Potassium Ion Mediated Living and Controlled Anionic Polymerization of 2-Vinylnaphthalene (2VN). Synthesis of P2VN-*b*-poly(α-methylstyrene) and P2VN-*b*-poly(9,9-dimethyl-2-vinylfluorene) Block Copolymers

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ABSTRACT: The anionic polymerization is reported of 2-vinylnaphthalene (2VN) initiated with potassium naphthalide (K-Naph), potassium 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene (K-OMOHN), and α-methylstyryldipotassium oligomers (AMS-K_2) in tetrahydrofuran at −78 °C. Narrow molecular weight distributions are obtained with good agreement of calculated and observed molecular weights. It is also possible to prepare poly(2-vinylnaphthalene) (P2VN) of very high molecular weight (as high as 90 000) and narrow polydispersity indices (PDI as low as 1.06). Under the above conditions, the P2VN-K_2 has a shelf life exceeding 1 h as indicated by polymerization resumption experiments giving P2VN with statistical narrowing of the molecular weight distribution. The living character of the P2VN-K_2 dianion was also demonstrated by the synthesis of narrow molecular weight distribution poly(α-methylstyrene)-*b*-P2VN-*b*-poly(α-methylstyrene), P2VN-*b*-poly(α-methylstyrene)-*b*-P2VN, and poly(9,9-dimethyl-2-vinylfluorene)-*b*-P2VN-*b*-poly(9,9-dimethyl-2-vinylfluorene) triblock copolymers and by quantitative end-functionalization with 1,4-bis(bromomethyl)benzene.

Introduction

In the past few years there has been a renewed interest in the synthesis and properties of macrocyclic vinylaromatic polymers.[1−11] We and others have shown that macrocyclic polymers differ from the corresponding linear precursors in their hydrodynamic, thermal, and spectroscopic properties.[1−8] For instance, compared to the matching linear polystyrene (PS), low MW (M_n < 10 000) macrocyclic PS shows higher emission, the differences increasing with decreasing MW.[8] The potential of macrocyclic aromatic vinyl polymers in modeling natural light-harvesting systems[12,13] prompted us to investigate the synthesis of macrocyclic poly(2-vinylnaphthalene), one of the most extensively studied vinylaromatic polymers other than polystyrene.[14−16] As this requires the synthesis and quantitative intramolecular alkylation of narrow molecular weight distribution (MWD) P2VN dianion, following previous methods, the living polymerization of 2VN is of interest.

Although the well-controlled anionic polymerization of 2-isopropenylnaphthalene (2IPN) has been reported,[17] the corresponding polymerization of 2-vinylnaphthalene (2VN) has not. 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 produces low MW P2VN (M_n < 5000) with broadened molecular weight distributions.[18] A more careful investigation 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.

Table 1. Radical Anion Initiated Polymerizations of 2-Vinylnaphthalene in THF at − 78 °C[a]

no.	initiator I	[I], mM	[2VN], mM	DP_n (calcd)	P2VN-MeOH M_n	P2VN-MeOH PDI
1	Li-Naph	6.5	55	17	2300	1.40
2	Li-OMOHN		44		9500	1.30
3	K-Naph	6.1	91	30	3900	1.15
4	K-OMOHN	2.6	62	48	5600	1.10
5[b]	K-OMOHN		90		88000	1.15
6	AMS-K_2	2.0	65	65	7600	1.07

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

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. Here we report that 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, P2VN can be prepared with very high molecular weight (as high as 90 000) and 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.

Experimental Section

Materials. 2-Vinylnaphthalene (2VN, Alfa Aesar, 95%) was dissolved in THF and purified by two vacuum sublimations from CaH_2 (method A, experiments 3, 4, 6, Table 1) or dissolved in toluene, stirred over solid $LiAlH_4$, and vacuum-sublimed from $LiAlH_4$ followed by one sublimation from CaH_2 to remove residual $LiAlH_4$ (method B).[18] Purified THF was then added to give THF/toluene (90/10 v/v) mixtures that were used

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Table 2. Restart and Block Copolymerization Involving P2VN-K$_2$[a]

		P(M1)						P(M2)-*b*-P(M1)-*b*-P(M2)				
no.	[I],[b] mM	M1	[M1], mM	t_1, min	$M_{n,th}$	M_n	PDI	M2	[M2], mM	t_2, min	M_n	PDI
1	3.1	2VN	26	60	1740	1550	1.14	2VN	100	10	14500	1.06
2	4.0	2VN	34	10	1770	2040	1.13	DMVF	85	15	9500	1.07
3	5.4	2VN	48	15	1850	3000	1.14	AMS	200	70	4170[c]	1.13
4	17	AMS	150	180	1840	1750[d]	1.09	2VN	250	5	11400	1.07

[a] Polymerizations of monomer 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. 2VN = 2-vinylnaphthalene, AMS = α-methylstyrene, DMVF = 9,9-dimethyl-2-vinylfluorene. [b] Initiator: K-OMOHN (nos. 1, 2), K-Naph (nos. 3, 4). Initiator concentrations are based on 100% conversion of aromatic hydrocarbon into radical anion. [c] Conversion of AMS (gravimetrically) is 8%. [d] Conversion of AMS (gravimetrically) is 50%.

