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Synthesis and Thermal Properties of Macrocyclic Poly(9,9-dimethyl-2-vinylfluorene) Containing Single 1,4-Benzylidene or 9,10-Anthracenylidene Linking Units

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ABSTRACT: Narrow distribution macrocyclic poly(9,9-dimethyl-2-vinylfluorene) (PDMVF) and the matching linear precursors with the same degree of polymerization (DP_n from 12 to 145) were synthesized via anionic polymerization followed by the end-to-end coupling with 1,4-bis(bromomethyl)benzene (DBX) or 9,10-bis(chloromethyl)anthracene (BCMA). The molecular characterization was carried out by size exclusion chromatography (SEC), proton NMR, and MALDI. The ratios of apparent molecular weights (MW's) of the macrocycles and those of the matching linear polymers decreased with increasing molecular weights as seen with other vinylaromatic macrocycles. However, in contrast to all other vinylaromatic macrocycles, the PDMVF macrocycles showed increases in glass transition temperature with decreasing MW.

Introduction

There has been a revived interest in recent years in the synthesis and properties of macrocyclic vinyl aromatic polymers.[1−15] The hydrodynamic,[16] thermal,[4a,6−8,13,15] and spectroscopic[17] properties of these macrocycles differ from those of the matching linear polymers. We have successfully synthesized and characterized macrocyclic and matching linear polystyrene (PS),[13] poly(2-vinylpyridine) (P2VP),[3,13] poly(α-methylstyrene) (PAMS),[14] and poly(2-vinylnaphthalene) (P2VN)[15] by end-to-end cyclization of the corresponding dianions with bifunctional electrophiles, such as 1,4-bis(bromomethyl)benzene (DBX) and dibromomethane, under highly dilute solutions (10^{-5}−10^{-6} M). Similar macrocyclic polystyrene (PS)-*b*-poly(dimethylsiloxane)[18,19] and PS-*b*-P2VP[20] and block copolymers have also been synthesized.

Vinyl aromatic polymers containing fluorene pendent groups have interesting photoluminescent properties and good chemical and thermal stabilities.[21,22] The molar absorptivity of fluorene in the near-UV region is on the order of 10^4, and its fluorescence quantum efficiency is relatively high (about 0.80).[23] Such polymers or copolymers may be of interest in the studies of energy transfer[23−25] and light harvesting materials.[26,27] It has been found that cyclic vinyl aromatic polymers show more efficient emission than their matching linear analogues.[17]

Here we report the synthesis of narrow MW distribution macrocyclic poly(9,9-dimethyl-2-vinylfluorene) (PDMVF) and the matching linear precursors via the anionic polymerization followed by the end-to-end coupling with DBX or 9,10-bis(chloromethyl)anthracene (BCMA). The incorporation of BCMA is of interest as anthracene is a useful fluorescent probe[28] in the study of energy migration.[29]

Experimental Section

Materials. Iodomethane (Aldrich, 99%) was distilled twice from CaH_2 prior to use. Tetrabutylammonium iodide (Aldrich, 98%) and dimethyl sulfoxide (DMSO) were used as received. THF was purified by distillation from Na/K alloy followed by distillation from 1,4-dipotassio-1,1,4,4-tetraphenylbutane ($DD-K_2$) carbanion solution. Potassium naphthalide (K-Naph), the initiator, was prepared by stirring naphthalene in THF over a potassium mirror for 15−20 min at 0 °C and used immediately. 1,4-Bis(bromomethyl)benzene (DBX, TCI, 99%), was recrystallized three times from $CHCl_3$ (mp 146−147 °C), dried under high vacuum, and dissolved in purified THF to desired concentrations. 9,10-Bis(chloromethyl)anthracene (BCMA, TCI, 99%) was recrystallized from $CHCl_3$ and dried under vacuum before being dissolved in purified THF to needed concentration.

Monomer Synthesis and Purification. 2-Vinylfluorene (2-VF) was synthesized as reported.[21] The DMVF monomer was prepared by bis-alkylation of the 9-position using a modified prosedure.[30] Thus, to a solution of 3.95 g of 2-VF (20.6 mmol) in 80 mL of dimethyl sulfoxide (DMSO) under argon was added 40 mL of 50 wt % aqueous NaOH solution and 0.37 g (1.0 mmol) of tetrabutylammonium iodide. The mixture turned pink, and upon dropwise addition of 7 mL (50 mmol) of CH_3I the pink color turned dark purple. After stirring vigorously at room temperature for 16 h, 100 mL of water and 100 mL of ether were added, and the mixture was stirred for 15 min and then separated. The aqueous layer was extracted with two portions of 30 mL of ether, and the combined ether extracts were washed with 20 mL of 5% HCl (twice) and then water until the aqueous solution was neutral. The ether extracts were dried with anhydrous $MgSO_4$, and the solvent was removed, leaving an orange solid. Purification with column chromatography (silica gel, J.T. Baker, 60−200 mesh) using hexane as eluent gave a white crystalline solid in 91% yield (mp 81.9−82.4 °C). It was then dissolved in purified THF, stirred over freshly crushed CaH_2, purified with cross-linked polystyrene−fluorene beads containing pendent fluorenyllithium anions,[22] and then distributed into ampules equipped with break-seals. ^1H NMR: δ (ppm) 7.80−7.30 (m, 7H), 6.90−6.70 (dd, 1H), 5.90−5.75 (dd, 1H), 5.30−5.20 (dd, 1H), 1.50 (s, 6H).

