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

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ABSTRACT: The first synthesis of well-defined narrow molecular weight (MW) distribution macrocyclic poly(2-vinylnaphthalene) (P2VN) containing a single 1,4-benzylidene or 9,10-anthracenylidene unit is reported. The synthesis involves the potassium naphthalide (K-Naph) or potassium 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene (K-OMOHN) initiated polymerization of 2-vinylnaphthalene (2VN) in THF at −78 °C, followed by end-to-end coupling of the resulting P2VN dianions under high dilution conditions (10^{-6}−10^{-4} M). Narrow MW distribution (1.11−1.26) P2VN macrocycles with MW's between 740 and 13 200 have hydrodynamic volumes that are between 5% and 29% smaller than those of the matching linear chains. The glass transition temperatures of macrocyclic P2VN do not deviate from the limiting value (151 °C) of the high MW P2VN, decreasing only below a DP_n of about 20. Compared to the linear analogues, macrocyclic P2VN shows higher nonoxidative thermal decomposition stability.

Introduction

The synthesis of polymers with unconventional architectures, such as stars, combs, and rings, has received increased attention in recent years.[1−23] In particular, the topological restraints in macrocyclic polymers are manifested in their thermal and spectral properties that differ from those of the matching linear polymers of the same molecular weight (MW). For instance, low MW polystyrene[1,11,19] or poly(2-vinylpyridine) macrocycles[6,19] have significantly higher glass transition temperatures than their linear analogues.[1,6,19] Furthermore, the restricted mobility in low MW macrocycles appears to result in enhanced fluorescence.[20]

Macrocyclic polystyrene and similar vinylaromatic polymers were first synthesized by the naphthalene radical anion mediated initiation of the vinyl monomers and the end-to-end cyclization through alkylation of the resulting polymer dianions with coupling agents such as 1,4-bis(bromomethyl)benzene (DBX).[1−6] The reactions in THF are rapid as they involve highly reactive carbanions. The stoichiometric balance of carbanions and coupling agents is achieved by simultaneous addition of solutions of polymer dianion and coupling agent through internal dilution titration-like procedures in which a slight excess of the carbanions is maintained. These procedures allow high yields of unfractionated macrocycles in some cases (>90%). The reaction products usually are readily fractionated to give narrow MW distribution macrocycles. We have recently reported the synthesis of macrocyclic block copolymers using similar techniques.[22,23]

An alternative intramolecular coupling of α,ω-heterobifunctional polymers at high dilution has been successfully used to synthesize well-defined macrocyclic polymers.[11−15] Also, the "electrostatic self-assembly and covalent fixation" method has been used to prepare macrocyclic polystyrene (PS) and polytetrahydrofuran.[16,17]

Given the unusual fluorescence enhancements of low MW macrocyclic PS,[20] the synthesis of macrocyclic P2VN with its greater emission quantum yield compared to polystyrene (PS) is of interest.[24−27] The direct synthesis by end-to-end coupling of PS, P2VN and similar dianions in principle is especially desirable, as specific chromophores are conveniently introduced via the coupling reagent. Although the Li ion mediated anionic polymerization of 2VN in THF at −78 °C is living,[27] the degree of polymerization control was not sufficient to prepare P2VN rings and stars. Thus, the lithium naphthalide (Li-Naph)-initiated polymerizations produced polymers with relatively broad, nonsymmetrical MW distributions. (PDI's) of 1.40 and above, attributable to slow initiation−fast propagation as observed for many polymerizations of this type.[28] The use of a more efficient electron donor, 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene lithium (Li-OMOHN), did not significantly improve the polymerization control, giving polymers with MW distributions 1.30 and above.[29] However, the anionic polymerization of 2VN in THF −78 °C in the presence of potassium ion was shown to be both living and well controlled, giving predictable high MW's and narrow MW distributions (PDI < 1.10).[27] 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 a high efficiency of such coupling reactions.

Here we report the potassium ion 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^{-6}−10^{-4} M). Characterization of these polymers by size exclusion chromatography (SEC), proton NMR, UV−vis spectroscopy, and thermal methods indicates the synthesis of narrow MW distribution macrocyclic P2VN containing single 1,4-benzylidene or 9,10-anthracenylidene units.

