Chapter 4

Living t-BuLi Initiated Anionic Polymerization of 2-Vinylnaphthalene in Toluene-Tetrahydrofuran Mixtures

4.1 Introduction

Although the lithium naphthalide (Li-Naph) initiated polymerization of 2VN is living, as described in the previous chapter, it is not well controlled giving polymers with relatively broad MW distributions (1.40 and above). Thus, it is of interest to find conditions allowing a Li ion mediated living/controlled polymerization of 2VN and the formation of a P2VN dianion suitable for subsequent reactions leading to triblock copolymers and/or rings.

The alkyllithium initiated polymerization in hydrocarbons is well known to be complex. However, the presence of polar reagents such as alkoxides or THF may lead to the formation of fewer but more reactive ionic species such as complexed ion pairs rather than ion pairs and ion pair aggregates. As the reaction rates including the rates of exchange between the various ionic species increase, considerable control can be imposed on the rates of initiation/propagation allowing higher conversions and narrower distributions.[1-5]

In this chapter, the results on the t-BuLi initiated polymerization of 2VN in toluene, in the presence of THF (5-20 equivalents with respect to the initiator), are summarized. The polymerizations involving carefully purified 2VN are found to be living and well controlled. Thus, there is good agreement between calculated and observed molecular weights, and the polymers have very narrow and symmetrical

MW distributions (D<1.10). High degrees of end-functionalization with chlorotrimethylsilane (>95%) and coupling with 1,4-bis(bromomethyl)benzene indicate excellent stability of the P2VN-Li living polymers.

4.2 Experimental

In a typical polymerization run, the reaction apparatus (Figure 2.6) was evacuated and flamed and t-BuLi in hexane (1.6×10^{-4} moles, 5 mL) was introduced into a reaction chamber. Hexane was distilled off and replaced with purified toluene (10-12 mL) at room temperature. After cooling to –78 °C varying amounts of THF were added giving characteristic light yellowish solutions. A solution of 2VN (1.8×10^{-3} moles, 4 mL) in toluene cooled to –60 °C was then added at once. The immediate formation of a dark red (burgundy) color indicated fast initiation. Immediately after initiation, argon, purified by bubbling through a t-BuLi/triphenylmethane/toluene solution cooled to –78 °C, was introduced into the reaction chamber. Over the course of the polymerizations, one mL aliquots were taken with a hypodermic syringe through a septum and reacted with methanol. Monomer conversions were determined by quantitative SEC analysis of polymer and monomer peaks through calibration with known 2VN/P2VN mixtures.

Polymerizations under high vacuum (Tables 4.2, 4.3) and the coupling of P2VN anions with bifunctional electrophiles were carried out as described in the Section 2.4. The P2VN-Li precursors were reacted with MeOH or TMSCl to serve as comparisons with the coupled polymers. The polymers dissolved in 10 mL of toluene were precipitated in methanol (100-150 mL), filtered and dried under high vacuum for 2 days at 50 °C. Monomer conversions in these experiments were determined gravimetrically.

4.3 Kinetic Studies of 2VN Polymerization

The first polymerizations were carried out with routinely purified 2VN (method A) in toluene at room temperature. Upon addition of 2VN to the colorless t-BuLi toluene solution a yellow color appeared instantly due to complex formation of t-BuLi with the monomer (see below) and this color slowly intensified to a brownish-red in 30-40 min. The color faded considerably after 4 hours. It is interesting that a similar yellowish color develops over about 10 minutes upon addition of 10-20 molar excess of naphthalene to t-BuLi/toluene at room temperature. This yellow color persists indefinitely but disappears upon addition of methanol. GC-MS analysis of the protonated reaction product shows only recovered naphthalene consistent with the formation of t-BuLi/naphthalene complexes.

As shown in Table 4.1 (# 57) and Figure 4.1, relatively broad MW distributions P2VN's are obtained and at least two low MW SEC peaks are observed that may correspond to the addition of one or two monomer units to t-BuLi. The elution volumes of these peaks are unchanged as the polymerization proceeds but their intensities relative to that of the polymer decrease indicating that they represent deactivated species. The use of conventionally purified monomer (method A) in these experiments (Table 4.1, # 55-57) makes it plausible that the deactivated oligomers were formed in the initial stages by reaction of P2VN-Li with 2-acetylnaphthalene (2AN) that has been shown to be present in the monomer in relatively large proportions (1.0 – 1.5 mol. %, Chapter 3). This reaction may proceed either by proton abstraction or by addition to carbonyl. The remaining anions slowly polymerize as shown by the clear shifts to higher MW's (Figure 4.1). However, the question remains why the low MW oligomers are trapped in the first place. It is possible that this is due to a relatively long life time of these oligomer anions that, in its own turn, may be due to the interaction of the propagating ion pair with a penultimate 2-naphthyl unit (see below). The stabilization of the propagating anion by cation coordination with penultimate pendent groups is well known.[6,7]

The broad SEC curves (Figure 4.1) with pronounced tailing are consistent with the slow initiation – fast propagation process described above. Monomer conversion reaches about 30 percent in 3 h after which the conversion slows and eventually stops possibly due to transfer to solvent.[4] The initiator efficiency in pure toluene calculated from the SEC and conversion data was found to be about 50 percent consistent with the formation of P2VN-Li/t-BuLi complexes.[4]

For the polymerization of 2VN (method A) at –78 °C in the presence of 10 equivalents of THF with respect to t-BuLi, the rates of both initiation and propagation are increased as indicated by high conversions (>75%) after 4 hours (Table 4.1, # 55, Figure 4.2). In this case again, the formation of what appears to be the dimer anion is seen, but the terminated t-BuLi/2VN adduct is absent presumably due to its rapid reaction with 2VN. Otherwise, the polymerization appears to proceed without deactivation as seen from the more narrow and symmetrical molecular weight distributions compared with the polymerization in toluene (Figures 4.1 and

4.2). Initiator efficiencies are quantitative in all cases where THF was used as an additive.

