Synthesis of Macrocyclic Polystyrene and Macrocyclic Poly(9,9-dimethyl-2-vinylfluorene) Containing a Single 9,10-Anthracenylidene Group

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ABSTRACT: Polystyryldilithium (PSLi$_2$), polystyryldipotassium (PSK$_2$) or poly(9,9-dimethyl-2-vinylfluorene)yl dipotassium (PDMVF-K$_2$), generated by electron transfer initiated polymerizations, were reacted with 9,10-bis(chloromethyl)anthracene (BCMA) under high dilution conditions to afford 9,10-anthracenylidene labeled PS or PDMVF macrocycles. However, only potassium ion mediated coupling reactions with BCMA gave high extents of 9,10-anthracenylidene incorporation (>90%) while analogous lithium ion systems afforded no more than 50% incorporation. Coupling reactions of PSK$_2$ with 9,10-bis(bromomethyl)anthracene (BBMA) also gave lower degrees of coupling and 9,10-anthracenylidene incorporation. Metal−halogen exchange or electron-transfer reactions may be responsible for the lower degree of 9,10-anthracenylidene labeling.

Introduction

The direct incorporation of single anthracene or similar acceptor groups into polystyrene (PS) or other vinyl aromatic polymers is of interest,[1−4] as anthracene is a useful fluorescent probe[4] for instance in the study of energy migration,[5] and may undergo reversible photodimerization.[6,7] The availability of a single acceptor group is important as steady-state and time-resolved emission studies of such polymers allow insight into the nature of the energy transfer processes. The presence of multiple acceptors is less desirable in this respect especially if the relative placement of the acceptors is not well-defined. Although direct coupling of polystyryllithium (PSLi) with 9-chloromethylanthracene (CMA) has been reported to give high degrees of anthracene incorporation,[8] we[9] and others[6] have not been able to confirm this. For instance, attack on CMA by the living PS anion can lead to radicals[6] and/or radical anions,[10] giving rise to only partial anthracene labeling. In addition, metal halogen exchange reactions[11,12] may lead to “head-to-head” dimeric species lacking the anthracene chromophore, as reported in similar PSLi coupling reactions.[13−15]

Presumably to avoid these complications, PS ions have been reacted with end-capping agents, such as 1-(2-anthryl)-1-phenylethylene, followed by addition of ethylene oxide to afford a diblock polymer with a pendant anthracene at its junction.[16] Another method leading to anthracene labeled polymers involves end-capping PSLi with ethylene oxide, followed by coupling with 9-chloromethylanthracene via a Williamson reaction.[6] This method, although largely successful (>80% labeling), introduces heteroatoms into the polymer backbone which may complicate energy transfer studies. Less nucleophilic living polymers, such as poly(methyl methacrylate) (PMMA) initiated with 1,1-diphenylhexyllithium in THF at −78 °C, have been coupled with 9,10-bis(bromomethyl)anthracene (BBMA) with high degrees of anthracene incorporation.[17] Incorporation of groups via an initiator, for instance 9-lithiomethylanthracene, has been tried for the case of styrene and other monomers, but with limited success.[18,19] To our knowledge, direct incorporation of a 9,10-anthracenylidene group into a PS backbone has not been demonstrated.

In this paper, we report coupling reactions that lead to essentially quantitative incorporation of a 9,10-anthracenylidene unit into PS or poly(9,9-dimethyl-2-vinylfluorene) (PDMVF) macrocycles. This polymer architectures is of interest as cyclic vinylaromatic macrocycles appear to show more efficient energy transfer than their matching linear analogues.[20]

Experimental Section

Reagents and Solvents. THF was purified by distillation from Na/K alloy onto fresh Na/K alloy from which it was vacuum-distilled onto a carbanion THF solution such as 1,1-diphenylhexyllithium. It was finally distilled in vacuo into ampules that were stored at −15 °C. Hexane was purified in a similar manner. Styrene (99%, Aldrich) was stirred over freshly crushed sodium hydride for 24 h and then vacuum-distilled onto dried dibutylmagnesium (1.0 M in heptane, Aldrich), from which it was distilled into ampules and diluted with solvent (THF or hexane) to about 2 M solutions and stored at −15 °C. Naphthalene (99+%, Fisher) was recrystallized three times in methanol. 9,10-Bis(bromomethyl)anthracene (BBMA, 98%, Toronto Research Chemicals, Inc.), 9,10-bis(chloromethyl)anthracene (BCMA, 99%, TCI), and 9-(chloromethyl)anthracene (CMA, 95+% Aldrich) were recrystallized from chloroform and vacuum-dried 24 h before being dissolved into purified THF and stored as about 1×10^{-3} M solutions. 1,1-Diphenylethylene (DPE, 99+%, Aldrich) was used as received for making the THF solutions of the corresponding dimer dilithio or dipotassio dianions that were used to remove protic impurities in the polymerization apparatus.

tert-Buytllithium (1.7 M in heptane, Aldrich) was diluted with purified hexanes to between 0.1 and 0.5 M, divided into ampules, and stored at −15 °C. The naphthalide radical anion solutions are prepared by stirring about 70 mg of naphthalene with about 1 g of cleaned potassium (99%, Aldrich) chunks at 0 °C in THF with rapid stirring under high-vacuum conditions. Within seconds a green color appeared, and the solution is filtered after 15 min and stored in ampules.