Experimental Section

Materials. 2-Vinylnaphthalene (2VN, 5 g, Alfa Aesar, 95%) was dissolved in toluene (10 mL) and stirred under high

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Table 1. Formation of Macrocyclic P2VN by Coupling of P2VN-K_2 and DBX or BCMA in THF at −78 °C[a]

			P2VN linear			P2VN cyclic			
no.	[I], mM	$M_n^{th} \times 10^{-3}$	$M_n \times 10^{-3}$	PDI	$M_p{}^b \times 10^{-3}$	$M_n \times 10^{-3}$	PDI	$M_p{}^b \times 10^{-3}$	$\langle G \rangle^c$
1	3.2	5.70	6.00	1.12	7.00	11.7	5.22	5.45	0.78
2	2.2	5.70	5.60	1.12	6.50	11.5	3.86	5.24	0.80
3	30	0.55	0.74	1.34	0.95	0.94	2.65	0.91	0.95
4	15	1.10	1.15	1.16	1.25	1.15	2.48	1.07	0.86
5	8.0	1.50	1.60	1.16	1.80	1.67	2.87	1.53	0.85
6[d]	7.5	1.60	1.60	1.14	1.85	2.20	2.28	1.50	0.82
7	5.0	3.40	3.80	1.12	4.40	4.00	2.79	3.35	0.76
8	1.5	11.0	13.2	1.16	14.8	1.50	2.18	10.6	0.71
9[e]	4.5	2.30	2.50	1.15	2.89	4.70	2.83	15.0	
10[e]	20	0.85	1.00	1.18	1.10	1.15	2.70	0.98	0.89
11[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. Coupling agent was 1,4-bis(bromomethyl)benzene (DBX), except as indicated. [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.

vacuum over solid $LiAlH_4$ for 5 h at room temperature. Toluene was then distilled into a side flask, and the remaining 2VN sublimed at 60 °C into this flask. To remove residual $LiAlH_4$, toluene was distilled into the trap, and the monomer was sublimed 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.[29] THF was purified by distillation from Na/K-benzophenone followed by distillation from the stable carbanion 1,4-dipotassio-1,1,4,4-tetraphenylbutane (DD-K_2). Naphthalene (Aldrich, 99+%) and 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,-10-octahydronaphthacene[30] (OMOHN) were recrystallized from methanol, dried in vacuo, and dissolved in purified THF. Potassium naphthalide (K-Naph) and the corresponding salt of OMOHN were prepared by stirring naphthalene or OMOHN in THF over a potassium mirror for 15−20 min at 0 °C. The initiators were used immediately after preparation. The coupling reagents 1,4-bis(bromomethyl)benzene (DBX, TCI America, 98+%) and 9,10-bis(chloromethyl)anthracene (BCMA, TCI America, Inc., 98%) were recrystallized twice from chloroform, dried on a vacuum line for 24 h, and dissolved in purified THF to needed concentrations.

Polymerization. Polymerizations and cyclizations were run under high vacuum in THF at −78 °C in flamed glassware using Teflon valves and break-seal techniques as reported elsewhere.[31] Prior to polymerization, the entire apparatus 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 dropwise addition of 2VN (0.5 g in 5 mL, 3.3×10^{-3} mol, Table 1, no. 7) in a THF/toluene mixture (90/10 v/v) into a THF solution of potassium naphthalide (K-Naph, 2×10^{-4} mol 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^{-6}−10^{-4} M) by simultaneous dropwise addition of 30 mL of P2VN-K_2 (7.5×10^{-5} mol) and a THF solution of 1,4-bis(bromomethyl)benzene (DBX, 80 mL, 1×10^{-4} mol) 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 (2.5×10^{-5} mol) 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 precipitate macrocyclic P2VN of low molecular weight (DP_n < 20). The polymers were dried in a vacuum at 40 °C for 2 days.