As seen from the polymerization profile (Table 4.1, # 56, Figure 4.3), the rate of propagation is even higher in the presence of 20 molar equivalents of THF, as expected. The appearance of a slight shoulder in curve (d) in the SEC chromatogram at 14.4 mL corresponds to a MW that is double that of the peak at 15.3 mL. The occurrence of such MW shoulders is also visible in curve (c) and in the high conversion polymers in Figure 4.2 indicating coupling reactions at longer reaction times.

The kinetics of the polymerization was tested by evaluating the relationships between DP_n and monomer conversion as well as polymerization rate vs. time using equation (1). The linearity of this plot was shown to be necessary and sufficient to exclude termination and transfer reactions. [8]

$$\ln\left(1 - \frac{[I]_0}{[M]_0} DP_n\right) = -k_p [I]_0 t \tag{1}$$

The DP_n values were obtained by dividing respective SEC-RI number-average MW's by the molecular weight of styrene (see below). As shown in Figure 4.4, after a few minutes, the slope decreases consistent with the presence of the 2AN impurity that decreases the concentration of active chain ends. Complex processes of formation of stable oligomers described above may also influence the polymerization rate at the initial stages. Furthermore, the presence of a significant fraction of the lithium alkoxide introduced due to the reaction of P2VN-Li with 2VN may decrease the rate as well.[7,9,10] Larger deviations from linearity appear after 3 hours for # 55 (Table 4.1) (~10 equiv. THF) and after 2 h for # 56 (Table 4.1) (~20 equiv. THF) corresponding to roughly 70% monomer conversion. The spontaneous deactivation by reaction of P2VN-Li with a penultimate pendent group followed by LiH elimination proposed for poly(2-isopropenylnaphthalene) anion in THF at ambient temperatures,[11] may occur and this would be consistent with the formation of the P2VN dimer traces which are visible in Figures 4.2 and 4.3.

The kinetic plot of the carefully purified 2VN (method B) polymerization (Table 4.1, # 105, Figure 4.4 b), except for the first few minutes, does not show significant deviation from linearity. In addition, except for slight deviations at very high monomer conversions, the plot of M_n vs. conversion (Figure 4.5) is linear confirming the absence of chain-transfer at these conditions. Thus, it would appear that this polymerization of carefully purified monomer under the above conditions is subject to control of MW and MW distribution. Indeed, the polymerizations run under vacuum (Tables 4.2-4.3) proceed to high monomer conversions (90%) without noticeable deactivation as indicated by narrow and symmetrical MW distributions (Figure 4.6). Experimentally determined molecular weights correlate well with calculated ones based on monomer to initiator ratio (see below). From Figure 4.4 the polymerization rate constant is on the order of 0.05 L mol^{-1} sec^{-1} which is about four orders of magnitude lower than obtained for the polymerization of 2VN in THF at ambient temperatures in the presence of Na ion.[12]

4.4 End-functionalization and Coupling Reactions

In order to determine the persistence of the polymer chain ends under the polymerization conditions, we used carefully purified 2VN (method B) and end-functionalized P2VN by the reaction of P2VN-Li in toluene/THF with 10-15 mol. equivalents of chlorotrimethylsilane (TMSCl). The ratio of the respective proton NMR integrals of the TMS and *tert*-butyl peaks in proton NMR (Figure 4.7) showed high degrees of end-functionalization (>95%) in broad range of the initiator concentrations and polymer molecular weights (Table 4.2).

The significant stability of P2VN anion in the presence of Li under our conditions is also indicated by the high efficiency of coupling reactions with dibromoxylene (DBX). For instance, the molecular weight of the DBX coupled product is doubled when compared to that of the precursor (Table 4.2, # 66, Figure 4.6 b). In the case of higher MW at otherwise identical conditions, around 5% of the precursor had not reacted with DBX (Figure 4.6 a) possibly due to slower coupling of longer polymer chains in the low polarity medium.

We observed a lower efficiency of P2VN-Li coupling-dimerization with 9,10-bis(chloromethyl)anthracene (BCMA), diiodomethane (DIM) and dichlorodimethylsilane (DCDMS), as shown in Table II. The coupled product of P2VN-Li and BCMA (Table 4.2, # 62) was formed in 80% yield as determined by SEC and the incorporation of anthracenylidene linkages was confirmed by UV-vis absorptions at 408, 386 and 364 nm characteristic of anthracenyl groups (Figures 4.8 and 4.9). The anthracenylidene content calculated from the reported extinction coefficients of 9,10-dimethylanthracene is nearly quantitative.[13] There is no indication of the presence of chromophores other than anthracene and naphthalene.[14]

Surprisingly, there was almost no coupling-dimerization upon reaction of P2VN-Li and DCDMS. Although the reaction between TMSCl and P2VN-Li is almost quantitative as shown above, the SEC data indicate only 15 and 10% dimer in # 69 and # 74 (Table 4.2), respectively. Proton NMR of the polymers subjected to methanolysis (Figure 4.10) revealed a broad and complex band centered at 3.20 ppm which is attributable to $–Si(CH_3)_2–OCH_3$ groups formed upon methanolysis of the $–Si(CH_3)_2–Cl$ chain-ends. Thus, the P2VN chains are end-functionalized with DCDMS rather than coupled. This unexpected behavior might be employed in P2VN post-polymerization reactions.