Polymerizations and Coupling Reactions. These were carried out in THF at −78 °C under high-vacuum conditions (10^{-5}−10^{-6} Torr) using break-seal techniques as reported elsewhere.[21] Polymerization reactions were performed by the addition of 1 mL of a 0.5 M *t*-BuLi/hexane solution (5×10^{-4}

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Table 1. Coupling of PSLi and BCMA or BBMA at −78 °C in THF[a]

	precursor		product					
run	M_n	PDI	M_n	PDI	% AN[b]	X	method[c]	% dimer
1	1600	1.15	3800	1.12	35	Cl	A	>95
2	2480	1.11	5000	1.10	38	Cl	B	>95
3	810	1.30	1800	1.20	33	Cl	A	>95
4	410	1.34	1300	1.19	45	Br	A	>95
5	650	1.33	1500	1.25	50	Br	B	>90

[a] Concentrations were [PSLi] = ~10^{-2} M and [XCH_2AnCH_2X] = ~10^{-3} M, both in THF. MW's determined by SEC using PS standards. [b] Percent 9,10-anthracenylidene incorporation determined by UV/vis; see text. [c] A = coupling agent added into anion, B = anion added into coupling agent.

mol) into a reaction flask via a break-seal and cooled to −78 °C. After addition of 10 mL of purified THF the solution instantly turns yellow, and 3 mL of a precooled 2.0 M solution (6×10^{-3} mol) of styrene/THF is added at one time. This rapidly stirred solution immediately turns reddish, indicating presence of the living PSLi. After 5 min of stirring at −78 °C, a small portion (20% of the total reaction mixture) is poured into a cooled side bulb which is closed off by Teflon stopcock and protonated with degassed methanol. To the remaining living polymer, a precooled BBMA or BCMA solution (10^{-3} M in THF) is added dropwise over about 10 min until the color of the living polymer is seen to fade. A small aliquot of the reaction mixture and precursor is removed for SEC analysis. The remaining precursor and coupled product are precipitated in excess methanol (~150 mL) and dried in a vacuum oven for 24 h before further analysis.

The reaction was also tried in the reverse manner. For example, 6.0×10^{-4} mol of a living polymer solution dissolved in 15.0 mL of THF was added dropwise (over about 10 min) into (2.5×10^{-4} mol) coupling agent dissolved in THF until the color of the living polymer barely persisted. Methanol was used to terminate the small amount of remaining living polymer.

Cyclization Reactions. About 10 mL of a 1,4-dilithio-1,1,4,4-tetraphenylbutane solution (10^{-2} M) prepared by the reaction of DPE with Li wire (98+%, Aldrich) in THF solution was added to 150 mL of THF that has been distilled through the vacuum line and into the cyclization apparatus. This solution was used to wash all walls of the entire apparatus and was stored in a reservoir bulb. About 10 mL of THF was distilled into the polymerization bulb and stirred rapidly at −78 °C to which the potassium naphthalide solution (5.4×10^{-4} mol in 10 mL) was added. To this solution the precooled styrene/THF solution (6.0×10^{-3} mol in 5 mL) was added one time, giving a reddish PSK_2 solution. After 5 min, 70% of this living polymer solution (2.1×10^{-4} mol in 20 mL) was transferred into a precooled addition funnel kept at −78 °C at all times. A very dilute solution of the BCMA coupler (70 mL of 3.0×10^{-3} M solution) and the solution of the living polymer (about 5×10^{-2} M), both precooled to −78 °C, were added simultaneously dropwise into about 150 mL of rapidly stirred THF at −78 °C over about 30 min. The addition rates were adjusted to allow a *faint* color of the PSK_2 to just persist in the cyclization mixture. The remaining PSK_2 (30%) was terminated with degassed methanol.

Crude cyclic polymer reaction mixtures were first concentrated by evaporation of excess solvent to allow for SEC analysis. Polymers were isolated by precipitation into a large excess of methanol (~150 mL). In some cases SEC analysis was carried out after precipitation as well, for instance during fractionations. Fractionations of the cyclized polymers were carried out by adding small aliquots of methanol (a few milliliters at a time) to a stirred THF solution of the crude polymer, allowing partial precipitation.[21] After centrifugation the resulting supernatant solution was analyzed by SEC. This procedure was repeated until the desired cycle (or other fraction) was obtained as determined by SEC. The purified cyclic polymer was then precipitated by addition of its solution into excess methanol and dried.