Fractionation. The crude dried macrocyclic polymers recovered in quantitative yield were dissolved in THF (0.3 g in 10 mL, Table 1, no. 7). 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. 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, obtained in 40−70% isolated yields, was then precipitated quantitatively by addition of large amounts of methanol (100 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 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 a 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 and after precipitation and/or fractionation. Proton NMR was run on a Bruker AM-250 FT instrument operating at 250 MHz in $CDCl_3$. In the cases of anthracenylidene containing macrocycles, polymers were subjected to SEC-UV analysis at both $\lambda = 405$ and 295 nm. UV−vis absorption was run on a Varian Cary 50 spectrometer with a baseline correction using 50 mg/L P2VN solutions in cyclohexane/THF (90/10 v/v) mixtures and 1 mm quartz cells. Glass transition temperatures (T_g) were acquired with 5−10 mg of P2VN using a Perkin-Elmer DSC-7 instrument with a scanning rate 10 °C/min in two consecutive runs for each polymer sample. The T_g values from the second run are reported as the maxima on the DSC curves. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument under nitrogen flow (40 mL/min) with 5 mg of P2VN.

Results and Discussion

1,4-Benzylidene P2VN Macrocycles. Narrow molecular weight distribution (PDI's in the range 1.11−1.26) macrocyclic P2VN with DP_n's from 7 to 120 were synthesized in THF at −78 °C in the presence of potassium ion by end-to-end coupling (10^{-6}−10^{-4} 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 structurally less regular than those with a single methylene group. Although the presence of a 1,4-benzylidene unit in macrocyclic PS affects its spectroscopic properties,[32] this should not be the case for P2VN as absorption and emission of 1,4-benzylidene is negligible compared with those of P2VN.[33,34] The use of coupling reagents, such as dibromomethane, is not desirable, as side reactions,

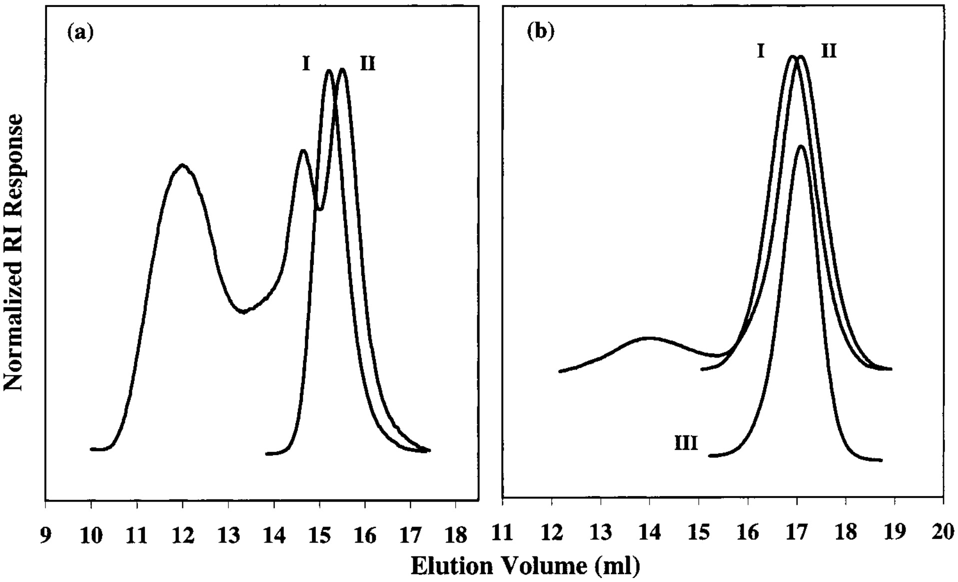

Figure 1. Normalized SEC (RI) traces of (a) poly(2-vinylnaphthalene) (P2VN) linear precursor (I) and reaction product of high concentration coupling with 1,4-bis(bromomethyl)benzene (DBX) (II) (Table 1, no. 1) and (b) precursor P2VN (I), product of coupling with DBX under high dilution (II) and fractionated macrocyclic P2VN (III) (Table 1, no. 5).

such as metal halogen exchange and elimination, will lead to the formation of spectroscopically active chain end groups or head-to-head coupled chains without the methylene unit.[35]