Polymerizations and Cyclization Reactions. Polymerizations and cyclizations were carried out in THF at −78 °C under high-vacuum conditions (10^{-5}−10^{-6} Torr) using break-seal techniques as reported elsewhere.[17] The needed amount of THF was distilled in, and the entire apparatus was rinsed with $DD-K_2$ carbanion solution. The precursor dianion, $PDMVF-K_2$, was prepared by a one time addition of a precooled DMVF/THF solution (1.0 g in 10 mL) to an about 20 mL solution of K-Naph (∼0.9 mmol) in THF stirred at −78 °C.

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Scheme 1. Synthesis of Macrocyclic PDMVF Containing Single 1,4-Benzylidene or 9,10-Anthracenylidene Linkages

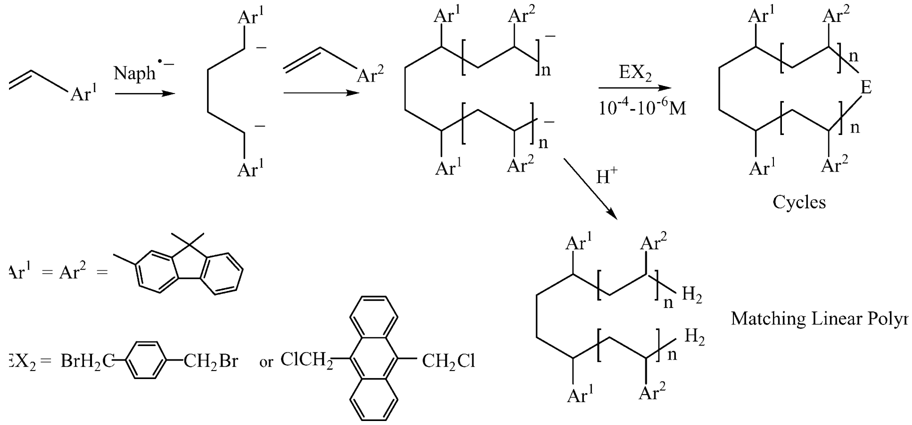

Table 1. Cyclization of DMVF Coupled with DBX or BCMA at −78 °C in THF[a,b]

		linear PDMVF			cyclic PDMVF				
no.	$M_{n,calcd}$	M_n	M_p	PDI	M_n	$M_p{}^c$	PDI	cycle yield^d (%)	$\langle G\rangle^e$
1	2200	2620	2920	1.12	2560	2600 (2640)	1.16	72	0.91
2	3300	3930	4420	1.12	3470	3930 (3910)	1.09	65	0.89
3^f	3530	4210	4970	1.13		− (4420)		50	0.89
4	6180	6560	7810	1.12	5860	6600 (6580)	1.14	50	0.84
5^g	8820	9710	11420	1.10	8080	8930 (8840)	1.12	66	0.77
6	9240	10320	11990	1.09	7910	8820 (8780)	1.09	70	0.73
7	26440	31240	34420	1.07	20840	24670 (24180)	1.08	38	0.71

[a] DBX is 1,4-bis(bromomethyl)benzene and BCMA is 9,10-bis(chloromethyl)anthracene. [Monomer] = 0.15 M; cyclization carried out over about 20 min at anion concentration of $\sim 10^{-4}-10^{-6}$ M. [b] Molecular weights were determined by SEC using polystyrene standards. See text. [c] The values in parentheses are M_p's of unfractionated cyclic PDMVF. [d] Percent yield of cycles estimated from SEC. [e] $\langle G\rangle = M_{p(\text{crude cyclic})}/M_{p(\text{linear})}$. [f] Cyclization carried out high concentration, [anion] $\sim 10^{-3}$ M. [g] BCMA was used as coupling reagent.