4.5 Molecular Weight Determination

In the course of our studies we have found that the number average molecular weights of P2VN's determined by the proton NMR integration of t-Bu and either aromatic or aliphatic hydrogen peaks (Figure 4.7) are always higher (40-70%) than those for the same samples determined by SEC using RI detector and PS standards (Table 4.3). This may be due in part to the presence of a solvent ($CDCl_3$) peak in the polymer aromatic resonances and of water in the methylene/methine P2VN resonances. In order to clarify this issue, we ran several NMR's in CD_2Cl_2 (5.30 ppm)[15] which does not interfere with the P2VN aromatic resonances.

As shown in Table 4.3 (# 90, 60), solvent interference in $CDCL_3$ gives a MW that is about ten percent too high. Nevertheless, even in CD_2Cl_2 there are obvious differences in the MW's with the NMR values being about 40-50% higher.

Given the absence of chain-end termination, the MW determinations by NMR should be considered as being more reliable especially at low MW's. As SEC elution volume reflects molecular size not weight, the lower apparent molecular weights obtained by SEC would appear to indicate that the P2VN molecular hydrodynamic volume is significantly smaller than that of polystyrene with the same mass. For example, the number average degree of polymerization (DP_n) of sample # 61 (Table 4.3) calculated by proton NMR is 40.2 and this almost the same as the value of 40.4 for the DP_n obtained by dividing the SEC apparent M_n by the mass of styrene monomer. Hence the hydrodynamic size of P2VN seems to correlate better with the degree of polymerization, and thus its contour length, rather than mass. Thus, we believe that the SEC MW values of P2VN determined with PS standards are underestimated by around 40-50 percent. A similar trend for other vinylaromatic polymers bearing large substituent groups has been reported[16] but we are not aware of similar observations for other vinyl polymers of this type.[17,18]

4.6 References

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Table 4.1. Polymerization of 2VN in toluene/THF. Effect of THF concentration on the polymerization kinetics[a]

#	[t-BuLi] mM	[THF] mM	[2VN] mM	DP_n^{th}	t_p min	P2VN-MeOH		
						M_n´10^{-3} (main peak)	M_w/M_n (main peak)	Conv.[e] %
57[b]	2.1[c]	0.0	140	67	30	1.48	1.22	
					60	3.46	1.40	
					120	5.31	1.64	
					180	5.87	1.68	28
					240[d]			
55	3.2[c]	31	150	47	5	0.82	1.06	
					15	1.10	1.09	
					45	1.87	1.10	
					110	2.82	1.10	
					180	3.37	1.11	
					240	3.53	1.11	
56	2.8[c]	58	167	60	5	1.02	1.08	
					15	1.70	1.11	
					45	3.24	1.11	
					90	4.59	1.13	
					240	5.86	1.12	
105	2.9	32	150	52	10	1.16	1.08	16
					40	2.17	1.15	34
					80	3.02	1.14	47
					120	3.63	1.10	61
					180	4.20	1.09	76
					240	4.45	1.09	84

a) One time addition of 2VN/toluene and stirring for t_p at –78 ºC under argon. t-BuLi sublimed. b) Polymerization at room temperature. c) Initiator concentration corrected for the presence of 1.5% mol 2AN impurity. d) Color considerably faded. e) Monomer conversions, determined as described in experimental section.

Table 4.2. Polymerization of 2VN in toluene/THF. End-functionalization and coupling reactions of P2VN-Li[a]

#	[tBuLi] mM	[THF] mM	[2VN] mM	t_p min	P2VN-EX[b]				P2VN-EX_2[b]		
					M_n ´10^{-3}	M_w/M_n	Conv[c] %	TMS %	M_n ´10^{-3}	M_w/M_n	EX_2
59	10	20	130	150	0.52	1.15	34				
60	3.6	28	135	165	3.3	1.08	86	95			
61	3.0	28	135	165	3.8	1.10	90	95			
63	4.2	30	125	120	2.4	1.09	70	97			
64	33	164	450	120	2.1	1.11	82	97			
65	0.8	3.4	120	120	11	1.04	64	95	21	1.13	DBX
66	4.5	22	125	100	1.6	1.09	53		3.2	1.13	DBX
62	3.0	26	140	125	3.6	1.10	70		6.3	1.18	BCMA
68	0.8	9.5	180	120	21	1.08	78		34	1.18	BCMA
78	5.0	26	180	120	2.3	1.08	69		3.5	1.27	DIM
69	3.8	15	210	90	2.3	1.08	37		2.7	1.16	DCDMS
74	4.5	20	180	100	2.7	1.07	61	95	2.9	1.15	DCDMS

a) One time addition of 2VN/toluene and stirring for t_p at –78 °C in high vacuum. t-BuLi was used as received. b) 10 time excess of EX added. EX_2 was added drop-wise for 15-20 min until decolorized. DBX: 1,4-bis(bromomethyl)benzene, BCMA: 9,10-bis(chloromethyl)anthracene, DIM: diiodometane, DCDMS: dichlorodimethylsilane. c) Monomer conversions; determined gravimetrically.