Two experiments (Table 1, no. 1 and 2) were run at relatively high polymer anion concentration (2.2×10^{-3} and 3.2×10^{-3} M, respectively) in order to determine the efficiency of the coupling reaction. The SEC chromatogram unexpectedly shows three new peaks (Figure 1a). The broad peak centered at 12 mL is the expected "polycondensation" product of high molecular weight (M_p = 112 000).[27] The peak at 15.5 mL represents a P2VN macrocycle with an apparent peak MW ($M_{p,c}$) of about 5500 that is appreciably lower than that of the matching linear P2VN precursor with a peak MW of 7000. The peak at 14.5 mL corresponding to M_p = 11 200 is almost exactly double that of the primary macrocycle, but not of the linear P2VN precursor (Table 1, no. 1) and is attributed to the macrocyclic dimer formed by one intermolecular and one intramolecular coupling. The clear shift from 15.0 to 15.5 mL for macrocyclic P2VN, the very similar shapes for the linear and macrocyclic P2VN, and the presence of a significant fraction of macrocyclic polymer dimer show an interesting tendency to form macrocyclic P2VN even at the high anion concentrations used in this case. 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 1). Following the simplified Carothers expression[36] for the degree of polymerization (DP_n) of this step polymerization, we have

$$DP_n = 2/(2 - pf_{av}) \quad (1)$$

$$DP_n = 2/(2 - f_{av}) \quad (2)$$

$$f_{av} = \sum N_i f_I / \sum N_i \quad (3)$$

where p and f_{av} denote the extent of reaction and the average functionality, respectively, and N_i and f_i are the number 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 since all the anion has reacted so that eq 1 reduces to eq 2. From eq 2, the apparent average functionality of P2VN-K_2 for our conditions is equal to 1.88 and shows that approximately 6% 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 linear precursor in the cyclization product appears to be negligible under these conditions.

There are several possible causes for this relatively minor termination, including impurities in the monomer and coupling agent and/or inadvertent termination of the anions during polymerization. However, these are most likely of minor importance given the polymerization conditions. The most plausible cause for the lower apparent "functionality" of the P2VN precursor is the occurrence of side reactions such as base-mediated intramolecular elimination reactions of 2-naphthyl bromide end group impurities generated by metal halogen exchange.[35] These are expected to give olefinic end groups, the fluorescence of which was detected in the formation of macrocyclic polystyrene by similar coupling reactions. Finally, although coupling appears to proceed cleanly at high concentrations, 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 reactions is not affected by the anion concentration. This is most likely not the case as the presence of free P2VN anions at the high dilution used in the cyclization−coupling reactions may lead to a greater fraction of side products. Thus, the presence of less than about 5% of linear chains, which appears to be the lowest detectable fraction, cannot be excluded. All other higher MW linear and macrocyclic polycondensates are readily removed from the mixture with the primary macrocyclic P2VN by fractionation procedures as described in the Experimental Section.

Under high dilution conditions, the more efficient formation of P2VN macrocycles is confirmed by the expected changes in hydrodynamic size (Table 1, no. 3−8). The elution volume of the main peak of the unfractionated cyclic polymer is larger than that of the

Table 2. Thermal Properties of Fractionated Macrocyclic and Matching Linear P2VN Containing Single 1,4-Benzylidene or 9,10-Anthracenylidene Units[a]

		P2VN linear				P2VN cyclic			
no.	DP_n[b]	$M_n \times 10^{-3}$	PDI	T_g, °C	TGA, °C	$M_n \times 10^{-3}$	PDI	T_g, °C	TGA °C
1	7	0.72	1.34	79		0.79	2.30[c]	76	
2	12	1.25	1.13	102		1.00	1.13	140	
3	17	1.75	1.13	113		1.58	1.12	150	
4	18	1.80	1.09	115	405	1.75	1.26	148	417
5[d]	39	4.00	1.11	132		3.15	1.13	151	
6	39	4.05	1.10	132	408	2.90	1.11	148	415
7	60	6.30	1.08	137					
8	118	12.3	1.16	145	401	11.1	1.12	151	406
9[e]	202	21.0	1.08	147					
10	330	34.3	1.10	150					
11	960	100	1.12	150					
12[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] This polymer contained 5% of "polycondensation" product. [d] Anthracene incorporation 90% as determined from DP_n and UV–vis. [e] See ref 50. [f] See ref 26.

matching linear polymer since the macrocycle has a smaller hydrodynamic volume (Figure 1b). As shown in Table 1 (no. 3–8), 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 0.95 to 0.71 as the polymerization degree (DP_n) increases from 7 to 125. The origin of this systematic trend is not completely understood but may be due to the severe conformational restraints in the cycles as the number of monomer units decreases. Such systematic trends are common for macrocyclic polystyrene (PS),[1–5,19] poly(2-vinylpyridine) (P2VN),[6,19] poly(α-methylstyrene) (PAMS),[21] and macrocyclic block copolymers such as PS-*b*-poly(dimethylsiloxane)[22] and PS-*b*-P2VP.[23] The existence of a clear decrease of ⟨*G*⟩ with increasing MW's would seem to be consistent with, if not provide support for, the formation of cycles.

