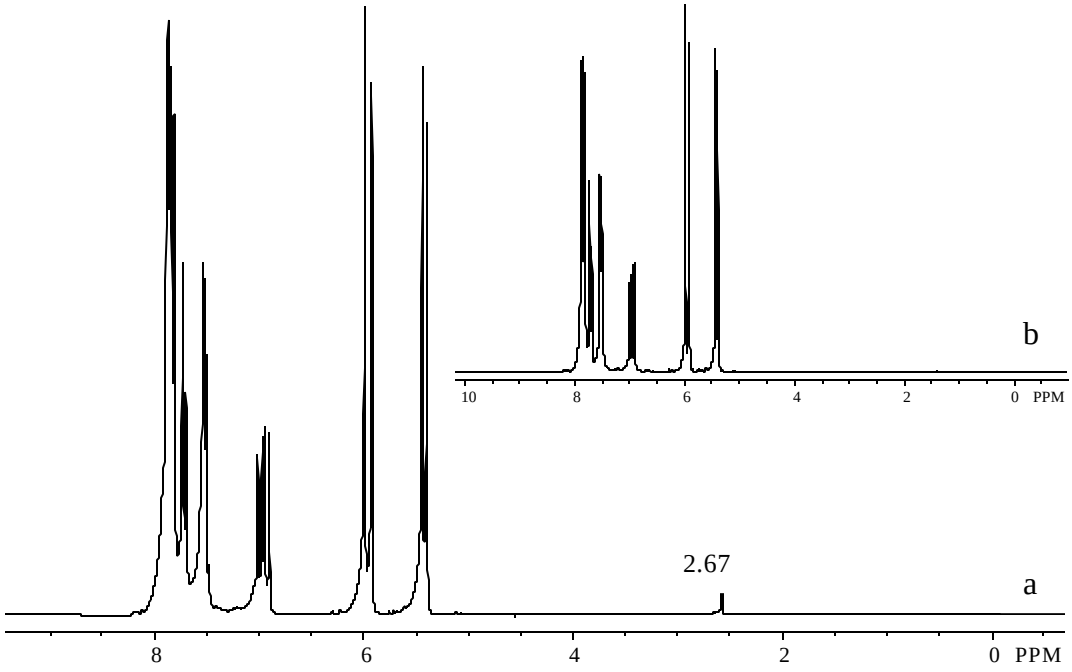

Figure 3.2. 250 MHz ^{1}H NMR of 2-vinylnaphthalene in $CDCl_3$ a) sublimed 2 times from CaH_2 and b) sublimed from $LiAlH_4$ followed by sublimation from CaH_2.