Characterization. Polymers (both linear and cyclic) were analyzed by SEC *prior* to precipitation by removing a small aliquot of the polymerization/reaction mixtures. Measurements were done in THF at a flow rate of 1 mL/min, using a LC system consisting of a Waters 510 HPLC pump, 410 refractive index detector, and a U6K injector. Two "Ultrastyragel" columns containing 10 μm beads with pore sizes of 500 and 10 000 Å and calibrated with PS standards gave linear separation in the 100−500 000 molecular weight range. Proton NMR measurements were carried out on a Bruker AC-250 FT-NMR in chloroform-*d* (Aldrich, 99+%).

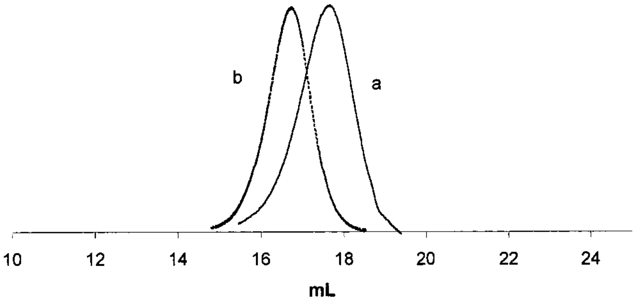


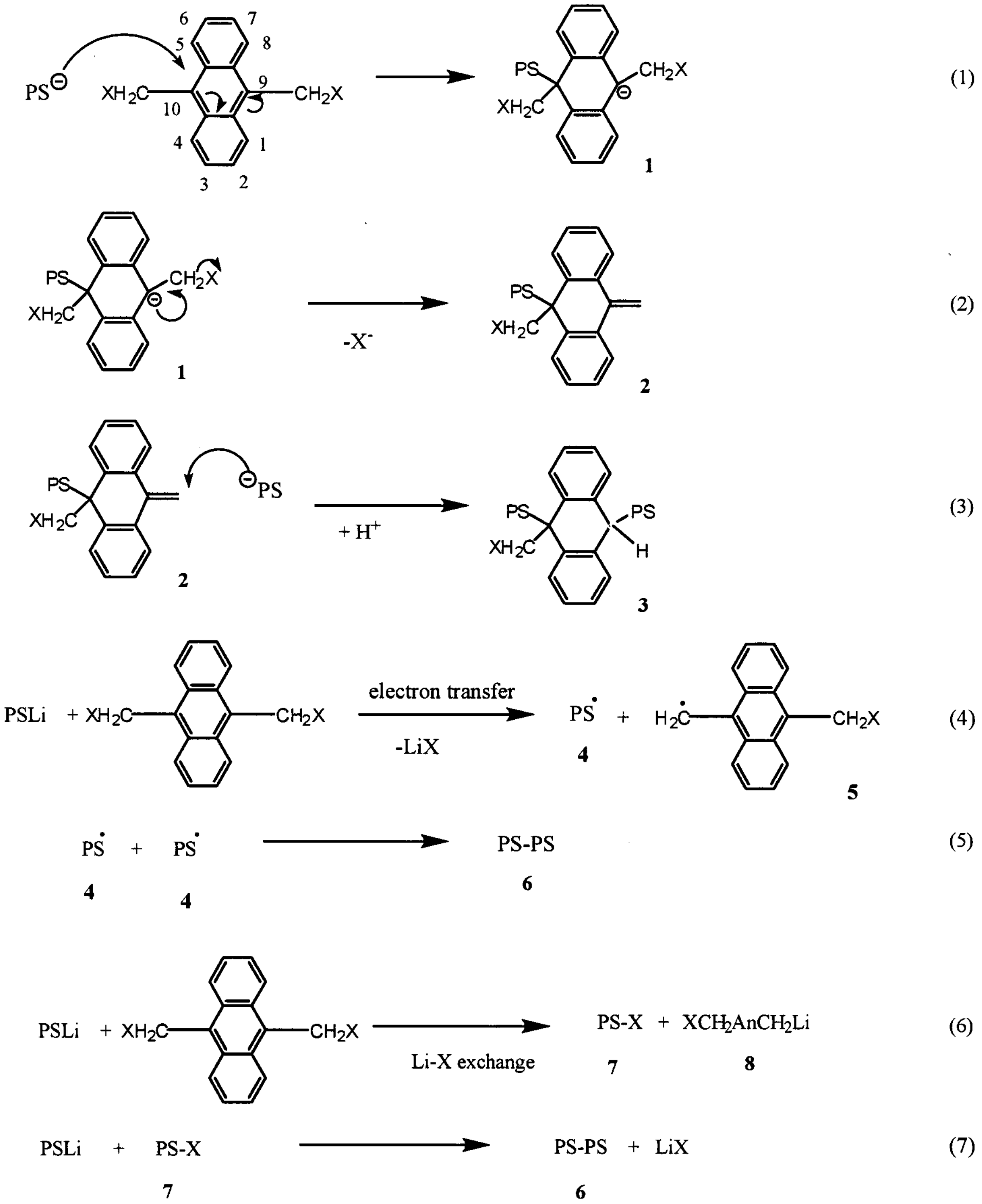
Figure 1. SEC (RI trace) of PSLi coupled with BCMA in THF at −78 °C (Table 1, no. 3): (a) precursor; (b) coupled product.

