Chapter 5

Synthesis and Characterization of Macrocyclic Poly(2-vinylnaphthalene) Containing Single 1,4-Benzylidene or 9,10-Anthracenylidene Groups

5.1 Introduction

The anionic polymerization of 2VN in THF –78 °C in the presence of potassium ion was shown (Chapter 3) to be both living and well controlled. Potassium ion mediated anionic polymerization of 2VN allows preparation of polymers with predictable high MW's and narrow MW distributions (below 1.10). The high degree of P2VN anion stability was confirmed by the preparation and characterization of block-copolymers. Also, a high MW P2VN was formed by step polymerizations of P2VN dipotassium (P2VN-K_2) with bifunctional electrophiles (DBX) indicating that such couplings proceed without significant side reactions.

In this chapter, the potassium mediated intramolecular cyclization of P2VN-K_2 in THF with 1,4-bis(bromomethyl)benzene (DBX) or 9,10-bis(chloromethyl)anthracene (BCMA) under high dilution conditions (10^{-4} – 10^{-6} M) is presented. The characterization of these polymers by size exclusion chromatography (SEC), UV-Visible spectroscopy and thermal methods indicates the synthesis of narrow MW distribution macrocyclic P2VN containing single 1,4-benzylidene or 9,10-anthracenylidene units. The investigation of linear and macrocyclic P2VN containing benzylidene or anthracenylidene groups as hole transporting materials for organic light emitting devices (OLED's) is presented.

5.2 Experimental

Prior to polymerization, the entire apparatus (Figure 2.7) was washed with 1,4-dipotassio-1,1,4,4-tetraphenylbutane (DD-K_2). The dipotassium salt of poly(2-vinylnaphthalene) (P2VN-K_2) was prepared at –78 °C via electron-transfer by drop-wise addition of 2VN (0.5 g in 5 mL, 3.3×10^{-3} moles, Table 5.1, # 84) in THF/toluene mixture (90/10 v/v) into a THF solution of potassium naphthalide (K-Naph, 2×10^{-4} moles in 35 mL). After stirring for 15 min, 30 mL of this P2VN-K_2 solution was transferred into a flask kept at –78 °C. Cyclization was performed at high dilution conditions (10^{-4} – 10^{-6} M) by simultaneous drop-wise addition of 30 mL P2VN-K_2 and a THF solution of 1,4-bis(bromomethyl)benzene (DBX, 80 mL, 2×10^{-4} moles) into a cyclization flask containing rapidly stirred THF (150 mL) at –78 °C. The rate of addition of the reactants was adjusted in such a way that a pale green P2VN-K_2 color just persisted. The remaining 10 mL of the P2VN-K_2 precursor solution was terminated with degassed methanol. This matching linear P2VN serves as the comparison for the cyclic P2VN. After evaporation of THF of the macrocyclic polymer solution to about 10-15 mL, a large excess of methanol (150 mL) was added to quantitatively precipitate polymers. The use of aqueous methanol (CH_3OH/H_2O, 5/1 v/v) was necessary to facilitate precipitation of macrocyclic P2VN of low molecular weight ($DP_n < 20$). The polymers were dried in vacuum at 40 °C for 2 days.

The dried polymers recovered in quantitative yield were dissolved in THF (10 mL). Small amounts of methanol were added slowly and with rapid stirring, until an opaque solution resulted. The solution was then centrifuged until phase separation, and the supernatant solution was analyzed by SEC-RI (SEC-UV for the case of anthracenylidene containing macrocycles). This procedure was repeated until the high MW fraction formed by intermolecular coupling was removed without affecting the SEC MW and MW distribution. The fractionated macrocyclic P2VN was then precipitated quantitatively by addition of large amounts of methanol (150 mL) or aqueous methanol (CH_3OH/H_2O, 5/1 v/v) for the case of samples with DP_n below 20. The cycles were then filtered and dried in vacuum at 40 °C for 2 days.

5.3 Macrocyclic P2VN Containing Single 1,4-Benzylidene Linkage

Narrow molecular weight distribution (PDI's in the range 1.11 to 1.26) macrocyclic P2VN with DP_n's from 12 to 120 were synthesized in THF at –78 ºC in the presence of potassium ion by end-to-end coupling (10^{-6}–10^{-5} M anion concentration) using 1,4-bis(bromomethyl)benzene (DBX). The linear analogues with the same MW were prepared by protonation of the P2VN dianion using methanol. The use of DBX as a coupling reagent introduces a 1,4-benzylidene unit into the polymer backbone that may affect some properties of macrocyclic P2VN, such as glass transition temperatures (T_g) or hydrodynamic size making the rings larger and less regular compared for instance with a single methylene group. Although the presence of 1,4-benzylidene unit in macrocyclic PS was found to affect spectroscopic properties,[1] this should not be the case for P2VN as absorption and emission of 1,4-benzylidene is negligible compared with those of P2VN.[2,3] The use of coupling reagents, such as dibromomethane, is not desirable, as in this case side reactions will lead to the formation of spectroscopically active vinylaromatic chain end groups or head-to-head coupled chains.[4]