After 5 min, about two-thirds PDMVF-K_2 and, simultaneously, a DBX or BCMA solution were added dropwise into a cyclization reactor containing ~250 mL of precooled and vigorously stirring THF. The addition rates were adjusted to allow a faint burgundy color of the anion to just persist in the cyclization mixture. The remaining PDMVF-K_2 was terminated with degassed methanol to give the matching linear polymer. After reaction THF was evaporated, and the residues were redissolved in 5−10 mL of CH_3Cl and washed with water to remove inorganic salts. The polymers were then precipitated in excess (about 200 mL) methanol. Fractionation was carried out by incremental addition of methanol into a THF solution of PDMVF (0.70−1.0 g dissolved in 5 mL of THF). As soon as precipitation was just visible (addition of 3−5 mL of methanol), the precipitate was filtered off and the solution was analyzed by SEC. This methanol addition filtration sequence was repeated until the shape and maximum of the SEC curve of the solution phase were similar to that in the crude product. Then the supernatant was isolated by solvent evaporation followed by drying in a vacuum oven.

Characterization. Size exclusion chromatography (SEC) was carried out at 25 °C with THF as mobile phase at a flow rate of 1 mL/min, using a Waters 510 HPLC pump, a Perkin-Elmer LC-30 refractive index detector, and two Polymer Laboratories PLgel 5 μm MIXED-C columns (linear range of MW: 200−2 000 000), calibrated with polystyrene standards (Polysciences). All polymers were analyzed prior to precipitation. Proton NMR was carried out on a Bruker AC 250 at 250 MHz using deuterated chloroform as solvent.

MALDI−TOF mass spectrometry was performed using an Applied Biosystems Voyager DE-STR mass spectrometer in a reflector mode using a nitrogen laser (337 nm) and an accelerating voltage of 20 kV. The MALDI mass spectra represent averages over 100 laser shots. The polymer solutions were prepared in dichloromethane. The matrix used was saturated dithranol solution doped with silver trifluoroacetate with a 100:1 volume ratio. The samples were prepared by mixing a 10 μL polymer solution with 50 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Default calibration from the Applied Biosystems software with accuracy of 0.01% was used to calibrate the mass scale.

Differential scanning calorimetry (DSC) was carried using 10 mg of precipitated and vacuum-dried polymer on a Shimadzu DSC-50 differential scanning calorimeter in the temperature range from 30 to 200 °C under a helium flow of 50 mL/min, with a 10 °C/min scanning rate in two consecutive runs for each polymer sample. The T_g determined from the second run is reported with a deviation of ±2 °C. Thermal gravimetric analysis (TGA) was carried out with a Shidmazu TGA-50 thermogravimetric analyzer under a 40 mL/min nitrogen flow with a heating rate of 10 °C/min using about 5−7 mg polymer sample.

Results and Discussion

Ring Formation. The synthesis of macrocyclic PDMVF with apparent number-average molecular weights ranging from 2600 to 31 200 was carried out in THF at −78 °C via DBX or BCMA mediated end-to-end cyclization at anion concentrations of $10^{-4}-10^{-6}$ M (Scheme 1, Table 1). The MW's directly determined from SEC using PS standards were corrected by multiplying this MW by a factor of 2.12 (= mass of DMVF/mass of styrene = 220/104). The fractionated macrocyclic polymers were obtained by incremental addition of methanol into a THF solution of the crude cyclization product (Experimental Section). This process was monitored by SEC analysis of the supernatant solutions (Figure 1b). Care was taken to ensure that the peak MW's and the low-MW portion of the MW distribution of the fractionated and crude macrocyclic polymer were identical.

As shown in Figure 1a, experiment 3 was carried out at a relatively high concentration ($10^{-2}-10^{-3}$ M) of

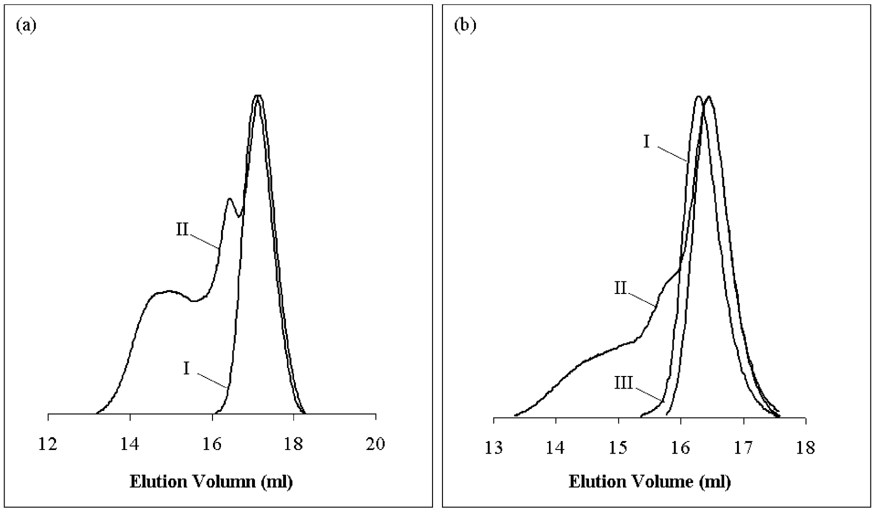

Figure 1. Normalized SEC chromatograms of PDMVF macrocycles (a) (Table 1, no. 3) and (b) (Table 1, no. 6): (I) linear PDMVF precursor, (II) crude cyclic PDMVF, (III) fractionated cyclic PDMVF.