UV/vis measurements were typically done at concentrations of ~10^{-4} M polymer solutions in purified cyclohexane on a Varian Cary 50 UV/vis spectrometer. 9,10-Dimethylanthracene (ϵ = 10 000 at 400 nm)[22] was used for determining the polymer anthracene content.

Results and Discussion

Reaction of PSLi with Anthracene Coupling Agents. Previous attempts to synthesize polystyrene (PS) macrocycles containing a 9,10-anthracenylidene group by high dilution coupling of dilithiopolystyrene ($PSLi_2$, formed by initiation of styrene with lithium naphthalide in THF at −78 °C) with 9,10-bis(chloromethyl)anthracene (BCMA) showed only a small fraction of anthracene incorporated into the cyclic product.[9] To simplify the study of these reactions, we started with the coupling of one-ended PSLi (1×10^{-2} M), formed by initiation with *t*-BuLi and BCMA or BBMA. The stoichiometry of these reactions was monitored by the fading of the reddish color of the PSLi upon addition of the coupling agent (about 10 min). The reverse sequence in which PSLi was added dropwise into BBMA or BCMA was also studied. In all cases, the solution turned from an orange/red of the PSLi solution to a dark brown/green during the course of the coupling reaction, possibly due to electron transfer or other side reactions leading to radical or anionic intermediates.[10] From the doubling of molecular weight of the coupled product nearly quantitative coupling of PSLi with either BBMA or BCMA occurs as shown in Table 1 and in Figure 1. However incorporation of the anthracene moiety is not quantitative (see below). Proton NMR analysis shows the expected broadened resonances between 3.2 and 3.7 ppm attributable to the benzylic protons of the coupling

Scheme 1



agent in all cases. However, peak broadening due to the diastereotopic protons of the methylene group and the lower mobility of the polymer made integration of the *t*-Bu initiator peaks unreliable in determining the degree of anthracene incorporation.

The large UV/vis absorptivity of 9,10-dialkylanthracenes (extinction coefficient of 9,10-dimethylanthracene is 1.0×10^{-4})[22] made spectrometry more useful in this respect. As shown in Figure 2 (Table 1, no. 3), a solution of the BCMA-coupled polymer in cyclohexane shows bands at 403, 381, and 362 nm, indicating the presence of a 9,10-disubstituted anthracene group.[23] However, UV/vis analysis indicated only 33% anthracene incorporation consistent with a previous report.[6] The identical run but with BBMA (Table 1, no. 4) resulted in only a slightly higher anthracene incorporation (45%). Performing the coupling reaction in excess BBMA, by dropwise addition of the PSLi solution into the BBMA solution until a slight color of the living polymer persisted, had little affect on the coupling reaction, with overall anthracene incorporation still not exceeding 50% (Table 1, no. 4).

Scheme 1 shows some possible side reactions. Attack of anthracene and its derivatives at the 9 or 10 position (Scheme 1, eq 1) by strong nucleophiles, such as carbanions, is a known reaction resulting in the demise of the anthracene chromophore.[10,24] It is unknown how such an intermediate may react, but it may undergo