Two experiments (Table 5.1, # 80 and 81) were run at a relatively high polymer anion concentration (2.2×10^{-3} and 3.2×10^{-3} M) in order to determine the efficiency of the intermolecular coupling reactions. The SEC chromatogram of this reaction product shows three new peaks (Figure 5.1). The broad peak centered at 12 mL is the intended "polycondensation" product of high molecular weight (M_p=112,000) (Chapter 3, # 80). The peaks at 15.5 and 14.5 mL represent, respectively, macrocyclic P2VN and macrocyclic dimer formed by one inter- and one intramolecular coupling. The clear and symmetrical shift in the SEC trace from the P2VN precursor at 15.0 to 15.5 mL for macrocyclic P2VN and the presence of a significant fraction of macrocyclic polymer dimer show an interesting preference for P2VN-K_2 to form macrocycles even at a relatively high anion concentration. The M_n of the high MW fraction (M_n = 101,600) indicates a high efficiency of coupling as this MW is 17 times that of the linear precursor (Table 5.1). Following the simplified Carothers expression[5] for the degree of polymerization (DP_n) of this step polymerization we have:

$DP_n = 2 / (2-pf_{av})$ (1) $DP_n = 2 / (2-f_{av})$ (2) $f_{av} = \Sigma N_i.f_I / \Sigma N_i$ (3)

where p, and, f_{av}, denote the extent of reaction and the average functionality, respectively, and where N_i and f_i are the numbers of "monomer" (i =1), "dimer" (i =2), "trimer" (i = 3), etc. molecules formed by this step polymerization. In the present case, the conversion, p, is taken as unity as all the anion has reacted so that equation (1) reduces to (2). From the equation (2), the average functionality of P2VN-K_2 for our conditions is equal to 1.88 and shows that under the reaction conditions approximately six percent of the total polymer anion might have been inadvertently terminated during the cyclization process. The probability that the P2VN chains are terminated at both chain-ends is equal to 0.0036 (0.06×0.06), so that the fraction of the linear precursor in the cyclization product appears to be negligible. This figure is probably overestimated given that the number average MW of the high MW polycondensate fraction is not corrected for the plausible presence of higher MW cycles that are not accounted for in the derivation of the Carothers equation and without which the experimental M_n values would have been higher. On the other hand, the extent of occurrence of side reactions under high dilution conditions may differ from that at higher concentrations (see below).

There are several possible causes for termination processes including the lack of purity in the coupling agent or the inadvertent termination of the anions during polymerization. However, these are most likely of minor importance given the rigorous purification procedures and polymerization conditions. The most plausible cause for the lower "functionality" is the occurrence of side reactions such as base mediated eliminations that have been demonstrated for the case of the formation of macrocyclic polystyrene by similar coupling reactions. As indicated above, the low estimated fraction of linear polymers with the same DP_n as the macrocycle is based on the assumption that the yield of the coupling reaction is not affected by the anion concentration. This is most likely not the case, and the presence of less than about 5 percent of linear chains can not be excluded. All higher MW linear and macrocyclic polycondensates are readily removed from the targeted macrocyclic P2VN by fractionation procedures as described in the Experimental Section.

A number of cyclizations were carried out at lower concentrations (Table 5.1). The efficient formation of P2VN macrocycles is confirmed by the expected changes in hydrodynamic size, compared to that of the matching linear chains.[6] The elution volume of the main peak of the unfractionated cyclic polymer is larger than that of the matching linear polymer since the macrocycle has a smaller hydrodynamic volume (Figure 5.2). As shown in Table 5.1 (# 83-99), the <G> values representing the ratio of the apparent peak MW (M_p) of the macrocycle in the unfractionated products divided by that of the linear precursor steadily decrease from 0.86 to 0.71 as the polymerization degree (DP_n) increases from 11 to 125. Such trends are common for macrocyclic polystyrene (PS),[7-10] poly(2-vinylpyridine) (P2VN),[10] poly(α-methylstyrene) (PAMS)[11,12] and macrocyclic block copolymers, such as PS-b-polydimethylsiloxane[13] and PS-b-P2VP.[14]

The above procedures allow the isolation of pure macrocyclic P2VN in high yields (> 70%) and preparation of matching pairs of linear and macrocyclic polymers (Table 5.2, Figure 5.2) having the same number average degree of polymerization (DP_n) and polydispersity (PDI). The fractionated macrocyclic P2VN's and corresponding linear precursors were used to study glass transition temperature (T_g) and thermal decomposition dependence with degree of polymerization. As shown in Table 5.2, the T_g values for linear P2VN are similar to those reported in literature.[15]

For a very high MW linear P2VN (DP_n = 8120) prepared by an inadvertent $LiAlH_4$ initiated polymerization in THF (sample X, Table 5.2, Chapter 3) we observed a 'limiting' value of T_g=152 ºC.[15,16] However, there are considerable differences for low MW P2VN prepared by different methods.[16,17] The T_g values reported here are the maxima of the respective DSC curves which deviate ± 2 º from the actual T_g values but were more straightforward to determine. The respective onset values are 6-8 º lower. This may account for discrepancies in the T_g values reported by different authors.