Table 4.3. Comparison of P2VN molecular weight determined by SEC and ^{1}H NMR[a]

#	**M_n^{SEC} $\times 10^{-3}$**	**PDI**	**M_n^{NMR} $\times 10^{-3}$**	**NMR solvent**	**M_n difference[b]**
63	2.4	1.10	4.0	$CDCl_3$	67
90	3.5	1.08	4.9	CD_2Cl_2	40
60	3.5	1.08	5.2	$CDCl_3$	50
61	4.2	1.10	6.2	CD_2Cl_2	48
65	11	1.04	16	$CDCl_3$	45

a) M_n^{NMR} calculated from the relative intensities of t-Bu and aromatic 2VN peaks. b) $(M_n^{NMR} - M_n^{SEC})\times 100/ M_n^{SEC}$

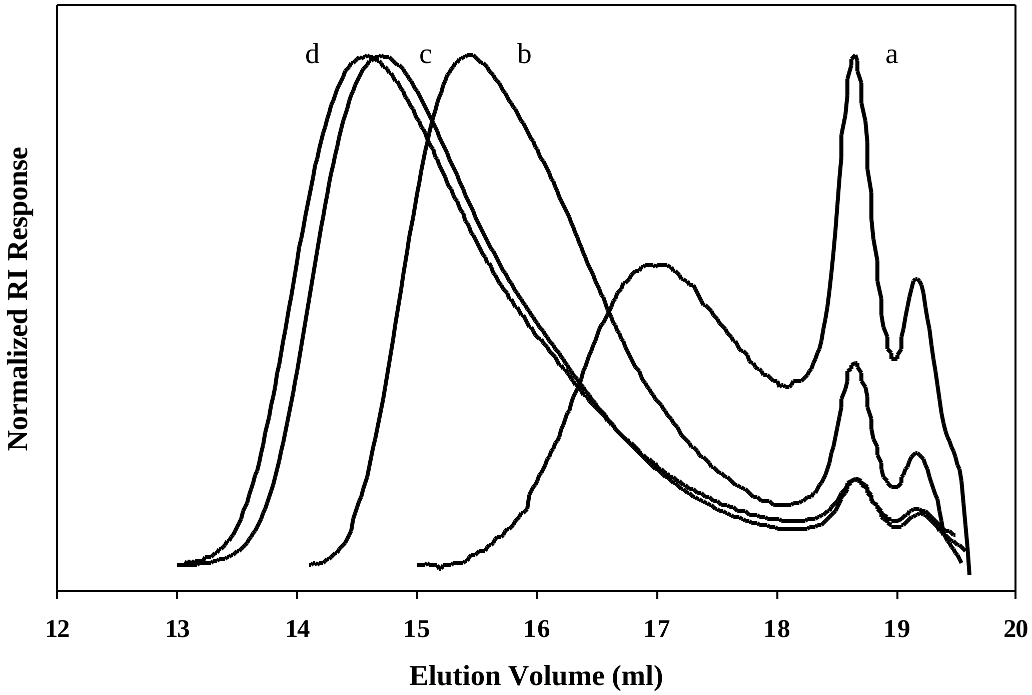

Figure 4.1. Normalized SEC chromatograms of P2VN initiated with t-BuLi in toluene at room temperature (Table 4.1, # 57) and terminated with MeOH after: a) 30 min, b) 60 min, c) 120 min, d) 180 min.

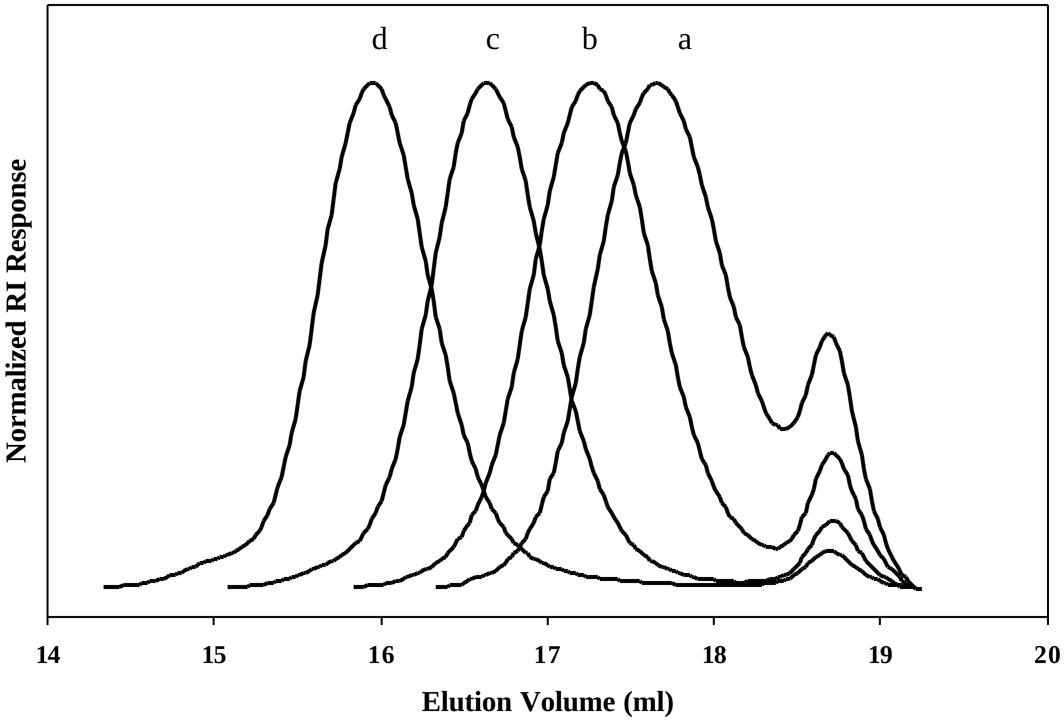

Figure 4.2. Normalized SEC chromatograms of P2VN initiated with t-BuLi in toluene in the presence of 31 mM THF at –78 °C (Table 4.1, # 55) and terminated with MeOH after: a) 5 min, b) 15 min, c) 45 min, d) 180 min.