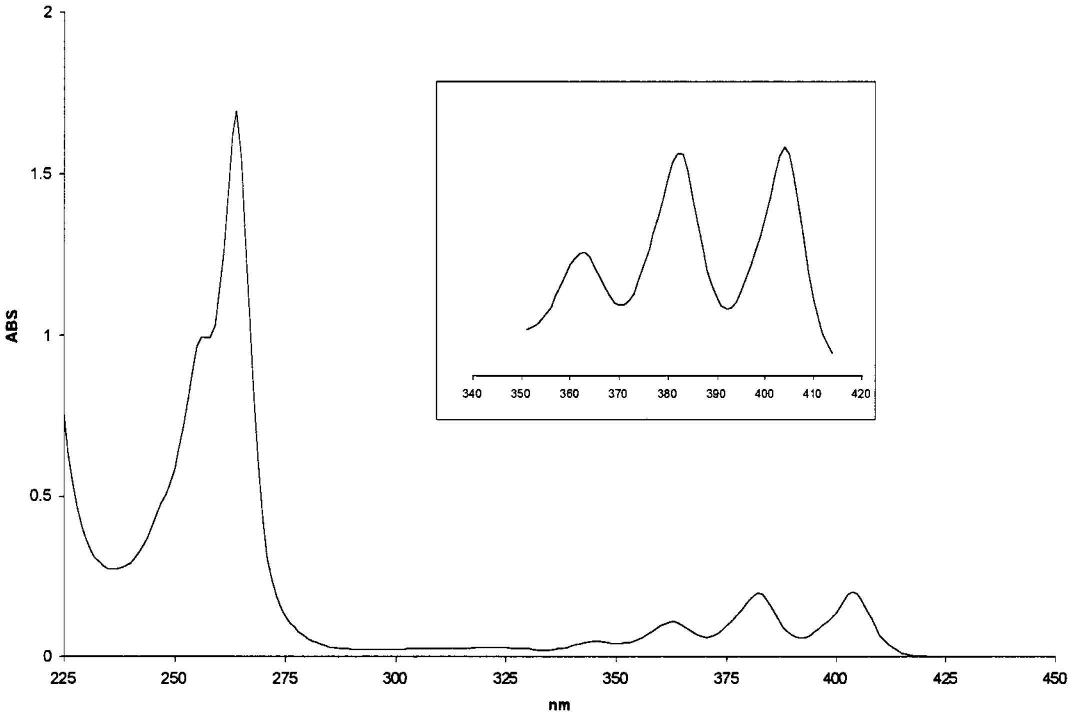


Figure 2. UV/vis spectra of coupled product of PSLi and BCMA (Table 1, no. 2). Inset shows anthracene absorption region.

halide elimination resulting in a methylene derivative, **2** (Scheme 1, eq 2). Coupling of this species with PSLi (eq 3) would result in a coupled product, **3**, lacking the anthracene chromophore. This may account in part for the less than quantitative 9,10-anthracenylidene incorporation into the coupled polymers (Table 1). Detection of **3** by ^{1}H NMR would be difficult due to overlapping of resonances of the PS-CH$_2$-anthracene protons with the methyl halo protons (both expected between 3.3 and 3.6).

Other side reactions may account for the poor anthracene incorporation in this system, for instance the formation of polystyrene radicals and subsequent coupling to form a "head-to-head" dimer, **6**, containing a 1,2-diphenyl linkage (Scheme 1, eqs 4 and 5).[6] However, lithium–halogen exchange to the "head-to-head" PS dimer would seem equally, if not more, likely (Scheme 1, eqs 6 and 7).[20,25,26]

Coupling in the Presence of Potassium Ions. Changing alkali counterions may profoundly affect the reactivity of carbanions and propagating vinyl–aromatic polymer anions in particular.[27] Possibly because Li ion solvation in ethers such as THF is stronger than that of K ion,[28] this ion is less prone to metal halogen exchange.[29] In addition, coupling of PS dianions with BBMA or BCMA under the above conditions is more likely to be a realistic model reaction for intramolecular coupling than the one-ended PS anion. For this reason we investigated next a series of step polymerizations of the potassium PS dianion (PS-K$_2$, formed by the potassium naphthalide initiated polymerization of styrene) with BCMA or BBMA. The number-average degree of polymerization (DP$_n$) of the resulting polymers is limited by side reactions of the PS dianion, the coupling agent, or other factors (discussed below). From the simplified Carothers equation (eq 8) a comparison of the DP$_n$ of the step polymerization with that of the protonated PS^{2-} precursor allows calculation of the apparent average functionality (f_{av}).[27,30]

$$\mathrm{DP_n} = 2/(2 - pf_{av}) \tag{8}$$

$$\mathrm{DP_n} = 2/(2 - f_{av}) \tag{9}$$

Here p and f_{av} denote the extent of reaction and the apparent average functionality, respectively, and N_I and f_I are the numbers of monomer ($i = 1$), dimer ($i = 2$), trimer ($i = 3$), etc. The conversion, p, is taken as unity as all the anion has reacted so that eq 8 reduces to eq 9, and an empirical apparent "number-average functionality" (f_{av}) of the two reagents can be calculated. It is worth noting that expression 8 does not account for the intramolecular formation of cycles, and the DP$_n$ values should be adjusted for this.