Table 3. Coupling Reactions of P2VN-K$_2$ and DBX in THF at −78 °C[a]

				P2VN-MeOH			P2VN-DBX		
no.	[I], mM	[2VN], mM	t_p,[b] min	M_n	PDI	M_p	M_n	PDI	M_p[c]
1	3.2	80	5	6000	1.12	7000	11 700	5.22	112 000
2	2.2	60	60	5600	1.12	6500	11 500	3.86	82 200

[a] 1,4-Bis(bromomethyl)benzene (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.

directly for polymerizations. 9,9-Dimethyl-2-vinylfluorene (DMVF) was synthesized and purified as reported earlier.[19] α-Methylstyrene (AMS, Aldrich, 99%) was distilled from CaH$_2$ followed by distillation from dibutylmagnesium. The monomers were then diluted to needed concentrations in purified THF and distributed into ampules equipped with break-seals. THF was purified by distillation from Na/K-benzophenone followed by distillation from 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[20] (OMOHN) were recrystallized from methanol, dried in a vacuum, and dissolved in purified THF. Potassium or lithium naphthalide (K(Li)-Naph) and corresponding salts of OMOHN were prepared by stirring naphthalene or OMOHN in THF over a potassium mirror or in the presence of carefully cleaned lithium chunks for 15−20 min at 0 °C. AMS-K$_2$ was prepared by addition of K-OMOHN into AMS/THF at 30 °C and stirring for 5 min at 30 °C and 10 min at −78 °C. The initiators were used immediately after preparation. The coupling agent 1,4-bis(bromomethyl)benzene (DBX, TCI America, 98+%) was recrystallized twice from chloroform, dried on a vacuum line for 24 h, and dissolved in purified THF to needed concentrations.

Polymerizations. Polymerizations were run in high vacuum in THF at −78 °C in flamed glassware using Teflon valves and break-seal techniques as reported elsewhere.[21] 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 via electron transfer from the 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. Thus, to a rapidly stirred K-Naph solution in THF (7 × 10^{-5} mol, experiment 1, Table 3) at −78 °C was added chilled with dry ice a 2VN solution in THF containing 5% v/v toluene (1.75 × 10^{-3} mol). 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) (7 mL, 1.4 × 10^{-2} M, 1 × 10^{-4} mol) was added into it dropwise until the solution decolorized. The remaining 7 mL of the P2VN-K$_2$ solution was terminated with degassed methanol. The polymers were precipitated by addition of methanol 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 precipitation. Proton NMR data were acquired on Bruker AM-250 FT instrument operating at 250 MHz with CDCl$_3$ used as a solvent.

Results and Discussion

We recently reported[18] that the removal of traces (1−1.5% molar) of 2-acetylnaphthalene from 2VN is critical to achieve a living anionic polymerization of this monomer in THF at −78 °C in the presence of Li ion. This impurity is present in commercial 2VN due to incomplete hydrogenation of 2-acetylnaphthalene, an important intermediate in the synthesis of 2VN.[22] It is not removed by conventional purification methods, such as recrystallization or vacuum sublimation/distillation. More rigorous purification methods, such as treatment with LiAlH$_4$ in toluene followed by vacuum sublimation, allowed the preparation of P2VN of the predicted high MW's (M_n > 100 000) and very narrow molecular weight distributions (MWD's) (PDI as low as 1.03 with *t*-BuLi as initiator). The inadvertent formation of very high MW P2VN (M_n = 850 000) with a relatively narrow MW distribution (PDI = 1.12) was also observed, confirming the high purity of the monomer.[18]

However, the lithium naphthalide initiated anionic polymerizations of 2VN in THF at −78 °C are not well controlled, giving wider polydispersities (Table 1). 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 1). 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 min 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 s. These color changes 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,[23,24] it may be sufficient to observe 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[20] (K-OMOHN) generally gives P2VN with even narrower polydispersities compared to P2VN initiated with K-Naph (Table 1).