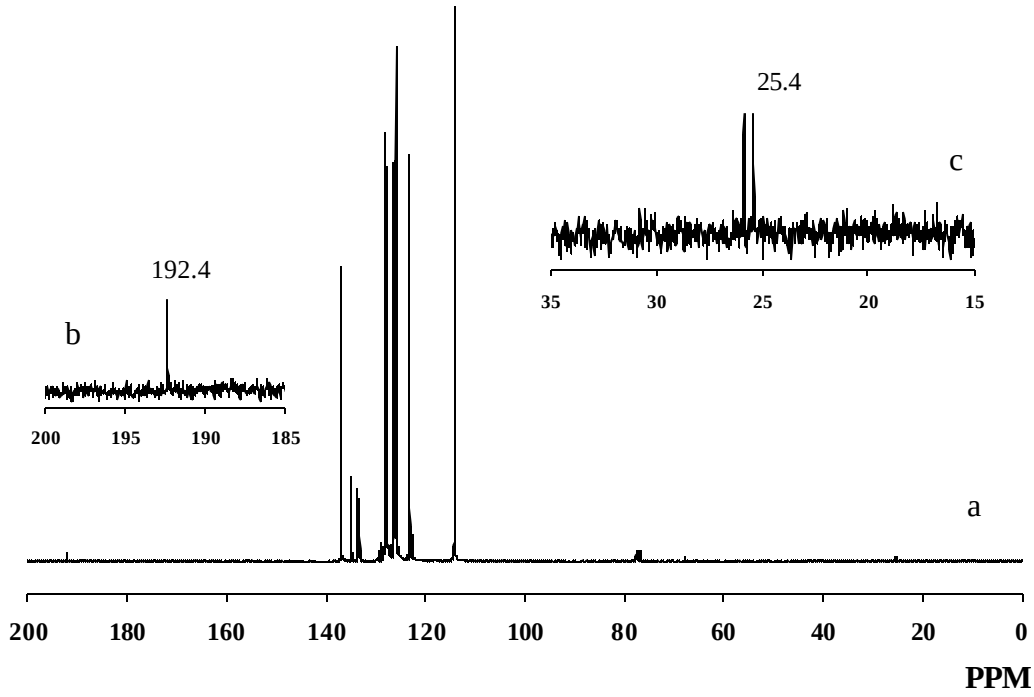

Figure 3.3. 62.9 MHz ^{13}C NMR of 2-vinylnaphthalene in $CDCl_3$ sublimed 2 times from CaH_2: a) the whole spectrum, b) the region showing carbonyl and c) methyl resonances.

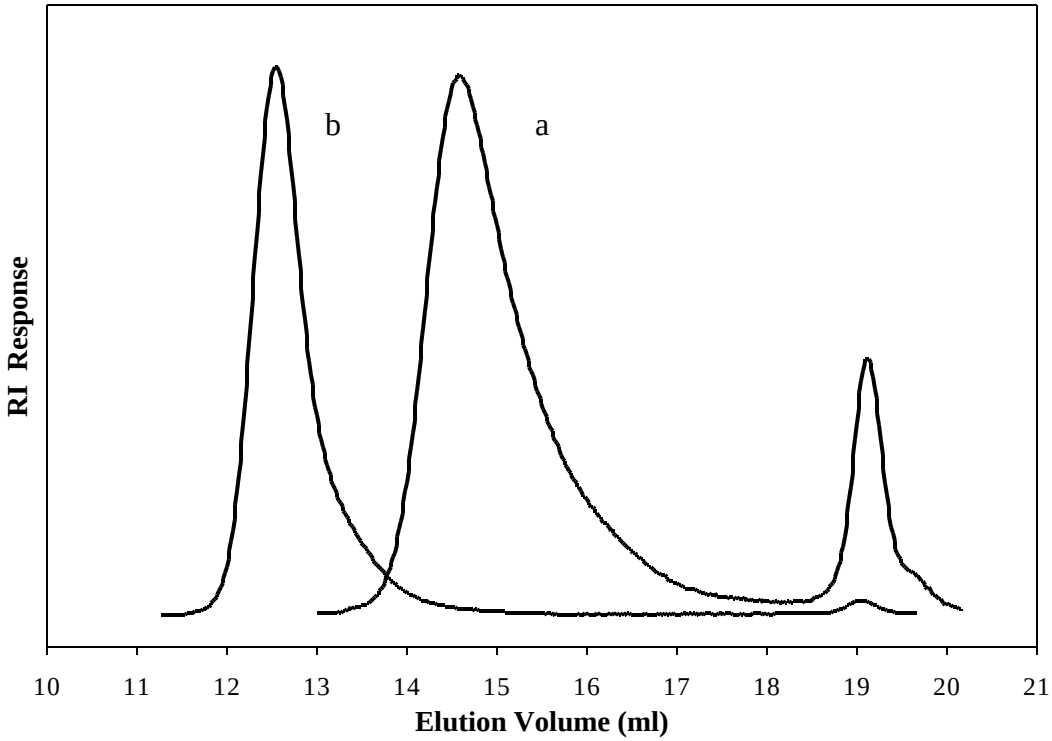

Figure 3.4. SEC curves of poly(2-vinylnaphthalene) from exp. # 88 (Table 3.2): a) P2VN precursor and b) P2VN after addition of the second 2VN portion after 1 h of storage at –78 °C (peak at 19 mL corresponds to OMOHN).