For linear P2VN the expected decrease of T_g is observed with decreasing molecular weight (Table 5.2, Figure 5.3). Thus, the difference in T_g between linear sample # 83 (DP_n = 18) and # 82 (DP_n = 960) is 35 ° (Table 5.2). The reported value[18] of T_g = 95±5 °C for linear P2VN with a DP_n of 10 fits this trend. However, it is of interest to note that, compared to the case of polystyrene, the glass transition temperatures of the P2VN macrocycles decrease relatively little with decreasing MW's giving rise to large T_g differences with the matching linear polymers (Figure 5.3). For instance, the ΔT_g value for sample # 83 (DP_n = 18) is 31 °, whereas for a PS of the same DP_n this difference is only 10 °.[10] The reason for this is unclear at present but may be due to lower flexibility of the conformationally more encumbered P2VN.

We also observed interesting differences in the thermal decomposition of linear and macrocyclic P2VN under non-oxidative conditions. A typical TGA curve for a low MW macrocyclic P2VN (Table 5.2, # 83) shows some decomposition at

300 ºC, seemingly at a lower temperature than the linear precursor that starts to decompose at 312 ºC (Figure 5.4). However, at higher temperatures the decomposition of the macrocyclic P2VN proceeds more slowly. Thus, a loss of 50 percent mass is observed at a temperature that is twelve degrees higher than that for the matching linear polymer. A similar trend was observed for cyclic PS-b-polydimethylsiloxane block copolymers where macrocycle was shown to have decomposition temperature 34 °C higher than that of the matching linear block copolymer.[14] These differences are probably attributable to the absence of chain ends in the macrocycles as the chain ends typically are involved in the initial cleavage reactions.[19] However, torsional and bond angle strain is expected to be higher in low MW macrocycles and this may be reflected in macrocyclic P2VN starting to decompose earlier (Figure 5.4 a). As the MW increases, the presence or absence of the polymer chain ends may become the factor that affects decomposition. Thus, the difference in decomposition temperatures becomes less pronounced in the case of higher MW P2VN (Figure 5.4 b) as the fraction of polymer chain ends decreases.

5.4 Macrocyclic P2VN Containing Single 9,10-Anthracenylidene Linkage

Incorporation of larger aromatic chromophores, such as anthracene, pyrene or perylene, into polymer main chain is of interest for studies of intramolecular energy transfer.[20,21] However, these molecules are prone to side reactions in the coupling of polymer anions with polycyclic aromatics due to their low oxidation-reduction potentials.[22] Thus, nucleophilic attack by PS anion on the anthracene moiety of 9,10-bis(chloromethyl)anthracene (BCMA) and similar derivatives gives reaction products lacking this chromophore or with multiple anthracene incorporation, presumably due to metal halogen exchange or electron transfer to anthracene.[23-27] Therefore we first tested the coupling reactions of P2VN-K_2 with BCMA at high anion concentrations (10^{-3} M, Table 5.1, # 103) in THF at –78 °C. As seen form Table 5.1, the apparent peak molecular weight of "polycondensation" product increases only by a factor of 5 which is considerably smaller than was observed for the DBX mediated coupling (Table 5.1, # 80) under similar conditions (Chapter 3). The SEC-RI trace of the BCMA coupled P2VN showed the presence of about 30 percent macrocyclic polymer and 10-20 percent of linear precursor in addition to the "polycondensation" product. In addition, the SEC-UV monitored at 405 nm where only anthracene absorbs showed multiple incorporation of AN into a "polycondensation"-type product. The coupling reactions of PSLi and BCMA in THF at –78 °C also gave multiple anthracene labeling consistent with lithium-halogen exchange.[27] The occurrence of significant side reactions at the high anion concentrations used here is in contrast to similar reactions of PS and poly(9,9-dimethyl-2-vinylfluorene) dianions with BCMA in the presence of potassium that allowed preparation of macrocycles containing a single anthracene unit.[28]