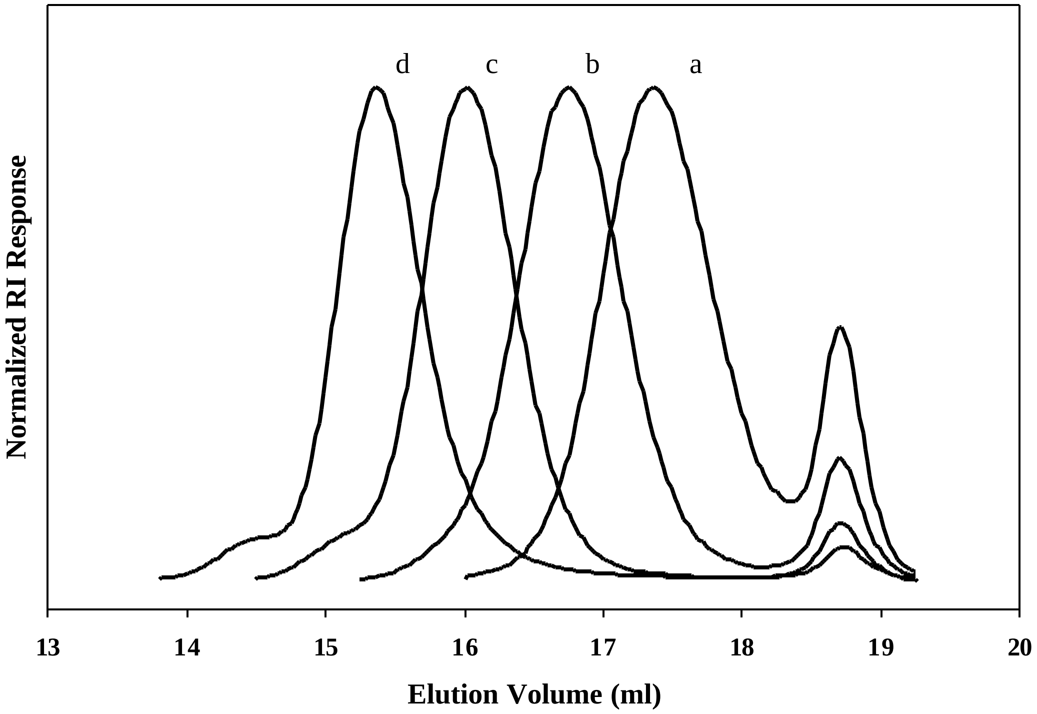

Figure 4.3. Normalized SEC chromatograms of P2VN initiated with t-BuLi in toluene in the presence of 58 mM THF at –78 °C (Table 4.1, # 56) and terminated with MeOH after: a) 5 min, b) 15 min, c) 45 min, d) 180 min.

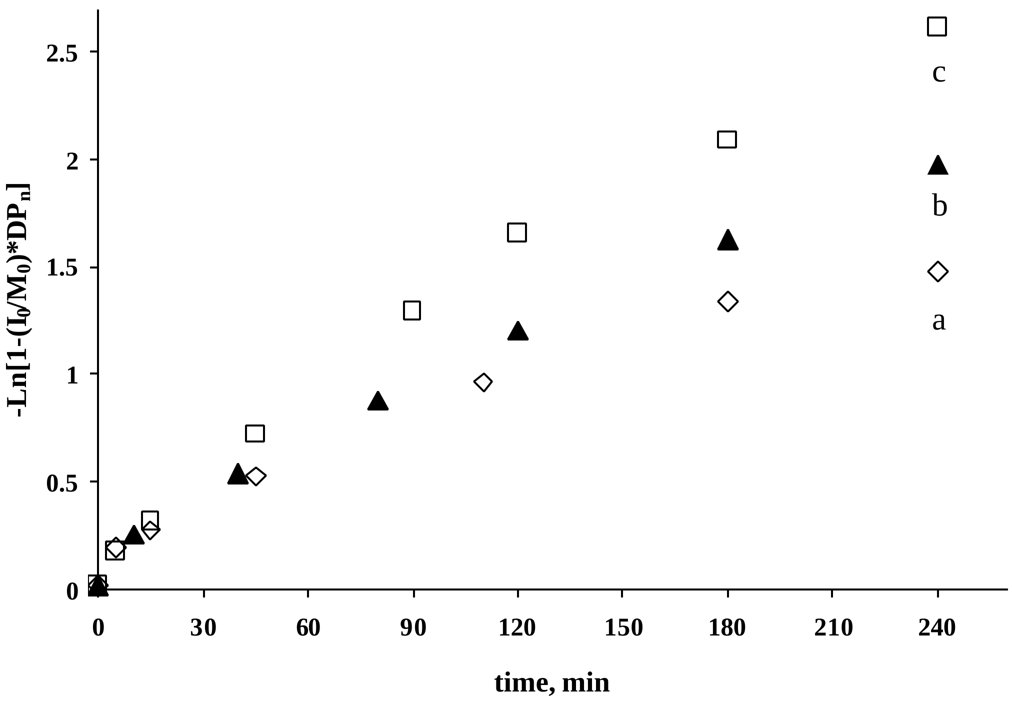

Figure 4.4. t-BuLi initiated polymerization of 2VN in toluene/THF. Dependence of Ln[1-(I_0/M_0)×DP_n] vs. time: a) Table 4.1, # 55, b) Table 4.1, # 105 and c) Table 4.1, # 56.