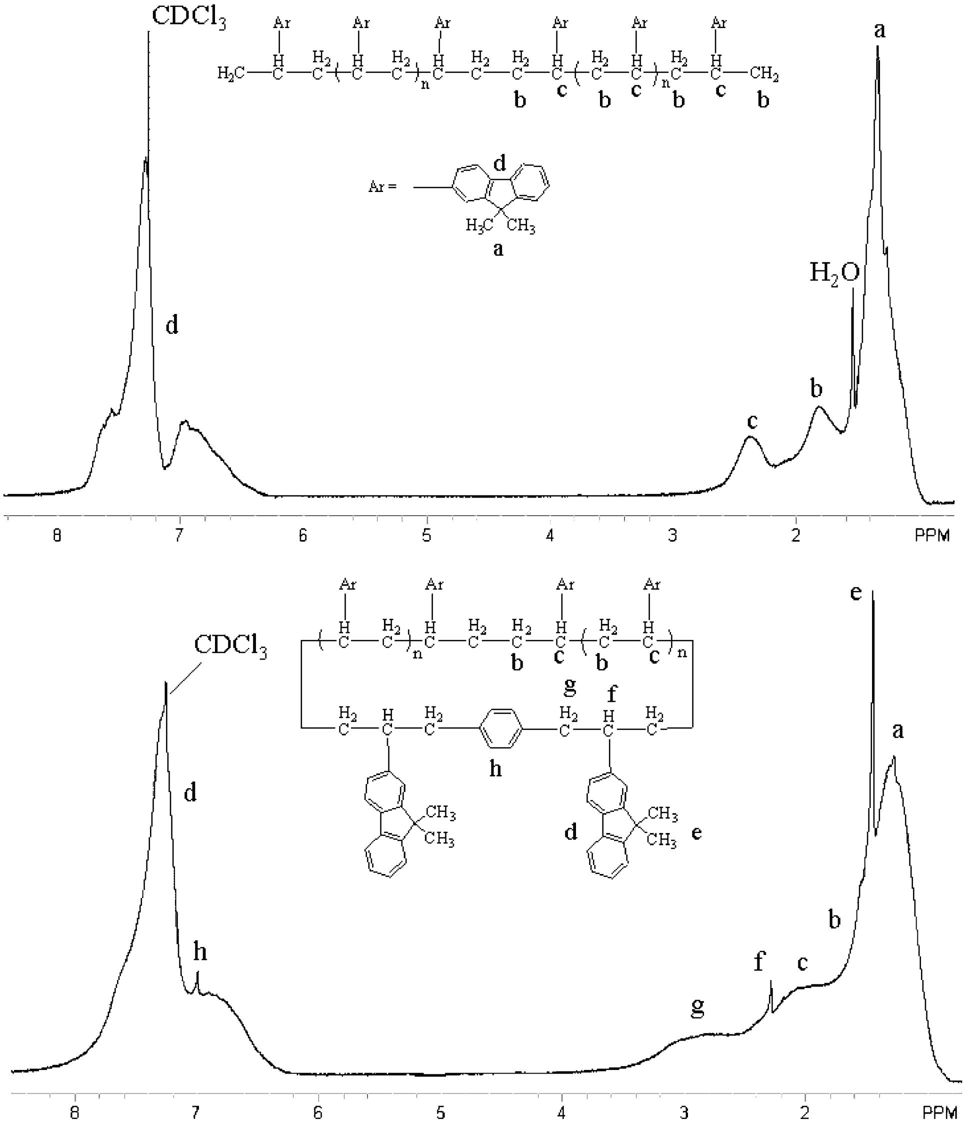

Figure 2. Proton NMR spectra (250 MHz) in CDCl$_3$ of protonated linear PDMVF (top) and fractionated macrocyclic PDMVF coupled with DBX (bottom) with a DP$_n$ of 12 (Table 1, no. 1).

polymer dianion and coupling reagent in order to determine the efficiency of the intermolecular coupling reactions. Nevertheless, this “step polymerization” between PDMVF-K$_2$ and DBX gave an appreciable yield (50%) of the macrocycle, as judged by the apparent peak MW that was 11% lower than that of the linear