Taking into account the fact that multiple anthracene incorporation was observed only in the "polycondensation" product, we investigated the coupling of P2VNK_2 with BCMA under high dilution conditions. Surprisingly, the formation of macrocyclic P2VN containing a single 9,10-anthracenylidene unit proceeded well as indicated by a SEC symmetrical peak and a clear shift to a higher elution volume and a high SEC (Figure 5.5) yield (~ 70%) of what appears to be a macrocyclic P2VN. In addition, the <G> values follow the same trends obtained for the above DBX mediated P2VN cycles being slightly higher for the same MW's most likely on account of the larger 9,10-anthracenylidene spacer (Table 5.1, # 100 and 102). In this case, the SEC-UV of the "polycondensation" product at 405 nm indicated the occurrence of multiple (at least twice the mole fraction with respect to naphthalene units) incorporation of anthracene compared to the single incorporation into the macrocyclic P2VN. However, fractionation allowed efficient removal of this high MW product giving macrocyclic polymers containing single 9,10-anthracenylidene unit. The uniform incorporation of a single AN into macrocyclic P2VN was confirmed by identical RI and UV SEC traces of the fractionated macrocycles run at both 405 nm (anthracene absorption, Figure 5.6) and 295 nm, the wavelength where only naphthalene absorbs. The anthracene content in the fractionated macrocyclic P2VN calculated using the DP_n from the linear precursor (Table 5.2, # 102), absorption at 405 nm (Figure 5.7) and the extinction coefficient for 9,10-dimethylanthracene ($\varepsilon = 10{,}000$)[27] was found to be 90% confirming a high degree of anthracene incorporation. Finally, the UV-Vis spectrum (Figure 5.7) does not show the presence of chromophores other than naphthalene and anthracene (346, 365, 385 and 406 nm).

5.5 Spectroscopic Studies of Macrocyclic and Linear P2VN

It was recently found of macrocyclic vinylaromatic polymers, such as macrocyclic polystyrene (PS)[1,29] and poly(9,9-dimethyl-2-vinylfluorene)

5.7 References

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Table 5.1. Formation of macrocyclic P2VN by coupling of P2VN-K_2 and DBX or BCMA in THF at –78 °C[a]

#	**[I] mM**	**M_n^{th} $\times 10^{-3}$**	**P2VN-MeOH**			**P2VN-EX$_2$**			
			M_n $\times 10^{-3}$	**PDI**	**M_p[b] $\times 10^{-3}$**	**M_n $\times 10^{-3}$**	**PDI**	**M_p[b] $\times 10^{-3}$**	**<G>[c]**
80	3.2	5.70	6.00	1.12	7.00	11.7	5.22	5.45	0.78
81	2.2	5.70	5.60	1.12	6.50	11.5	3.86	5.24	0.80
109	30	0.55	0.74	1.34	0.95	0.94	2.65	0.92	0.96
99	15	1.10	1.15	1.16	1.25	1.15	2.48	1.07	0.86
92	8.0	1.50	1.60	1.16	1.80	1.67	2.87	1.53	0.85
83[d]	7.5	1.60	1.60	1.14	1.85	2.20	2.28	1.50	0.82
84	5.0	3.40	3.80	1.12	4.40	4.00	2.79	3.35	0.76
85	1.5	11.0	13.2	1.16	14.8	1.50	2.18	10.6	0.71
103[e]	4.5	2.30	2.50	1.15	2.89	4.70	2.83	15.0[f]	-
100[e]	20	0.85	1.00	1.18	1.10	1.15	2.70	0.98	0.89
102[e]	4.5	3.70	4.00	1.11	4.43	4.40	2.39	3.48	0.79

a) K-Naph was used as initiator. SEC analysis using RI detector and polystyrene standards. b) Apparent peak molecular weight. c) Ratio of apparent peak molecular weights of macrocyclic and linear P2VN. d) K-OMOHN was used as initiator. e) 9,10-bis(chloromethyl)anthracene (BCMA) was used as coupling reagent. f) Apparent peak molecular weight of the "polycondensation" product.

Table 5.2. Thermal properties of fractionated macrocyclic and matching linear P2VN containing single 1,4 benzylidene or 9,10-anthracenylidene units[a]

#	DP_n[b]	**P2VN linear**				**P2VN cyclic**			
		M_n ´10^{-3}	PDI	T_g °C	TGA °C	M_n ´10^{-3}	PDI	T_g °C	TGA °C
109	7	0.70	1.35	79		0.78[c]	2.30	76	
99	12	1.25	1.13	102		1.00	1.13	140	
92	17	1.75	1.13	113		1.58	1.12	150	
83	18	1.80	1.09	115	405	1.75	1.26	148	417
102[d]	39	4.00	1.11	132		3.15	1.13	151	
84	39	4.05	1.10	132	408	2.90	1.11	148	415
80	60	6.30	1.08	137					
85	118	12.3	1.16	145	401	11.1	1.12	151	406
68[e]	202	21.0	1.08	147					
73	330	34.3	1.10	150					
82	960	100	1.12	150					
X[f]	8120	845	1.12	152					

a) SEC analysis using RI detector and polystyrene standards. T_g is glass transition temperature, and TGA is temperature for 50% weight loss under N_2. b) Approximate values obtained by dividing respective SEC M_n's by MW of styrene. c) Not fractionated macrocyclic P2VN; contains ~5% of "polycondensation" product with Mn approx. 2 kD. d) Anthracene incorporation 90% as determined from DP_n and UV-Vis. e) See Chapter 4. f) See Chapter 3.