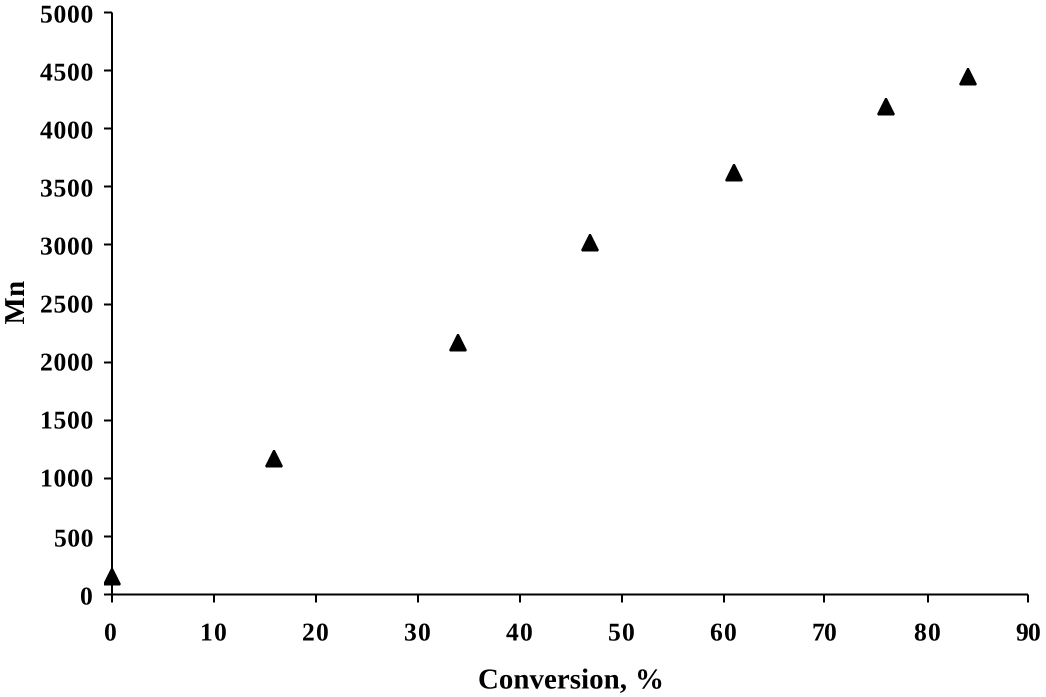

Figure 4.5. Relationship between number-average MW and monomer conversion for 2VN polymerization in toluene/THF (Table 4.1, # 105).

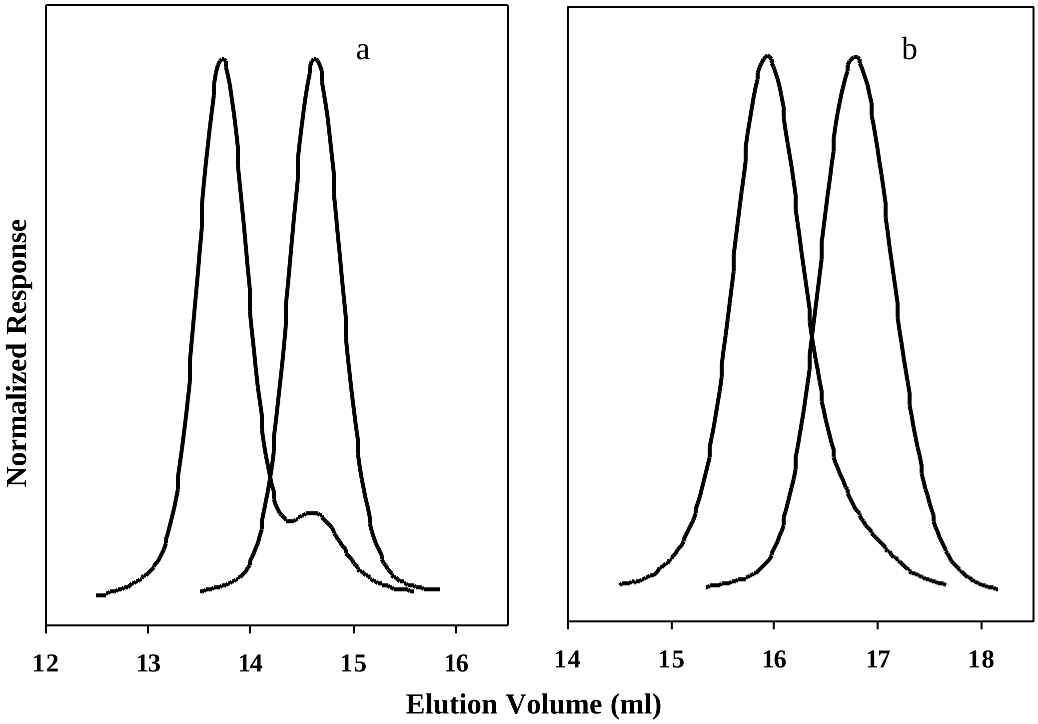

Figure 4.6. Normalized SEC chromatograms of P2VN initiated with *t*-BuLi in toluene/THF and coupled with DBX: a) Table 4.2, # 65 and b) Table 4.2, # 66.