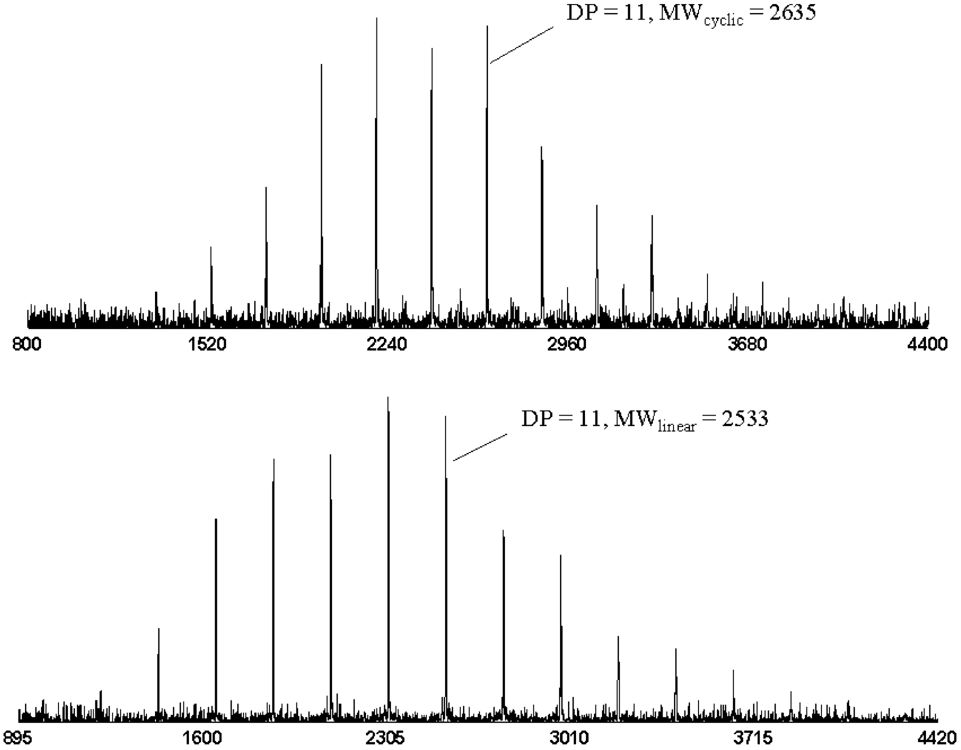

Figure 3. MALDI−TOF spectra of macrocyclic PDMVF (top) and the matching linear polymer (bottom). (Table 1, no. 1).

precursor. The small peak (M_p = 9300) was attributed to the macrocyclic dimer resulting from one intermolecular and one intramolecular coupling. The broad peak is due to a "polycondensation" product of high molecular weight (M_p = 42 100). This product is assumed to be linear[31,32] on the basis of the observed dehydrohalogenation for the DBX-mediated cyclization of polystyrene dianion.[17] Following the simplified Carothers equation (eq 1)[33] for the number-average degree of polymerization (DP_n), this gives

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

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

where p and f_{av} denote the extent of the reaction and the number-average functionality of the dianion and coupling reagents, respectively. The conversion, p, is taken as unity as all the anion has reacted so that eq 1 reduces to eq 2. The quantity of f_{av} denotes an *empirical apparent* functionality of the two reagents. This includes the loss of functionality resulting from the presence of impurities in either reagent, inadvertent protonation, for instance, due to reaction of the carbanions with solvent or the occurrence of side reactions.[17,31,32]

As the molecular weight of the high-MW fraction had a MW 10 times that of the precursor, the apparent value of f_{av} of PDMVF-K_2 is 1.8, which is 10% lower than the maximum functionality of 2.0. This corresponds to 10% termination of the polymer dianion so that the fraction of polymer dianion terminated at both chain ends is estimated as about 1%. Thus, the extent of contamination of the macrocycle with matching linear polymer is should be negligible at least at high concentrations.

The cyclization yields estimated from the SEC chromatograms varied from 38 to 72% and generally decreased with increasing DP_n, consistent with prediction.[34] Thus, the cyclization yield was only 38% for the very large size macrocycle (Table 1, no. 7) as the relatively large end-to-end distance between the anion and electrophile reaction sites favors the intermolecular coupling rather than the intramolecular coupling.