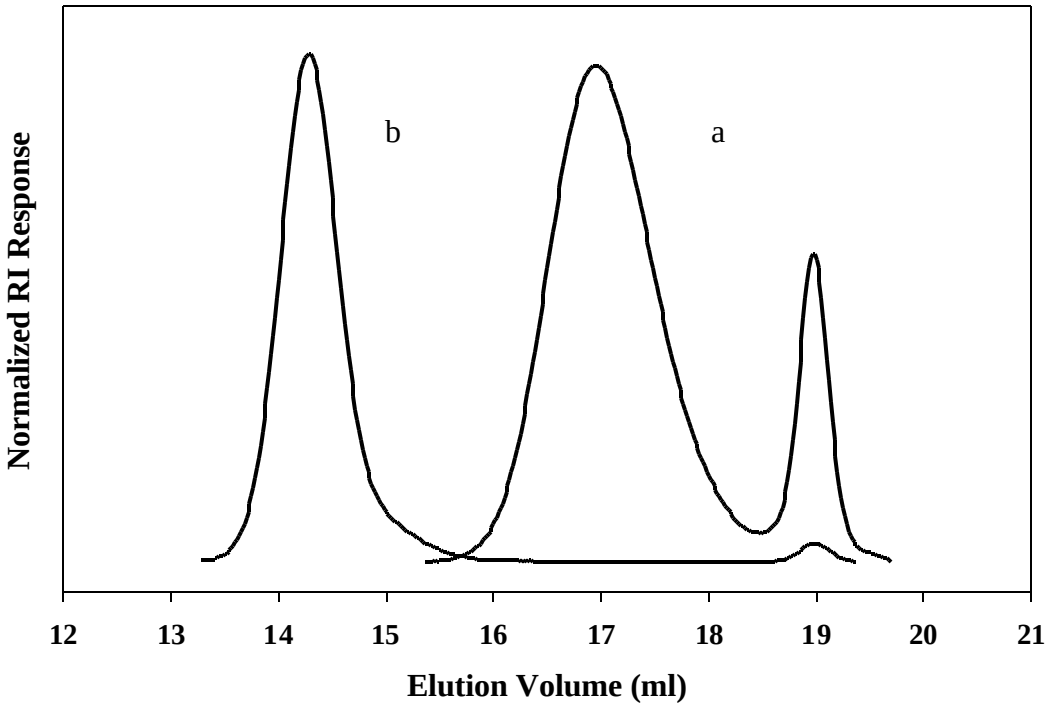

Figure 3.5. Normalized SEC curves of P2VN (Table 3.4, # 87): a) P2VN precursor and b) P2VN after addition of the second 2VN portion after 1 h of storage (peak at 19 mL corresponds to OMOHN).