The proton NMR spectra of a P2VN macrocycle coupled with DBX and its matching linear polymer (Table 1, no. 7; Table 2, no. 6) provide additional evidence for the presence of the benzylidene unit in the cycle (Figure 2). Thus, a new broad downfield resonance is visible at 3.40 ppm corresponding to four benzylic methylene protons. The broadness of this resonance is due in part to the geminal coupling of the methylene protons that are diastereotopic due to the presence of the nearby asymmetric center and to vicinal coupling with the 2-naphthyl methine proton that is also visible at 2.50 ppm. The resonance at 2.30 ppm for the linear P2VN is due to the 2-naphthylmethylene end group and differs from the corresponding 2-naphthylmethine proton in the cycle observed at 2.50 ppm.

The above procedures allow the isolation of macrocyclic P2VN in high chromatographic yields (>70%) and preparation of matching pairs of linear and macrocyclic polymers (Table 2, Figure 1b) 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 the dependence of the glass transition temperature (T_g) and thermal decomposition on the degree of polymerization. As shown in Table 2, the T_g values for linear P2VN are similar to those reported in the literature.[37–39] For a very high MW linear P2VN (DP_n = 8120) prepared by an inadvertent $LiAlH_4$-initiated polymerization in THF,[29] we observed a presumably limiting value of T_g = 152 °C.

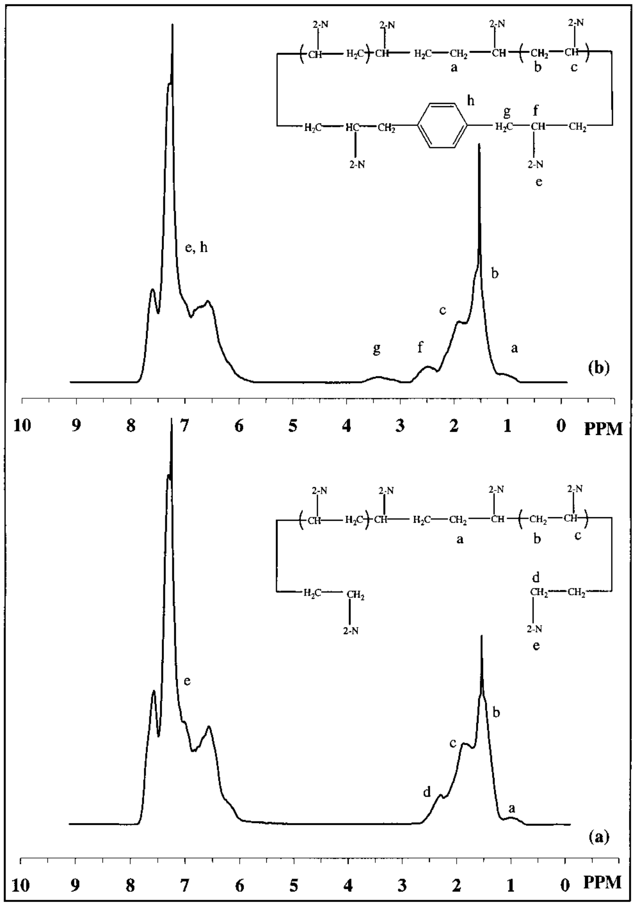

Figure 2. 250 MHz proton NMR of (a) linear protonated precursor poly(2-vinylnaphthalene) (P2VN) (DP_n = 39) and (b) 1,4-bis(bromomethyl)benzene (DBX) coupled fractionated macrocyclic P2VN (Table 1, no. 7; Table 2, no. 6).