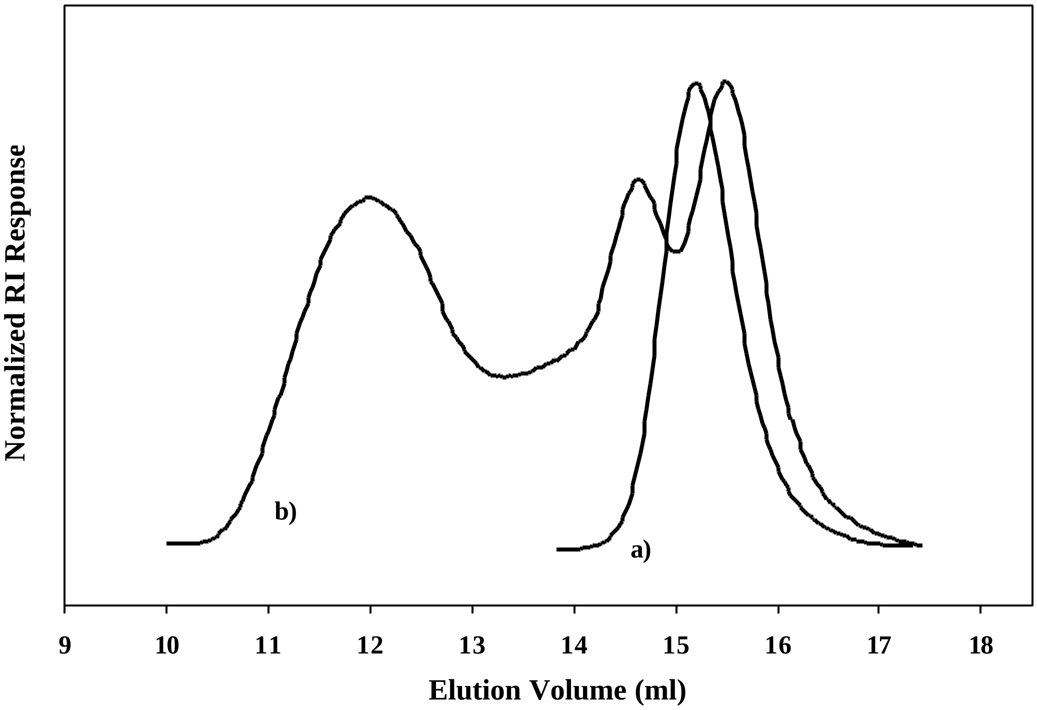

Figure 5.1. Normalized SEC (RI) traces of a) precursor P2VN and b) reaction product of high anion concentration coupling with DBX (Table 5.1, # 80).