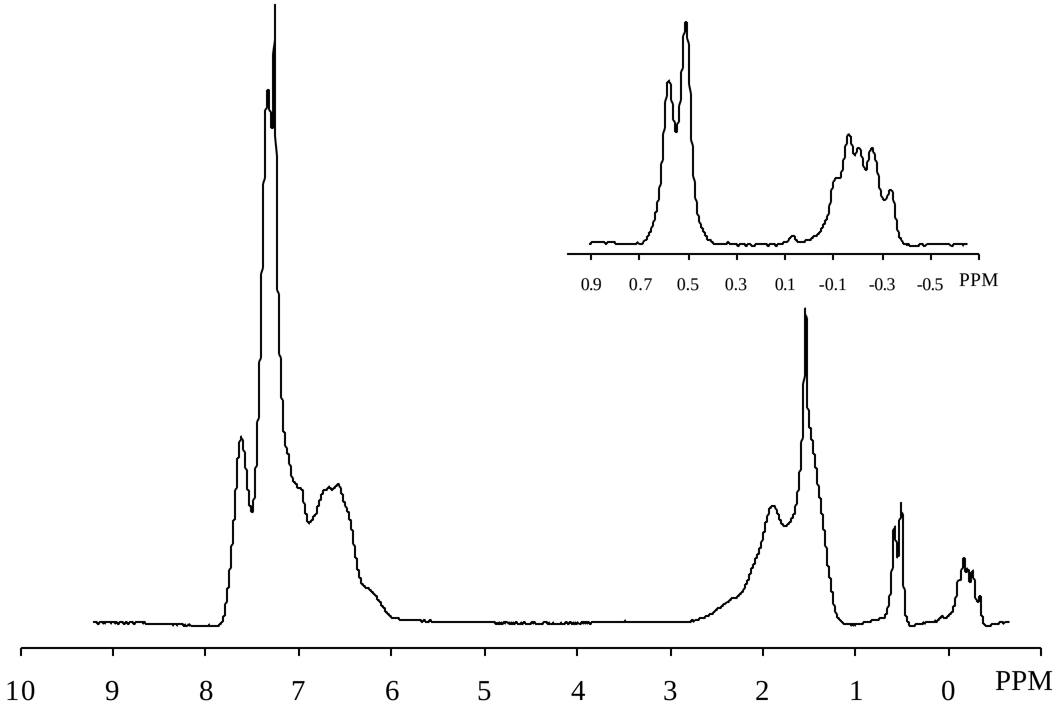

Figure 4.7. 250 MHz proton NMR spectrum in $CDCl_3$ of P2VN-Li terminated with TMSCl (Table 4.2, # 63).

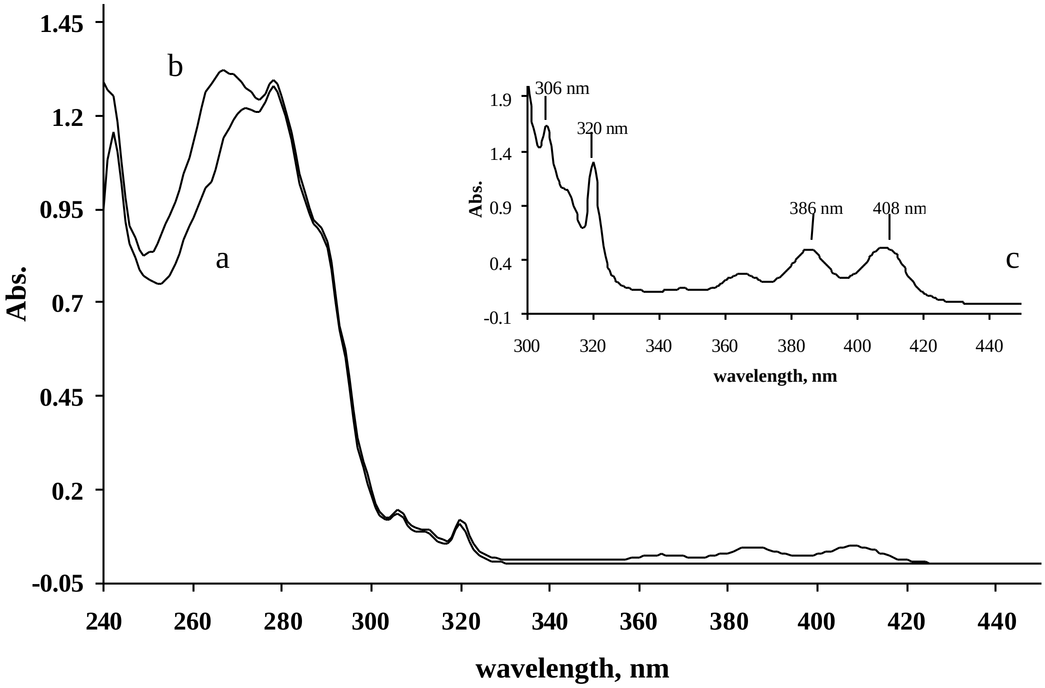

Figure 4.8. UV-Vis spectrum acquired in 10 mm quartz cell in cyclohexane/(20% v.) THF of a) P2VN terminated with MeOH (DP_n = 60, D = 1.12, conc. = 40 mg/L), b) P2VN coupled with BCMA (Table 4.2, # 62, DPn = 67, D = 1.13, conc. = 48 mg/L) and c) the trace b magnified 10 times.