The SEC chromatograms of the macrocyclic PDMVF showed a clear shift to lower MW, indicating a decrease of hydrodynamic volume compared to that of the matching linear precursor (Figure 1).[15] However, the ratios of apparent peak MW's of the unfractionated cyclic polymers and the matching linear polymers given as the $\langle G \rangle$ values increased from 0.71 (Table 1, no. 7) to 0.91 (Table 1, no. 1) as the molecular weights decreased. Similar trends were found for P2VP,[15] PS,[17] and PAMS[14] in the same molecular weight range. This effect is apparently due to severe steric restrictions in the smaller macrocycles.

The formation of catenanes, although a possible complication, is not considered to be a serious complication as they are isomeric with dimer cycles and are removed by precipitation. Furthermore, their formation has been shown to require large concentrations of the dianion precursors and the already formed rings.[12] Even then the yields are low.[12]

As shown in Figure 2 (bottom), the proton NMR spectrum of the smallest PDMVF cycle with a DP of 12 (Table 1, no.1) shows a clear resonance around 2.3 ppm, corresponding to the two methine protons (f) of the PDMVF end units. The resonances at about 2.6−3.4 and 7.0 ppm correspond to the four benzylic protons (g) and the four equivalent aromatic protons (h), respectively, of the 1,4-benzylidene coupling unit that is not present in the linear PDMVF. The broad resonance of the methylene g-protons is consistent with the presence of the nearby asymmetric centers of the chain ends that would be expected to render the geminal g-protons nonequivalent.

MALDI−TOF measurements of the fractionated macrocyclic PDMVF and the matching linear polymer (Table

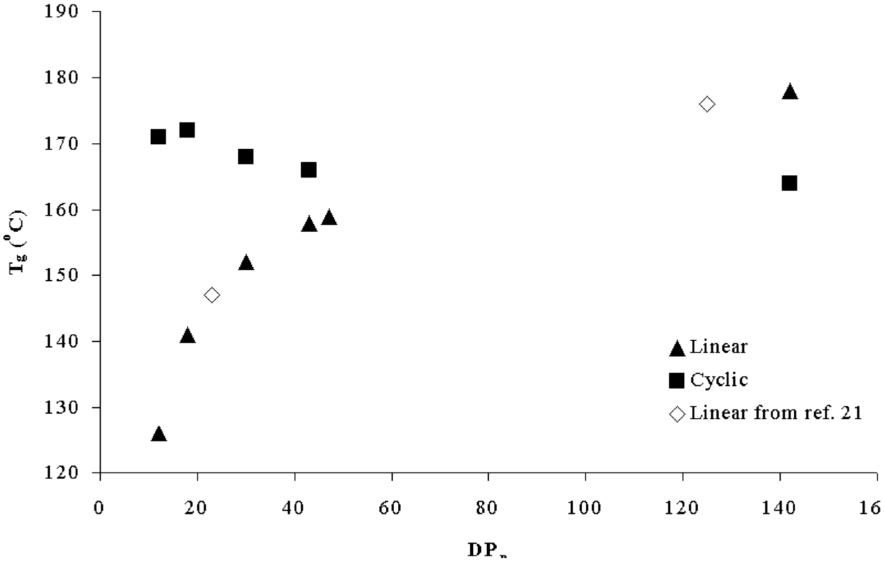

Figure 4. Relationship between glass transition temperature (T_g) and degree of polymerization (DP_n) of macrocyclic and linear PDMVF.

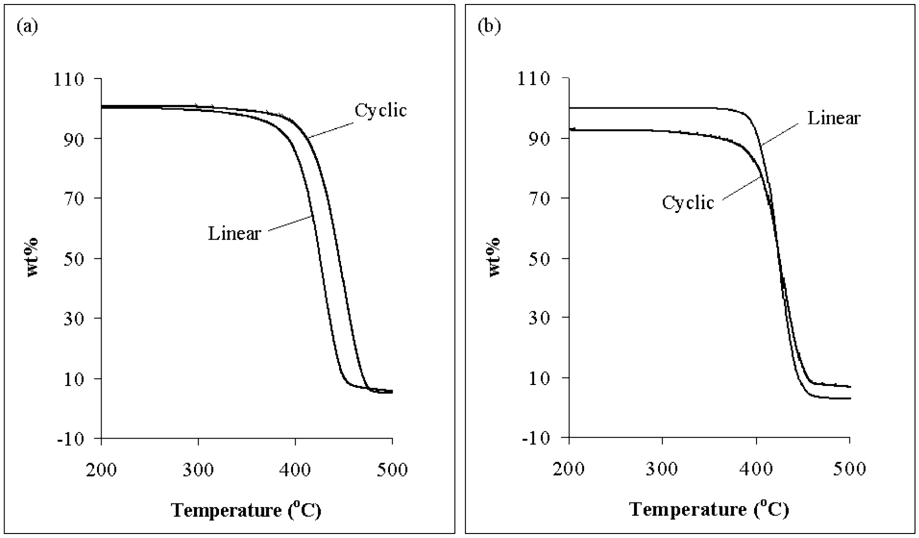

Figure 5. TGA of macrocyclic PDMVF and the matching linear analogue: (a) Table 2, no. 2; (b) Table 2, no. 8.