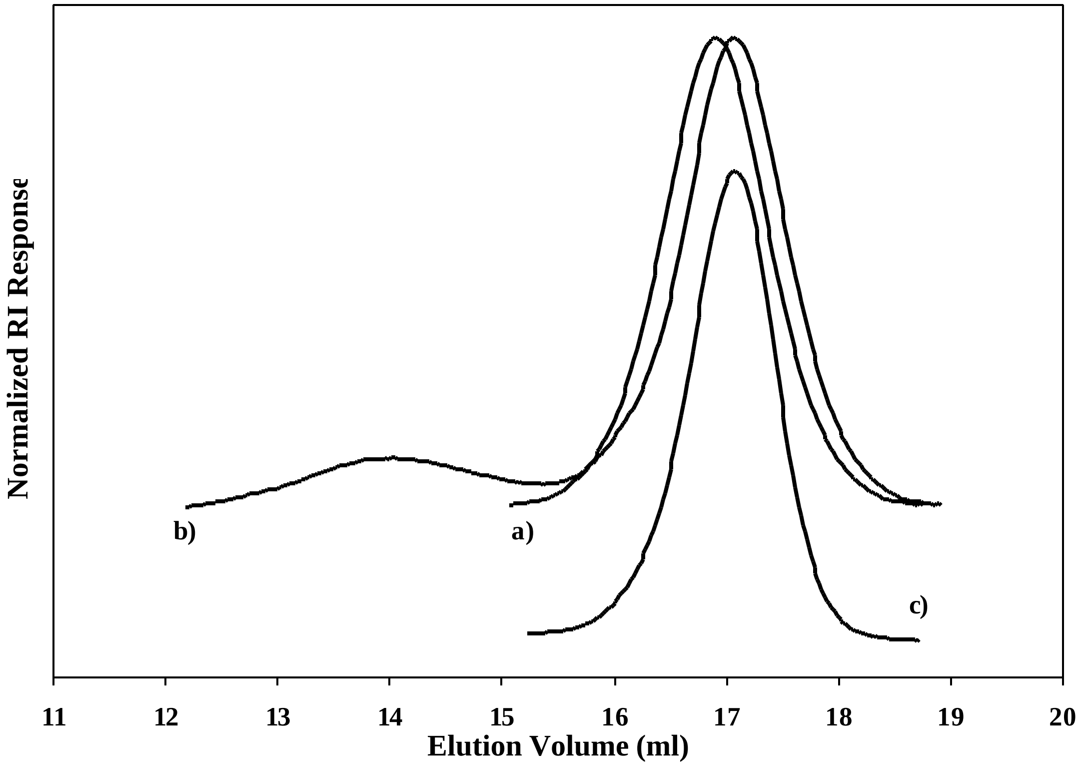

Figure 5.2. Normalized SEC (RI) traces of a) precursor P2VN, b) product of coupling with DBX under high dilution and c) fractionated macrocyclic P2VN (Table 5.1, # 92).

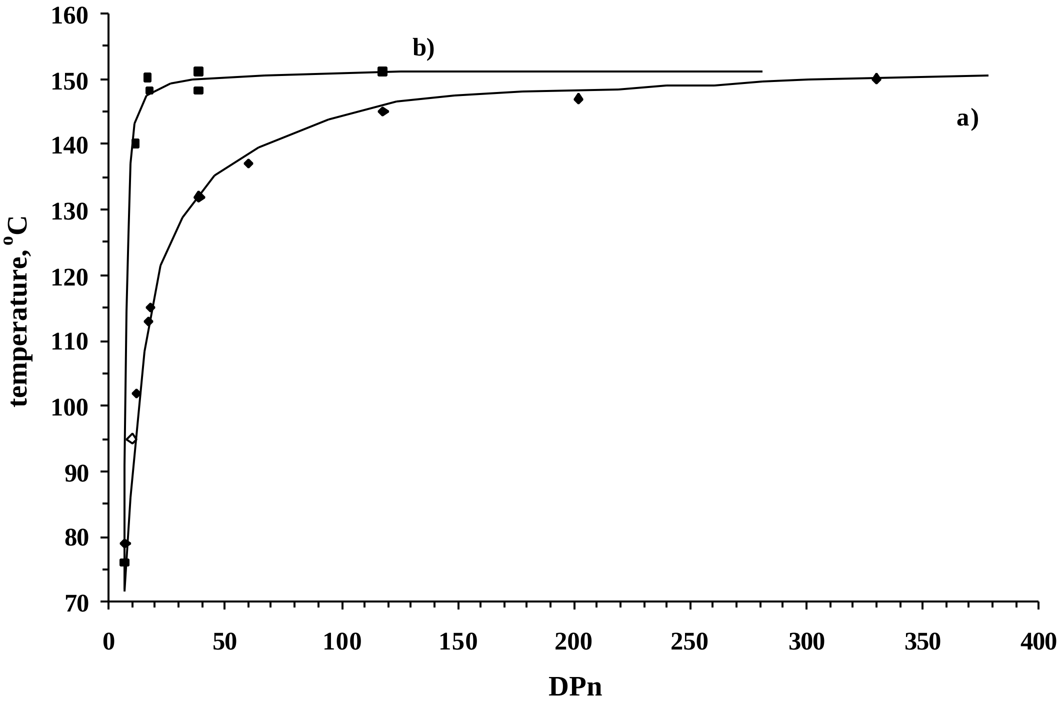

Figure 5.3. Relationship between glass transition temperature (T_g) and degree of polymerization of a) linear and b) macrocyclic P2VN (the data point of linear P2VN of a DP_n = 10 (open diamond) is taken from reference 18).