A step polymerization between PSK$_2$ and BBMA at high concentrations of both reagents (10^{-2}–10^{-3} M) gave a peak molecular weight (M_p) 5 times higher than the M_p of the precursor while the M_n of the product doubled (DP$_n$ = 2, Table 2, no. 1, Figure 3, top). From a DP$_n$ value of two eq 9 gives a value of f_{av} of about one so that the apparent fraction of inadvertent deactivation per chain end is about 0.5. Thus, the resulting probability of having deactivation at both chain ends in this case is quite high (0.25). The SEC UV (400 nm) (not shown) trace of this step polymer is nearly identical to that of the SEC RI trace, indicating that the anthracene group generally was incorporated by simple coupling and was incorporated nearly evenly, regardless of the molecular weight's of the coupled product. UV/vis analysis of the coupling product shows about 1.3 mmol of anthracene/mmol of polymer. Given the approximate doubling of M_n, this means only approximately 65% 9,10-anthracenylidene incorporation.

The same step polymerization using BCMA and PSK$_2$ gives rise to a much greater degree of coupling than the above BBMA system (Table 2, no. 2; Figure 3). In this

Table 2. Reactions of PSK_2 and $(PDMVF)K_2$ with DCMA or DBMA in THF at −78 °C[a]

	precursor		product[h]						
run	M_n	PDI	M_n (M_p)	PDI	X[d]	% cycle[e]	⟨G⟩	reaction type	% anthracene[f]
1[a]	3300 (3550)	1.08	6700 (18 500)	2.97	Br	0		step	65
2[a]	6750 (7025)	1.06	29 600 (118 000)	4.23	Cl	12	0.75	step	85
3[a]	2250 (2370)	1.12	2390 (1750)	2.34	Cl	67	0.74	cyclization	93
4[b]	8000[c] (8320)	1.12	9600 (7430)	1.68	Cl	65	0.85	cyclization	~100 (93[g])
5[b]	2500 (2700)	1.10	3050 (2300)	3.37	Cl	75	0.85	cyclization	95

[a] Molecular weights determined by SEC using PS standards; PS dianion precursor. [b] PDMVF dianion precursor. SEC molecular weight's of PDMVF are corrected (see text). [c] Precursor alkylated with 9-chloromethylanthracene. [d] Halogen in anthracene coupler. [e] Yield of cycles as a percentage of product determined by SEC. [f] Percentage of anthracene incorporated by UV/vis. [g] Percentage of anthracene in α,ω-disubstituted precursor. [h] Distribution of crude cyclization product determined by SEC; M_n and M_p refer to number and peak molecular weight.

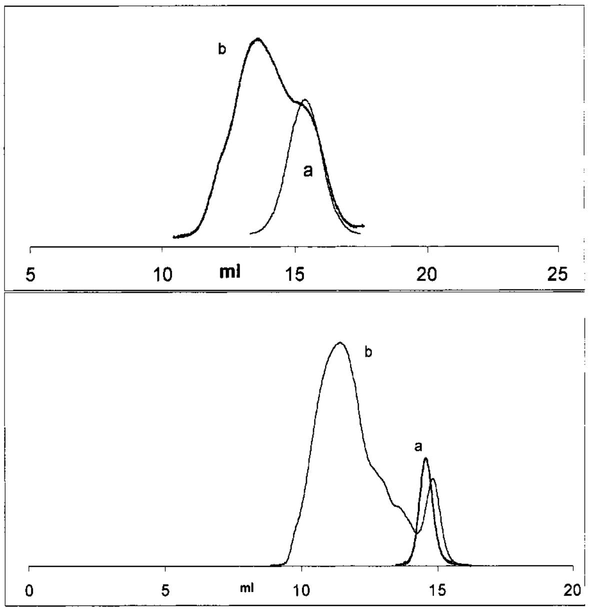


Figure 3. (top) SEC of PSK_2 coupled with BBMA (Table 2, no. 1): (a) precursor, (b) step polymerization product. (bottom) SEC of PSK_2 coupled with BCMA (Table 2, no. 2): (a) precursor, (b) step polymerization product.

case the SEC peak maximum (M_p value of about 120 000) of the polymer increased about 17-fold compared to the M_p of the precursor (~7000), and the overall DP_n of the product increased 5-fold, indicating an approximately 80% coupling yield. The UV/vis spectrum of the crude coupled product indicates a high anthracene content (about 85% of the calculated value) despite the fact that at such a high degree of chain extension the chance of inadvertent termination (for instance, by addition of the polystyryl anion to the anthracene ring) is greatly increased.

The narrow distribution low molecular weight polymer (about 12% of the product) with an elution volume that is significantly larger than that of the precursor (Figure 3, bottom) indicates the inadvertent formation of a macrocyclic polymer by end-to-end coupling even in these relatively concentrated solutions. The ratio $M_{p,c}/M_{p,l}$ of the apparent M_p values of cyclic over linear polymer (⟨G⟩) is about 0.75, which is roughly what is expected for vinyl−aromatic macrocycles in this molecular weight range.[31] This indicates that the cycle is not contaminated by a large fraction of the linear polymer. The UV (400 nm) and RI traces are essentially identical, confirming that the inadvertently formed cycle has approximately the same anthracene content (at least 85%) as the step polymerization product.