For linear P2VN, a T_g decrease is observed with decreasing molecular weight (Table 2, Figure 3), as expected. The reported value[40] of T_g = 95 ± 5 °C for linear P2VN with a DP_n of 10 fits this trend. However, the glass transition temperatures of the P2VN macrocycles (150 °C) are independent of MW above a DP_n of about 20. The slightly lower T_g value of macrocycle no. 4 (Table 2) may be due to the presence of some lower MW polymer consistent with the relatively wide MW distribution of this sample. However, there is a sharp decrease in T_g at lower DP_n's giving rise to large T_g differences with the matching linear polymers that vary

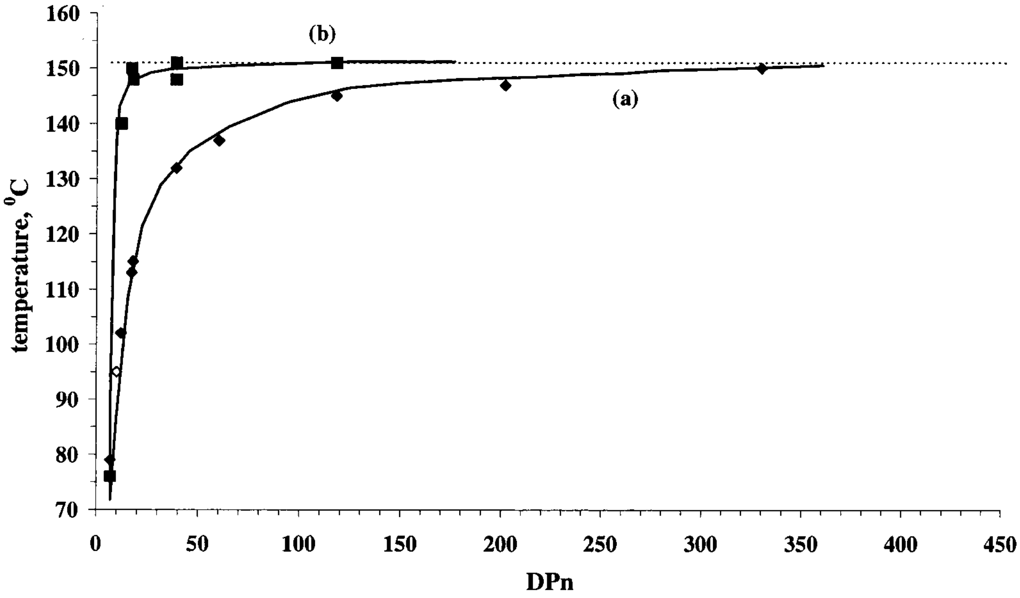

Figure 3. Relationship between glass transition temperature (T_g) and degree of polymerization (DP_n) of (a) linear and (b) macrocyclic P2VN. (The data point of linear P2VN of a $DP_n = 10$ is taken from ref 40.)