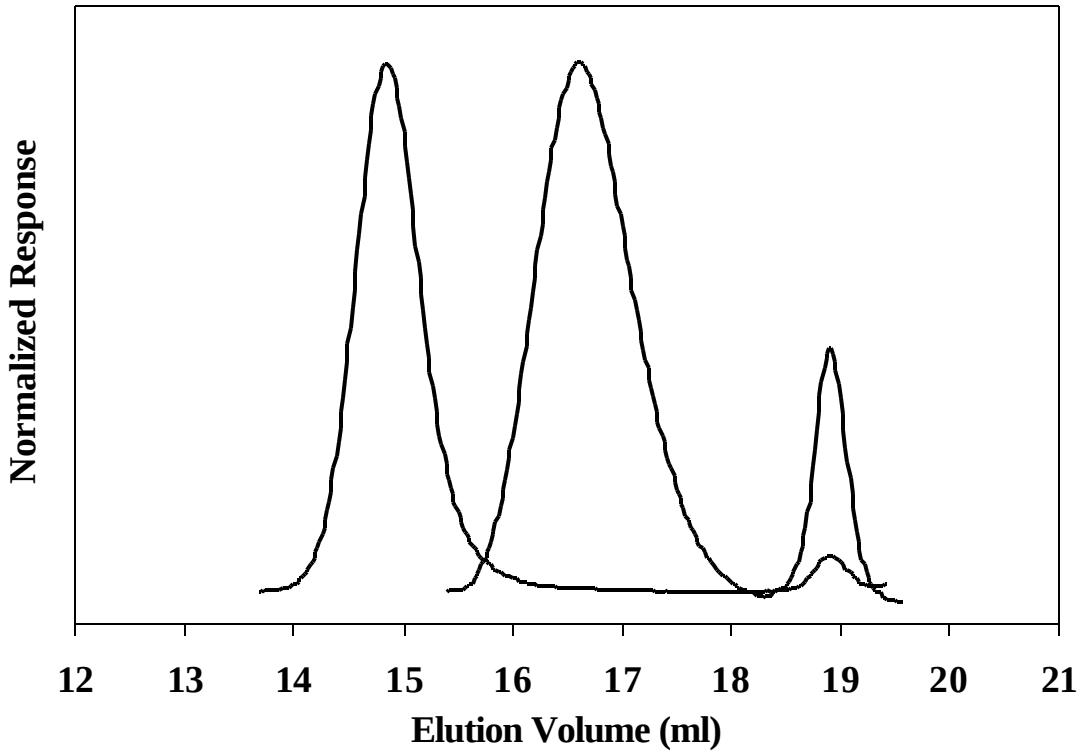

Figure 3.6. Normalized SEC curves of P2VN and PDMVF-*b*-P2VN-*b*-PDMVF (Table 3.4, # 91) (peak at 19 mL corresponds to OMOHN).