1, no. 1) showed further and clear evidence for ring formation (Figure 3). The interval between the peaks is 220 Da, corresponding to the molar mass of DMVF unit. For both polymers, the experimental and calculated mass numbers were in good agreement. The formation of the ring structure was supported by the 102 Da mass difference between 1,4-benzylidene linkage of the macrocycle and the two protonated chain ends of the matching linear precursor. For instance, the masses of cyclic PDMVF with a DP of 11 and its linear precursor were observed at 2635 and 2533 Da, respectively, which agreed well with the calculated values ($MW_{cyclic(calcd)} = 2635.5$ Da, $MW_{linear(calcd)} = 2533.3$ Da). There was also good agreement with the SEC MW data (Table 1).

PDMVF Macrocycle Containing 9,10-Anthracenylidene. Incorporation of larger aromatic chromophores, such as anthracene, pyrene, or perylene, into a polymer main chain is of interest for the studies of intramolecular energy transfer.[24,27] Macrocyclic poly(2-vinylnaphthalene)'s (P2VN) containing a single 9,10-anthracenylidene linking unit have been prepared through cyclization of the polymer dianion with 9,10-bis(chloromethyl)anthracene (BCMA).[15] A macrocyclic PDMVF containing a 9,10-anthracenylidene linking unit with DP_n of 11 was successfully prepared, and UV analysis indicated 95% anthracenylidene incorporation.[35] The $\langle G \rangle$ value of 0.85 of this macrocycle was reasonable. However, an earlier attempted synthesis of a larger size PDMVF macrocycle ($DP_n = 36$) using BCMA coupler failed, as judged by an abnormally high $\langle G \rangle$ value of 0.85 for this MW. This may have resulted from significant contamination by linear PDMVF due to the rather high concentration used in the coupling reaction.[32,35] However, the use of relatively low concentration (about 1×10^{-3} M) in our case produced a macrocycle ($DP_n = 44$) with a satisfactory $\langle G \rangle$ value of 0.77 (Table 1, no. 5), which followed the expected $\langle G \rangle$ vs DP_n trend.[12,14] The anthracene incorporation in this case is about 90% determined by UV–vis absorption at 406 nm using the extinction coefficient of 9,10-dimethylanthracene ($\epsilon = 10\,000$)[35] and the DP_n of the matching linear PDMVF precursor.

Thermal Properties. The fractionated macrocyclic PDMVF polymers and their matching linear analogues were used to study the dependence of the glass transition temperature (T_g) and thermal decomposition, on the

Table 2. Thermal Properties of Fractionated Macrocyclic PDMVF and the Matching Linear Polymers

		linear PDMVF		fractionated cyclic PDMVF	
no.	DP_n[a]	T_g (°C)[b]	$TGA^{50\%}$ (°C)[c]	T_g (°C)[b]	$TGA^{50\%}$ (°C)[c]
1	12	126	424	171	441
2	18	141	417	172	445
3[d]	23	147			
4	30	152	420	168	435
5[e]	44	158		166	
6	47	159	421		429
7[d]	125	176			
8	142	178	423	164	425

[a] Obtained by SEC analysis using PS standards. [b] Glass transition temperature. Second run, scanning rate 10 °C/min under He. [c] Temperature for 50% weight loss under N_2. [d] See ref 21. [e] Anthracene incorporation 90% as determined from DP_n and UV–vis.

molecular weight. As shown in Table 2**,** the T_g values of linear PDMVF, varying from 126 °C ($DP_n = 12$, Table 2, no. 1) to 178 °C ($DP_n = 142$, Table 2, no. 8), are comparable to those reported.[21]

Thus, for linear PDMVF, T_g was observed to decrease with decreasing molecular weight and glass transition temperatures of linear PDMVF. Number 3 ($T_g = 147$ °C, $DP_n = 23$) and no. 7 ($T_g = 176$ °C, $DP_n = 125$) of Table 2 fit this trend (Figure 4).[21] However, the glass transition temperatures of the macrocyclic PDMVF did not follow the trend previously reported for PS,[13] PAMS,[14] P2VP,[15] and P2VN.[13] In those cases the T_g values were identical to those of high-MW linear polymers and practically independent of MW above a DP_n of about 10–30. In the present case, the T_g's of PDMVF macrocycles *decreased with increasing* DP_n's from from 171 °C ($DP_n = 12$, Table 2, no. 1) to 164 °C ($DP_n = 142$, Table 2, no. 8). In contrast to all other vinyl aromatic macrocycles, we have studied this value of 164 °C was 14 deg lower than the matching linear polymer (Table 2, no. 8). This indicates that the MW of the highest DP cyclic polymer is still below the limiting value at which the T_g's of linear and cyclic polymers converge.[13–15]