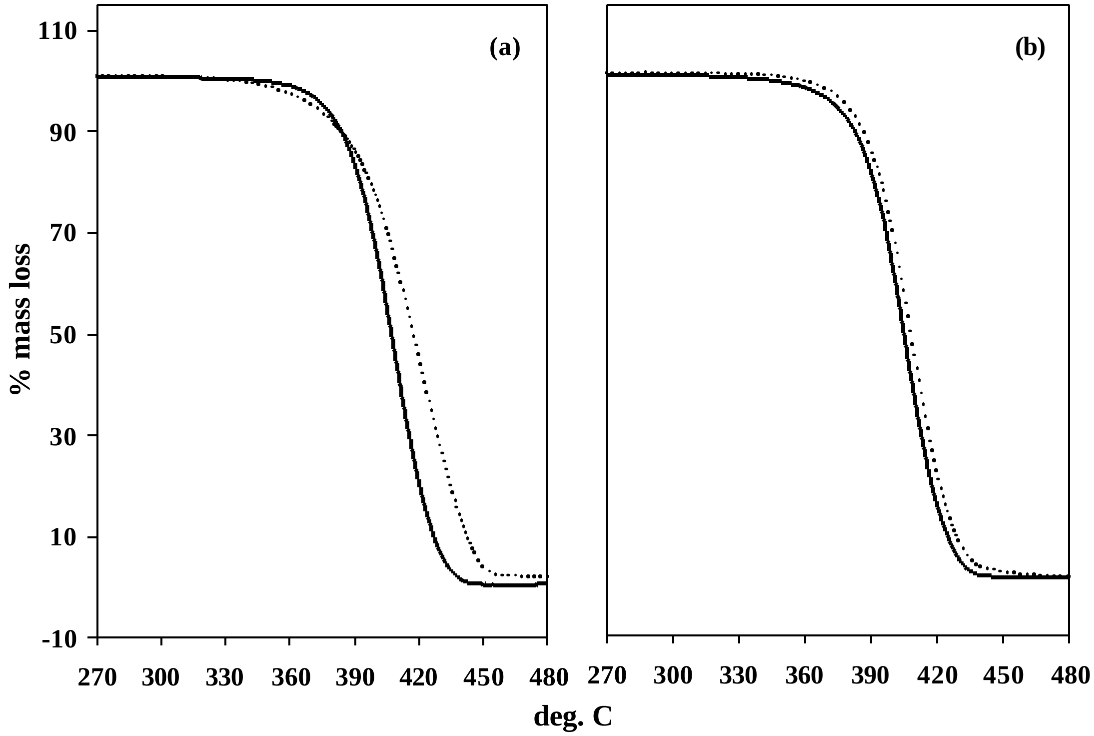

Figure 5.4. Differences in thermal non-oxidative decomposition (TGA) for linear(solid line) and macrocyclic P2VN (dashed line) with DP_n values of a) 18 (Table 5.2, # 83) and b) 125 (Table 5.2, # 85).

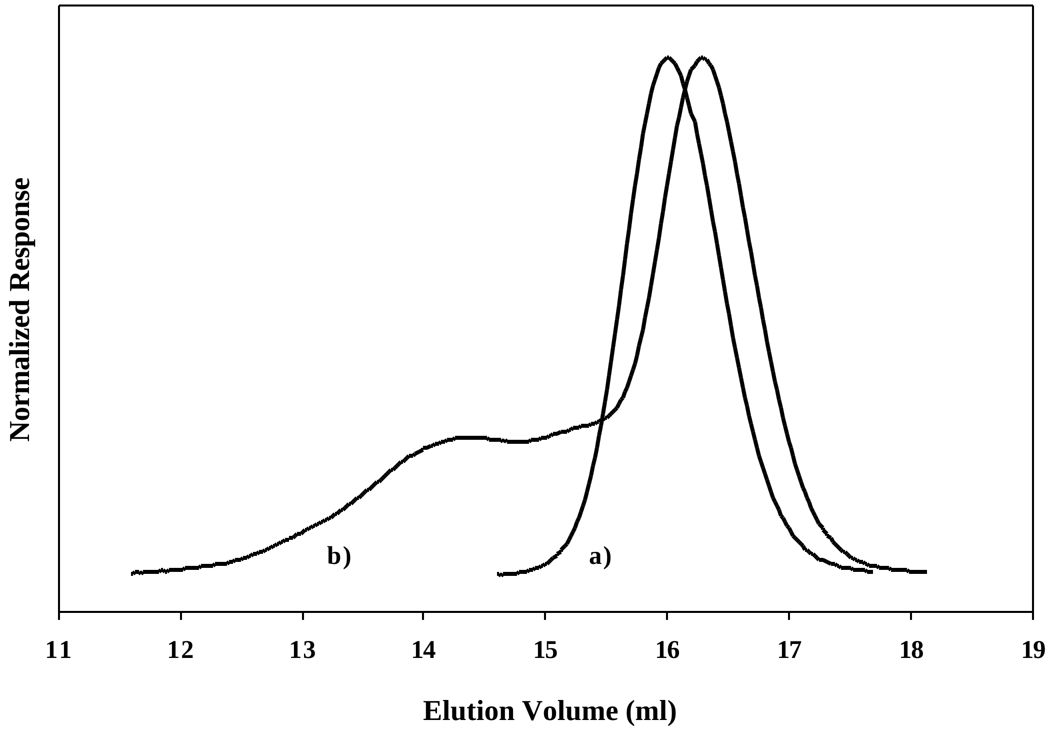

Figure 5.5. Normalized SEC (RI) traces of a) linear precursor and b) unfractionated product of high dilution coupling of P2VN-K_2 with BCMA (Table 5.1, # 102).