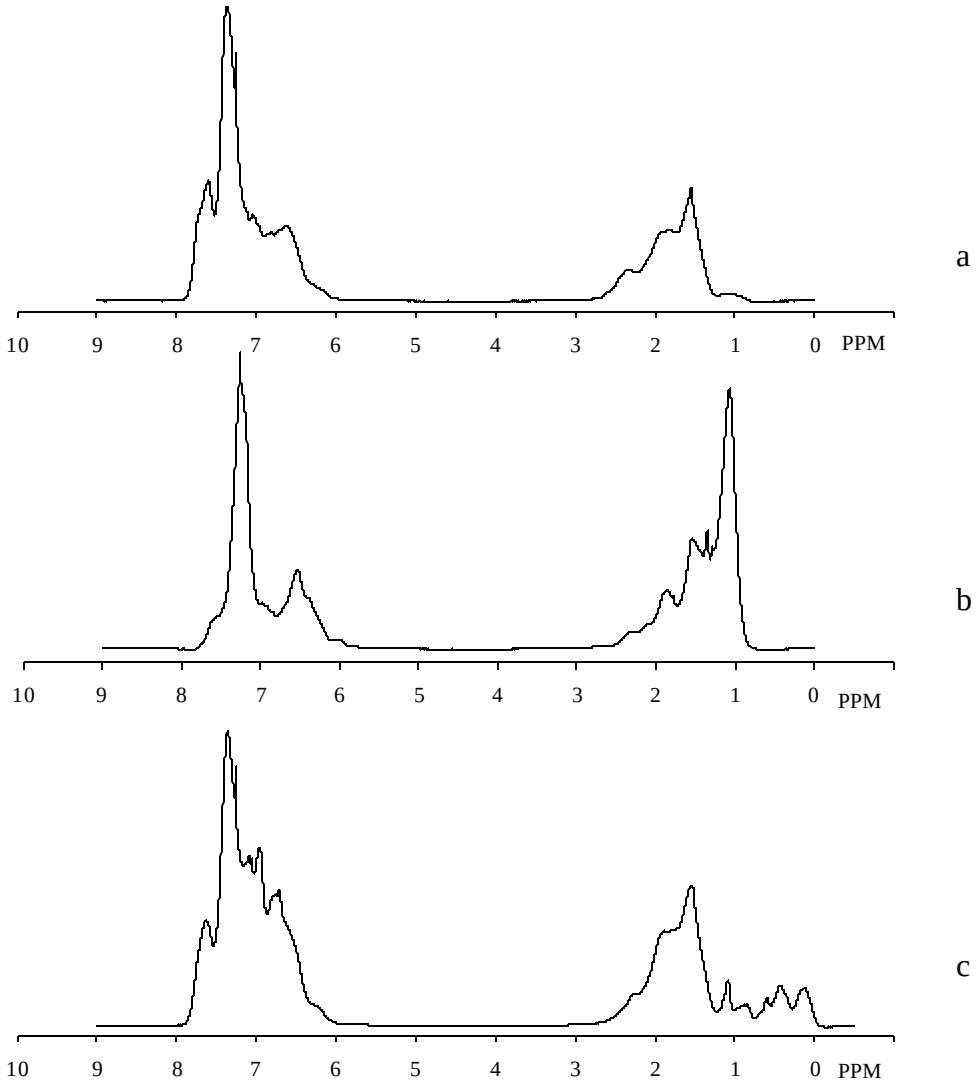

Figure 3.7. 250 MHz ^{1}H NMR of a) P2VN (Table 3.4, # 94), b) PDMVF-*b*-P2VN-*b*-PDMVF (Table 3.4, # 91) and c) PAMS-*b*-P2VN-*b*-PAMS (Table 3.4, # 94).

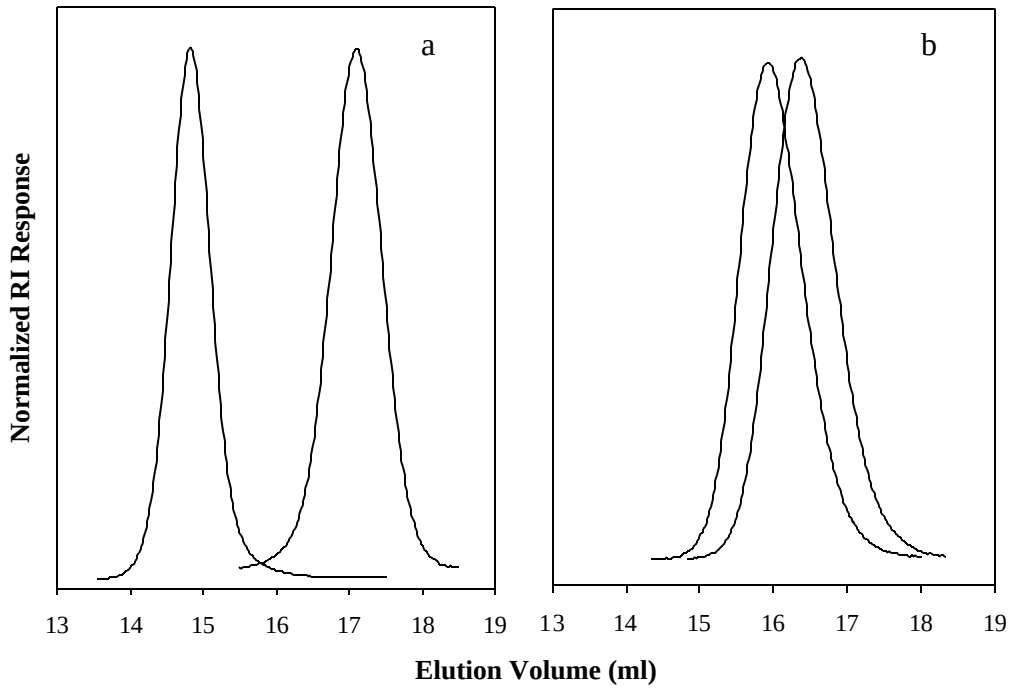

Figure 3.8. Normalized SEC curves of a) P2VN and P2VN-*b*-PAMS-*b*-P2VN (Table 3.4, # 95), b) P2VN and PAMS-*b*-P2VN-*b*-PAMS (Table 3.4, # 94).