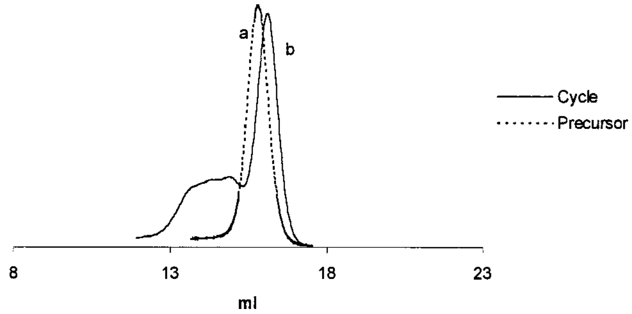


Figure 4. SEC of PS macrocycles containing anthracene (Table 2, no. 3): (a) precursor, (b) cyclization product.

Correcting the SEC chromatogram for the presence of cycles (recalculation of M_n by correcting for the presence of cycles) and assuming all remaining polymer to be linear, the M_n of the remaining coupled product is about 75 000, a nearly 11-fold increase over that of the precursor. From eq 9 the f_{av} is about 1.8 so that the extent of inadvertent termination (of anion or halide group) is less than 10%. Assuming that the extent of anion termination is 10%, the probability of anion termination at both ends is only about 1%. This is important as terminated and thus linear precursors are not easily differentiated or separated from the cyclic product. Thus, the formation of cycles containing single 9,10-anthracenylidene groups under these reactions conditions is feasible.

Formation of 9,10-Anthracenylidene-Containing Macrocycles. A cyclization reaction (Table 2, no. 3) was carried out the by slow simultaneous addition of dilute THF solutions of PSK_2 (~5 × 10^{-3} M) and BCMA (~(1−2) × 10^{-3} M) at −78 °C into 150 mL of rapidly stirred THF at −78 °C. From the SEC data shown in Figure 4, the hydrodynamic volume of the cyclization product (formed in 67% yield) is about 26% lower than that of the linear precursor (⟨G⟩ value of 0.74). The UV (400 nm) and RI SEC traces are essentially identical, indicating that the macrocycles are singly labeled. UV/vis analysis of the fractionated polymer confirms a high degree of 9,10-anthracenylidene incorporation (93%) into this cycle.

The success of the potassium ion mediated cyclization with BCMA prompted us to synthesize other anionic vinyl−aromatic polymers that are more promising for