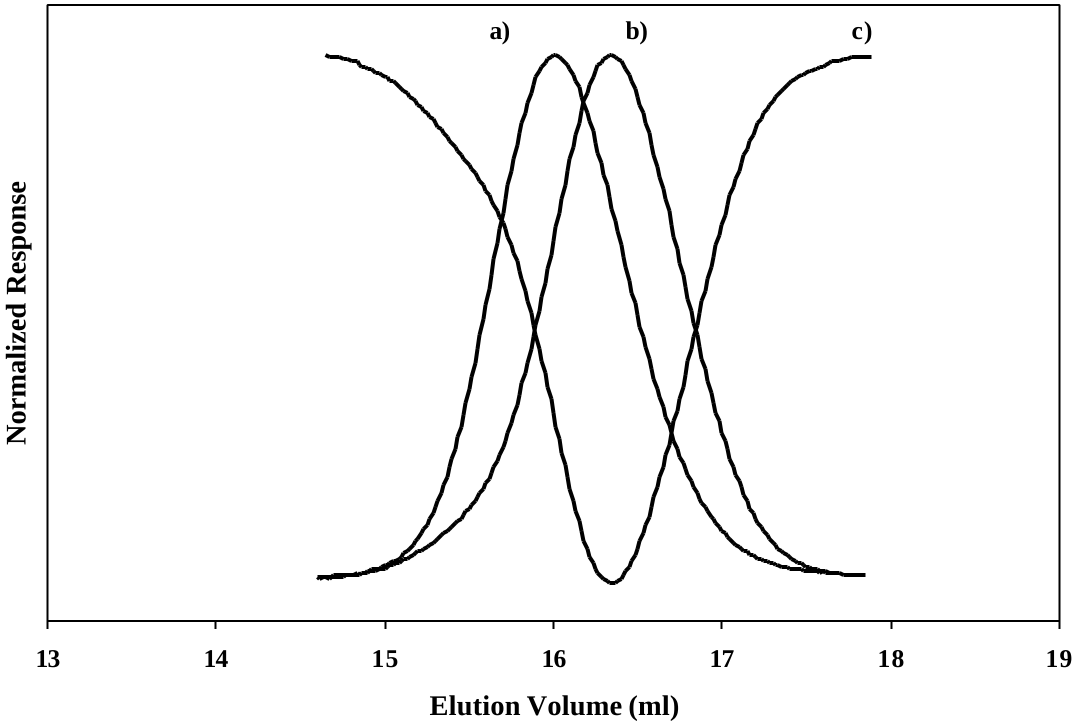

Figure 5.6. Normalized SEC traces of a) precipitated linear and b) fractionated macrocyclic P2VN acquired using RI and c) UV at 405 nm detectors (Table 5.2, # 102).

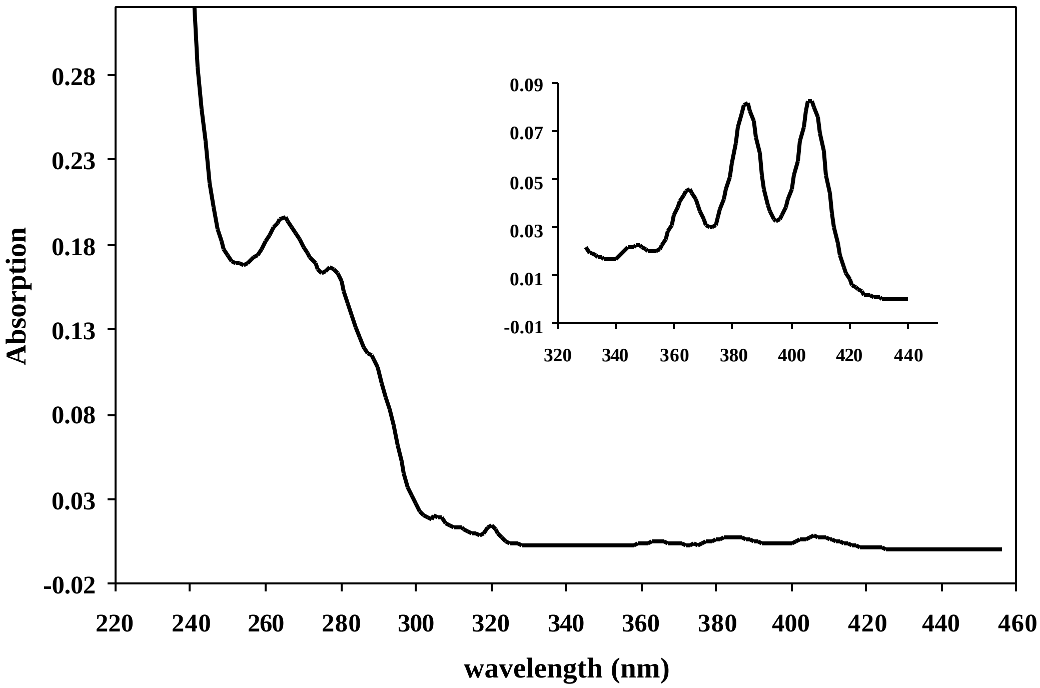

Figure 5.7. Absorption spectrum of fractionated macrocyclic P2VN with DP_n=39 (Table 5.2, # 102). containing 9,10-anthracenylidene group (54 mg/L in cyclohexane/THF : 80/20, v/v), 0.1 cm cell). Insert: is magnified 10×.