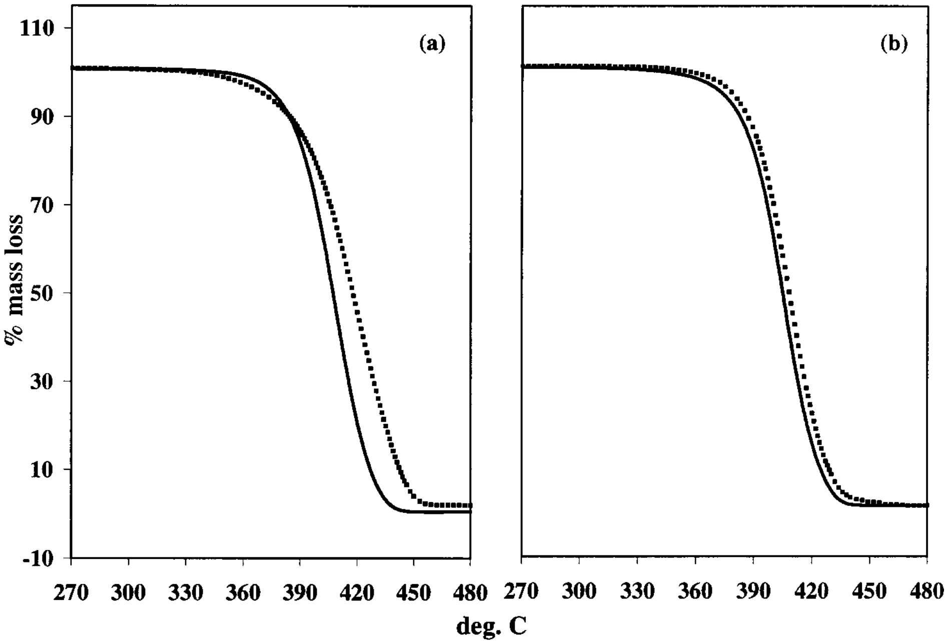

Figure 4. Differences in thermal nonoxidative decomposition (TGA) for linear (—) and macrocyclic P2VN (· · ·) with DP_n values of (a) 18 (Table 2, no. 4) and (b) 125 (Table 2, no. 8).

from about 30 to 40 °C (Figure 3). These differences for macrocyclic and linear PS in this DP_n range are 10−20 °C.[19] The reason for this is unclear at present but may be due to the lower flexibility of the conformationally more encumbered macrocyclic P2VN.

We also observed interesting differences in the thermal decomposition behavior of linear and macrocyclic P2VN under nonoxidative conditions. A typical TGA curve for a low MW macrocyclic P2VN (Table 2, no. 4) shows some decomposition at 300 °C, seemingly at a lower temperature than the linear precursor that starts to decompose at 312 °C (Figure 4). However, at higher temperatures the decomposition of the macrocyclic P2VN proceeds more slowly. Thus, a loss of 50% mass is observed at a temperature that is 12 °C higher than that for the matching linear polymer. Similar trends are observed for cyclic PS and PS-*b*-poly(dimethylsiloxane) block copolymers.[22] These differences are probably attributable to the absence of chain ends in the macrocycles.[41]

9,10-Anthracenylidene P2VN Macrocycles. Incorporation of larger aromatic chromophores, such as anthracene, pyrene, or perylene, into a polymer main chain is of interest for studies of intramolecular energy transfer.[25,26] However, these chromophores are prone to side reactions in the coupling of polymer anions with polycyclic aromatics due to their low oxidation−reduction potentials.[42] Thus, nucleophilic attack by PS anion on the anthracene moiety of 9,10-bis(chloromethyl)anthracene and similar derivatives leads to multiple anthracene incorporation, presumably due to metal halogen exchange or electron transfer to anthracene.[43−47] Therefore, we first tested the coupling reactions of P2VN-K_2 with BCMA at high anion concentrations (10^{-3}

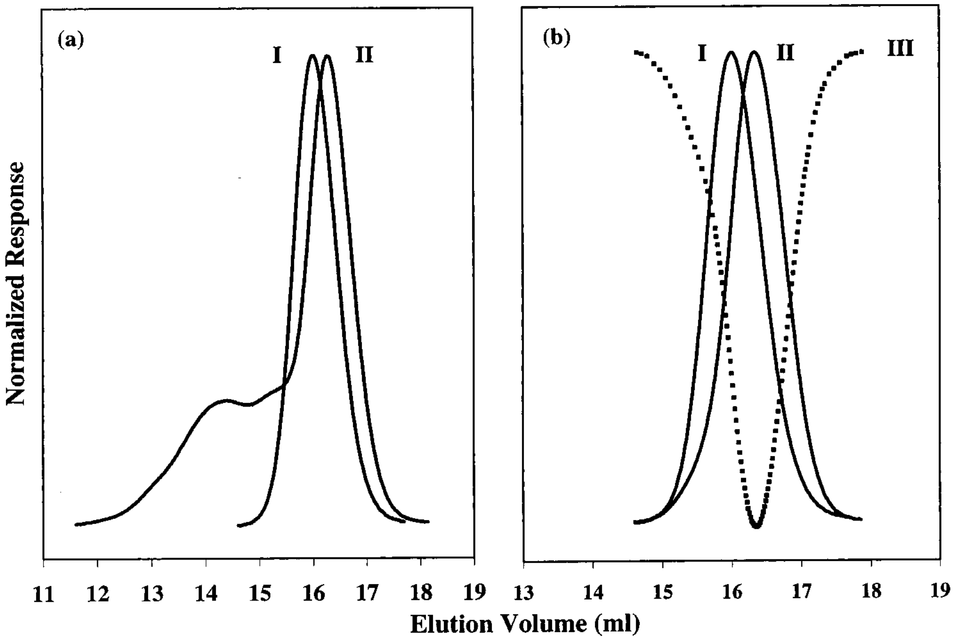

Figure 5. Normalized SEC (RI) traces of (a) linear precursor (I) and unfractionated product of high dilution coupling of P2VN-K_2 with 9,10-bis(chloromethyl)anthracene (BCMA) (II) (Table 1, no. 11) and (b) fractionated linear (I) and macrocyclic P2VN acquired using RI (II) and UV at 405 nm (III) detectors (Table 2, no. 5).