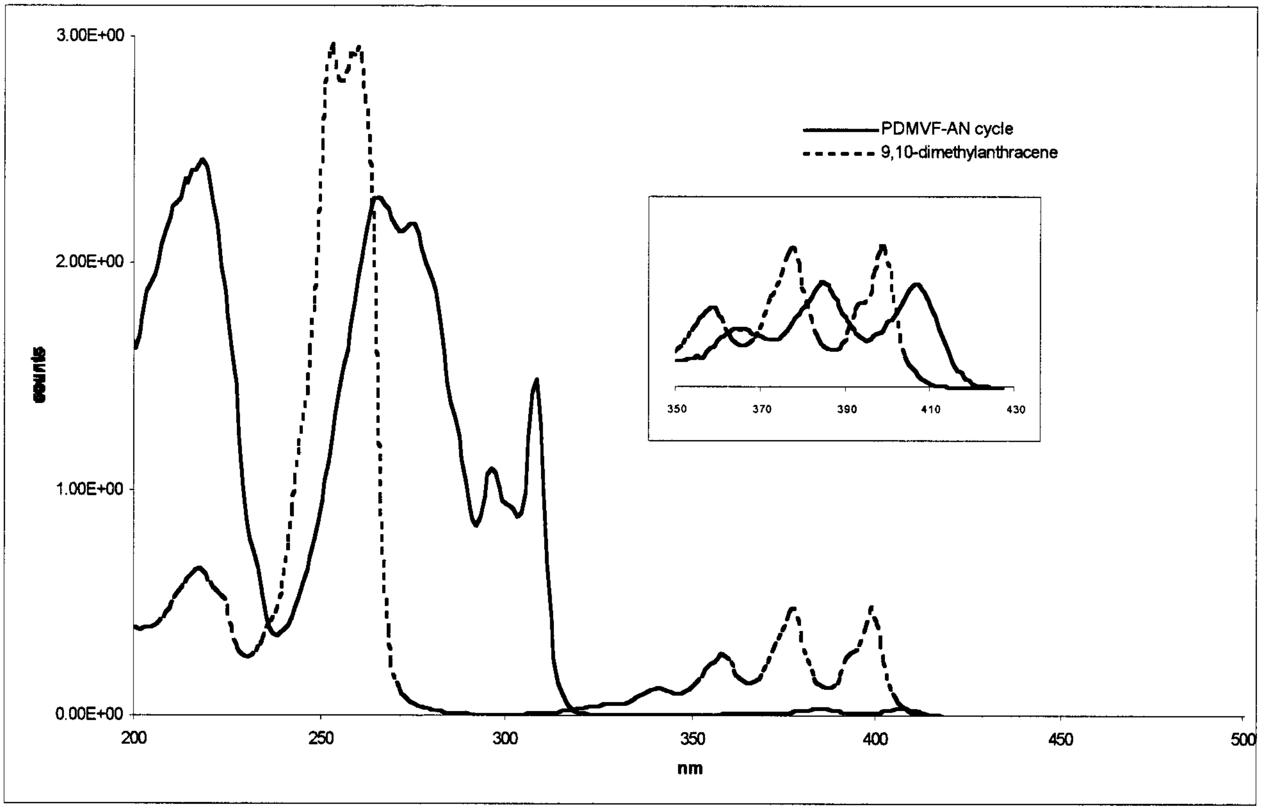


Figure 5. UV/vis of 9,10-dimethylanthracene and macrocyclic PDMVF containing anthracene unit (Table 2, no. 4).

photochemical studies. Thus, the cyclization was attempted of poly(9,9-dimethyl-2-vinylfluorenyl)dipotassium (PDMVF-K_2), obtained by reaction of potassium naphthalide with 9,9-dimethyl-2-vinylfluorene at −78 °C in THF, with BCMA under the above conditions (Table 2, no. 4).[32] The precursor dianion was terminated with 9-chloromethylanthracene to afford a telechelic α,ω-9-anthracenyl linear PDMVF. As the apparent molecular weight values of PDMVF, as determined by SEC with PS standards, do not appear to be realistic as determined by ^{1}H NMR,[32] the reported values have been corrected (Table 2, nos. 4 and 5). The SEC of the cyclic material has a $\langle G\rangle$ value of 0.85, with the cycle formed in a 65% yield. The $\langle G\rangle$ value is somewhat large for a DP of about 32 may indicate that the concentration of BCMA in the cyclization reaction (about 3×10^{-3} M in this case) was too high, resulting in end-functionalized products as well as cyclic products. Thus, UV/vis analysis of the fractionated cyclization material shows quantitative 9,10-anthracenylidene incorporation (∼100%), while the end functionalized “precursor” shows 93% 9,10-anthracenylidene content.

The use of a lower BCMA concentration (about 1×10^{-3}) under otherwise identical conditions produced a cycle (about 75% yield) with a $\langle G\rangle$ value of 0.85 (Table 2, no. 4). Because the number-average DP of the protonated precursor in this case was low (DP of about 11), this $\langle G\rangle$ value is roughly what is expected for cycles in this range.[31] Also, the peak width of the cyclic product (at half-height) was found to be essentially identical to that of the precursor, indicating that contamination by linear precursor was minimal. UV/vis of the fractionated cycle revealed a high degree of 9,10-anthracenylidene incorporation (95%).

Figure 5 shows the UV/vis spectra of a PDMVF macrocycle containing 9,10-anthracenylidene (Table 2, no. 4) and of model compound 9,10-dimethylanthracene. The shift from 400 to 407 nm of the cycle compared to the model compound may indicate an interaction between the pendant groups and the 9,10-anthracenylidene chromophore. This shift is essentially the same for the lower molecular weight PDMVF cycle (Table 2, no. 5). The strong absorption of the PDMVF and the absence of 9,10-dimethylanthracene around 300 nm will allow energy transfer studies by selective excitation of the PDMVF segment and the observation of the 9,10-anthracenylidene emission. Collaborative studies along these lines are currently being carried out.

The reasons for the better potassium- rather than lithium ion-mediated coupling of the living PS and PDMVF anions with BCMA is interesting. It is possible that this is due to the higher reactivity of lithium salts of delocalized carbanions on account of the higher fraction of solvent-separated ion pairs. For instance, this was shown to be the reason for the higher reactivity of polystyrryllithium compared with that of all other cations in the polymerization of styrene. In the present case the situation is not that simple as the relative rates of competing side reactions (i.e., halogen exchange, electron transfer, addition to the anthracene ring) compared with that of the desired substitution determine the overall coupling yield.

Conclusions

Direct incorporation of single 9,10-anthracenylidene units into macrocyclic polystyrene and poly(9,9-dimethyl-2-vinylfluorene) was achieved through high dilution end-to-end coupling of the polymer dianion potassium salts and 9,10-bis(chloromethyl)anthracene in THF at −78 °C. Identical runs with 9,10-bis(bromomethyl)anthracene as the coupling agent or lithium as the counterion resulted in poorer coupling yields and lowered 9,10-anthracenylidene incorporation.

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