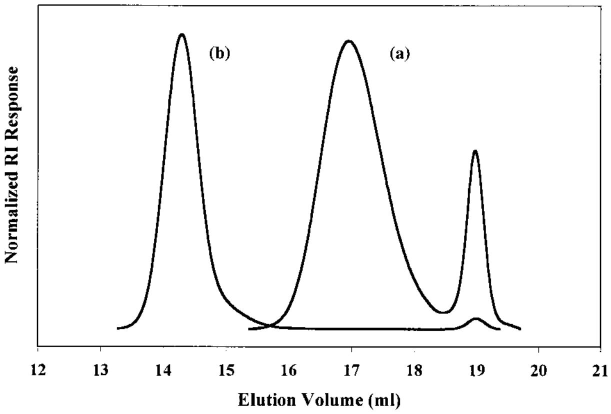

Figure 1. Normalized SEC curves of P2VN (Table 2, no. 1): (a) P2VN precursor and (b) P2VN after addition of the second 2VN portion after 1 h of storage (peak at 19 mL corresponds to OMOHN).

The MW distributions of the polymerizations initiated with simple anionic initiators are consistently narrower than with the radical anions. Thus, AMS-K_2 or *t*-BuLi initiators give polymers with narrower polydispersities than the radical anion initiators (Table 1, nos. 3, 4, 6).[18] These differences may indicate that one or more steps in the radical anion mediated initiation process are slow on the polymerization time scale.[23] 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, should be a better electron donor toward 2VN. Thus, the electron transfer to 2VN from K-OMOHN should 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.

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 formed anions 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.[25] 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 25 °C.[26] 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 2, upon addition of a second portion of 2-vinylnaphthalene to the P2VN-K_2 stored for periods up to 1 h at −78 °C, the polymerization proceeds to give narrow distribution higher molecular weight P2VN with complete absence of the P2VN precursor (Figure 1).

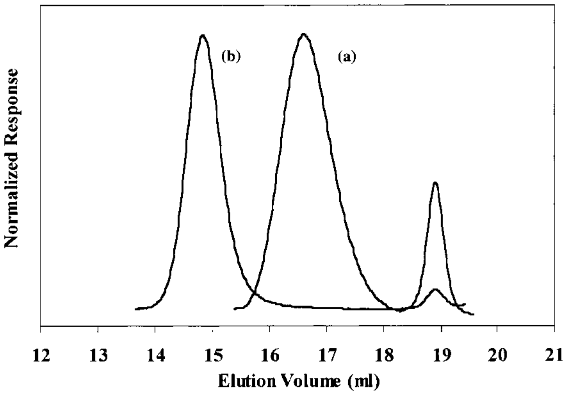

Figure 2. Normalized SEC curves of (a) P2VN and (b) PDMVF-*b*-P2VN-*b*-PDMVF (Table 2, no. 2) (peak at 19 mL corresponds to OMOHN).

The calculated molecular weight of the polymers in Table 2, $M_{n,th}$, is determined using MW of styrene, as it was found that SEC M_n of P2VN correlated well with the polymer contour length rather than its mass.[19] The discrepancies between $M_{n,th}$ and SEC M_n determined using RI detector and PS standards are attributed to overestimated initiator concentrations due to incomplete conversions of aromatic hydrocarbons into the respective radical anions.

Although storage for times longer than 1 h was not tested, the persistence of P2VN-K_2 anion is apparently sufficient to allow convenient end-functionalization and block copolymerizations.

Formation of Block Copolymers. Addition of a recently reported new vinyl monomer, 9,9-dimethyl-2-vinylfluorene (DMVF),[19] quantitatively gives narrow distribution higher MW PDMVF-*b*-P2VN-*b*-PDMVF block copolymers (Table 2) with the expected statistical narrowing of polydispersity.[27] As judged by the rapid color change from dark green to the dark red characteristic of the poly(9,9-dimethyl-2-vinylfluorenyl) anion, 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 2). These observations confirm the significant stability of the P2VN anion in the presence of potassium ion under the above conditions.

The appearance of new resonances centered at 7.25 and 1.10 ppm, due to 9-methyl hydrogens, in the proton NMR of the PDMVF-*b*-P2VN-*b*-PDMVF copolymer shows clearly the presence of the PDMVF block (Figure 3b). Because of the high PDMVF content, the block copolymer NMR closely resembles the reported PDMVF spectrum.[19]

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.[28] 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 2, no. 4, Figure 4a).