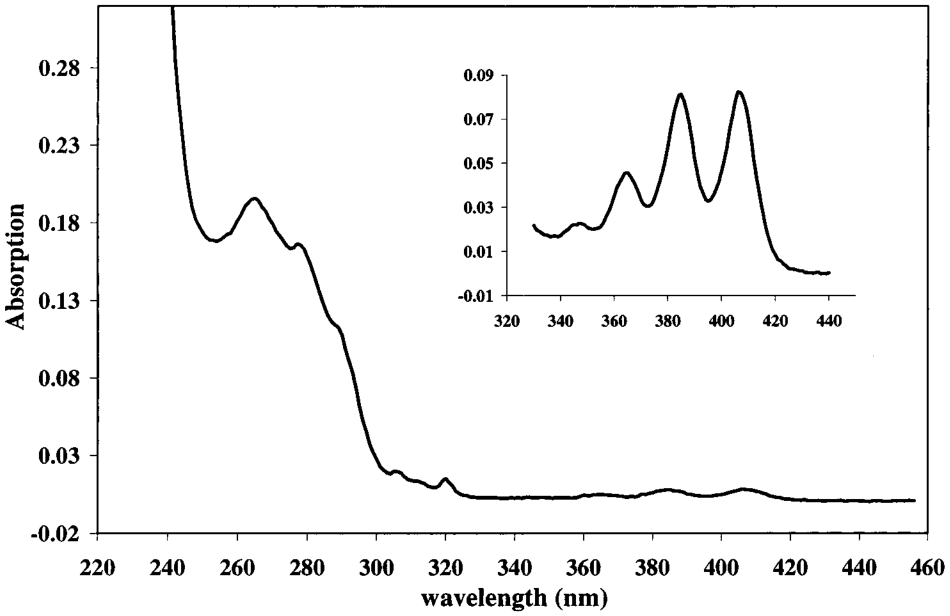

Figure 6. Absorption spectrum of fractionated macrocyclic P2VN (Table 2, no. 5) containing 9,10-anthracenylidene group (54 mg/L in cyclohexane/THF: 80/20, v/v, 0.1 cm cell). Inset is magnified 10 times.

M, Table 1, no. 9) in THF at −78 °C. As seen form Table 1, the apparent peak molecular weight of "polycondensation" product increases only by a factor of 5, which is considerably smaller compared to DBX coupling (Table 1, no. 1) run at similar conditions.[27] The SEC-RI trace of the BCMA coupled P2VN showed the presence of 30% macrocyclic polymer and 10−20% 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. Similar reactions of PSLi and BCMA in THF at −78 °C also gave multiple anthracene labeling consistent with lithium−halogen exchange.[47] 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.[48]

Surprisingly, the BCMA mediated formation of macrocyclic P2VN containing a single 9,10-anthracenylidene unit proceeded well under high dilution conditions as indicated by a symmetrical SEC peak and a clear shift to a higher elution volume and a high SEC (Figure 5a) yield (70%) of what appears to be a macrocyclic P2VN. In addition, the $\langle G \rangle$ 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 1, no. 10 and 11). In this case, the SEC-UV of the "polycondensation" product at 405 nm indicated the occurrence of multiple (at least twice) 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 units. 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 5b) 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 2, no. 5), absorption at 405 nm (Figure 6), and the extinction coefficient for 9,10-dimethylanthracene ($\epsilon = 10\,000$)[48] was 90%, confirming a high degree of anthracene incorporation. Finally, the UV−vis spectrum (Figure 6) does not show the presence of chromophores other than naphthalene and anthracene (346, 365, 385, and 406 nm). Studies on the photophysics of these labeled macrocycles are being carried out.[49]

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