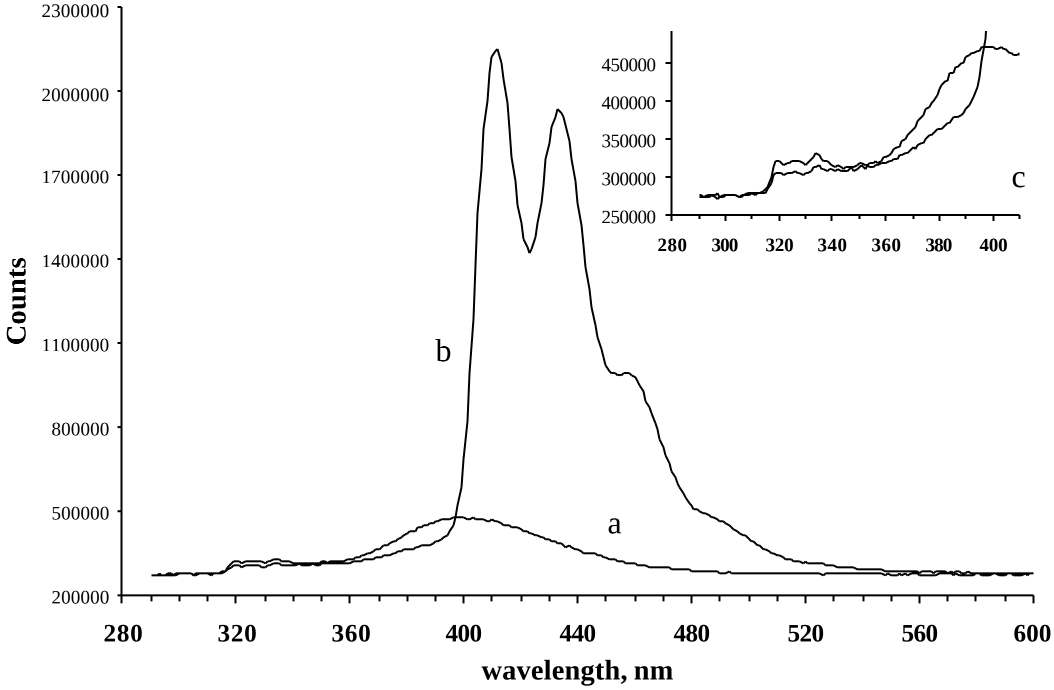

Figure 4.9. Emission spectrum acquired in 10 mm quartz cell in cyclohexane/(20% v.) THF of a) P2VN terminated with MeOH (DP_n = 60, D = 1.12, conc. = 48 mg/L), b) P2VN coupled with BCMA (Table 4.2, # 62, DPn = 67, D = 1.13, conc. = 48 mg/L) and c) the spectrum magnified 5 times.

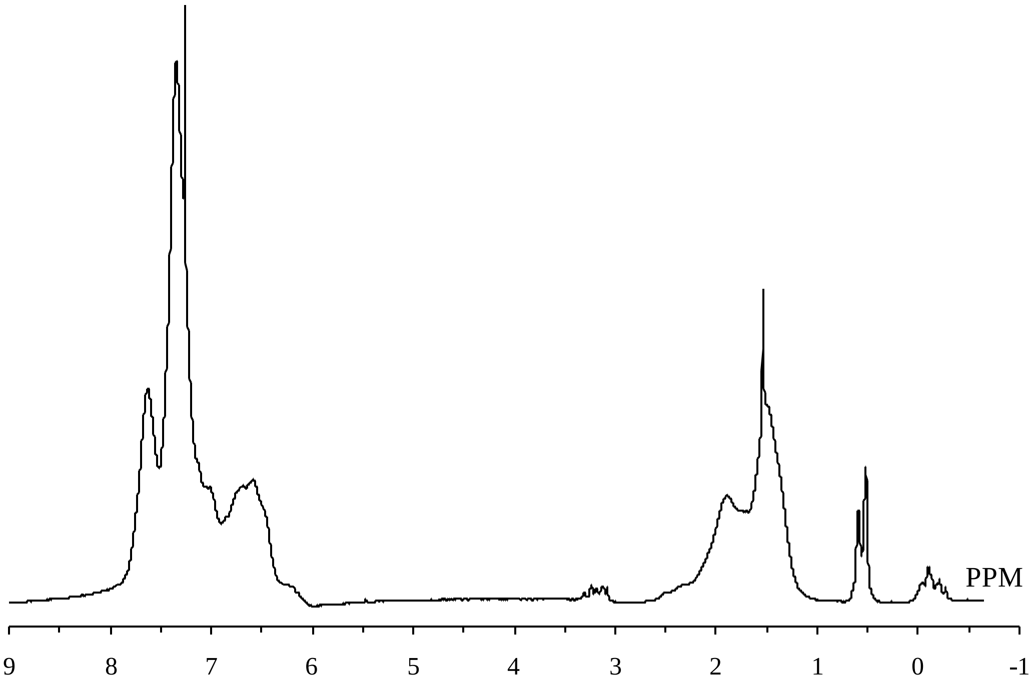

Figure 4.10. 250 MHz proton NMR spectrum in $CDCl_3$ of P2VN-Li coupled with DCDMS (Table 4.2, # 74).