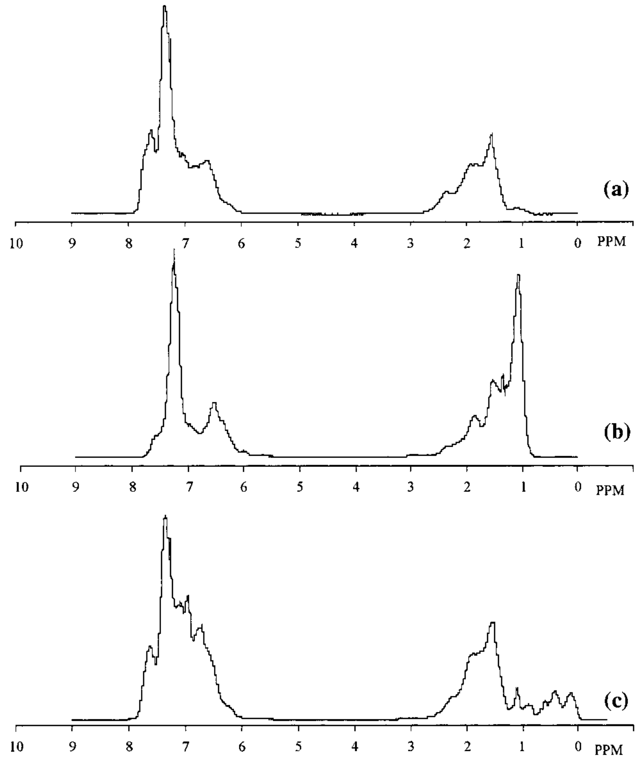

Figure 3. The 250 MHz ^{1}H NMR spectra of (a) P2VN (Table 2, no. 3), (b) PDMVF-*b*-P2VN-*b*-PDMVF (Table 2, no. 2), and (c) PAMS-*b*-P2VN-*b*-PAMS (Table 2, no. 3).

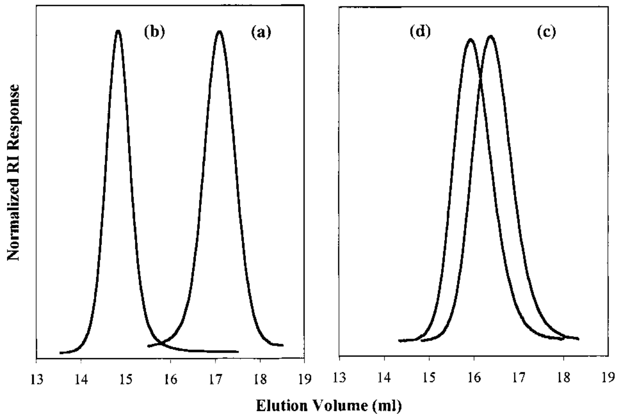

Figure 4. Normalized SEC curves of (a) P2VN, (b) P2VN-*b*-PAMS-*b*-P2VN (Table 2, no. 4), (c) P2VN, and (d) PAMS-*b*-P2VN-*b*-PAMS (Table 2, no. 3).

However, upon addition of AMS to a P2VN-K$_2$ solution at −78 °C, a *gradual* color change from dark green to dark red occurs over about 15 min, 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.[29] However, 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 2).

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. A process of this general type, for instance through a "complex formation" between chain end ion pair and penultimate naphthyl group, was proposed for the polymerization of styrene[25] or α-methylstyrene[30] initiated by poly(1-vinylnaphthalene) or poly(2-vinylnaphthalene) anions in THF at ambient temperatures in the presence of sodium ion. Similarly, to account for spontaneous termination in the polymerization of 2-isopropenylnaphthalene (2IPN) in the presence of Li ion in THF at 25 °C, the addition was proposed of the P2IPN anion to a penultimate pendent 2-naphthalene group.[25]

Neither of these processes seems likely in our case. Thus, the relatively narrow molecular weight distribution of the PAMS-*b*-P2VN-*b*-PAMS copolymer (Table 2, no. 3, Figure 4b) despite the slow rate of initiation of AMS by P2VN anion is probably due to the fact that the AMS homopolymerization is very slow as well. Thus, at an AMS anion concentration of approximately 3×10^{-3} M, only 8% of the AMS is converted after more than 1 h (Table 2, no. 3) from which an AMS homopolymerization rate constant on the order of about 7×10^{-3} L/(mol s) is estimated. This value is comparable to a previously reported value of 12×10^{-3} L/(mol s) at a slightly higher temperature (−59 °C).[31] A slow AMS initiation/propagation is consistent with the observed shift toward a symmetrical narrow distribution higher MW SEC curve without a clear indication of residual P2VN precursor (Figure 4). In this case, no significant 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 3c). Thus, the resonances of α-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.[32,33]

End-Functionalization Reactions. Although not strictly required for living polymerizations, the ease and degree of end-functionalization are 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.[34,35] Such reactions are also required for the synthesis of stars and macrocyclic vinylaromatic polymers.[1−5] 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 shows 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).

The high degree of end-functionalization is again consistent with the persistence and high reactivity and chemoselectivity of the P2VN anion under these conditions. Side reactions such as proton transfer and/or halogen exchange or elimination reactions not leading to the coupled products are apparently absent. Thus, it is expected 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.

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