As shown in Figure 4, the high T_g values, especially of the lower MW macrocycles, gave rise to significant T_g differences (as large as 45 °C, Table 2, no. 1) compared to those of the linear polymers. Smaller T_g differences between linear and cyclic polymers were reported for PS (10–20 °C)[13] and for P2VN (30–40 °C).[15] The larger differences in T_g observed in the present case may indicate greater rigidity of the smaller PDMVF macrocycles that are conformationally encumbered by the presence of the large fluorenyl pendent groups.

Differences were also observed in the thermal decomposition behavior of linear and macrocyclic PDMVF under nonoxidative conditions. In agreement with the thermal behavior of other vinyl aromatic macrocyclic polymers, the low-MW PDMVF macrocycles showed a higher thermal stability than the matching linear polymers, and this difference diminished with increasing MW's.[13,1536] For instance, a 50% weight loss was recorded at 445 °C for cyclic PDMVF with DP_n of 18 (Table 2, no. 2), 28 deg higher than that of the matching linear polymer (Figure 5a). The better heat resistance of macrocyclic polymers is attributed to the absence of chain ends that may be more susceptible to hydrogen abstraction and radical depolymerization.[36]

However, as shown in Figure 5b, a typical TGA curve for a high-MW macrocyclic PDMVF (e.g., Table 2, no. 8) showed about 5% "early" weight loss below 200 °C, possibly due to the release of moisture from the sample (Figure 5b). In this case a small loss of mass started at about 280–300 °C, lower than the decomposition temperature of the linear analogues (320–360 °C). A similar "early" decomposition was observed for MW macrocyclic PS, PS-*b*-poly(dimethylsiloxane)[18] block copolymers, and macrocyclic P2VN.[15] This phenomenon is not understood at present but may be related to structural imperfections in a small fraction of the macrocycles, for instance, the presence of allyl hydrogens resulting from the presence of vinylic impurities.[15] The thermal decomposition in the presence of oxygen was not explored. Further studies on these interesting macrocycles are in progress.

Conclusions

The synthesis of narrow distribution macrocyclic PDMVF containing a single 1,4-benzylidene or 9,10-anthracenylidene linking unit is reported. The SEC hydrodynamic size of the cycles with DP_n's between 12 and 142 was between 9 and 29% lower than that of the matching linear polymers with differences decreasing with increasing MW. The glass transition temperatures of low-MW macrocycles were as much as 30–45 deg higher than the matching linear polymers. In contrast with results obtained on other vinyl aromatic macrocycles, the T_g values of the PDMVF macrocycles increased significantly with decreasing degrees of polymerization. However, the T_g of the highest MW macrocycle ($DP_n = 142$) remained 14 deg lower than that of the matching linear polymer. Compared to their linear analogues, macrocyclic PDMVF polymers always exhibited higher nonoxidative thermal stabilities.

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References and Notes

(1) (a) Keul, H.; Höecker, H. *Large Ring Molecules*, 1st ed.; Semlyen, J. A., Ed.; John Wiley & Sons: New York, 1996; Chapter 10. (b) Ederle, Y., Naraghi, K., Lutz, P. J., Eds. *Synthesis of Cyclic Macromolecules*; Wiley-VCH: Weinheim, 1999.
(2) Roovers, J. *Macromolecules* **1985**, *18*, 1359.
(3) Hogen-Esch, T. E.; Sundararajan, J.; Toreki, W. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 23.
(4) (a) Rique-Lubet, L.; Schappacher, M.; Deffieux, A. *Macromolecules* **1994**, *27*, 6318. (b) Deffieux, A.; Schappacher, M. *Macromolecules* **2001**, *34*, 5827.
(5) Deffieux, A.; Schappacher, M.; Rique-Lubet, L. *Polymer* **1994**, *35*, 4562.
(6) Ishizu, K.; Kanno, H. *Polymer* **1996**, *37*, 1487.
(7) Pasch, H.; Deffieux, A.; Ghahary, R.; Schappacher, M.; Rique-Lubet, L. *Macromolecules* **1997**, *30*, 98.
(8) Kubo, M.; Hayashi, T.; Kobayashi, H.; Tsubo, K.; Itoh, T. *Macromolecules* **1997**, *30*, 2805.
(9) (a) Oike, H.; Imaizumi, H.; Mouri, T.; Yoshioka, Y.; Uchibori, A.; Tezuka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9595. (b) Oike, H.; Hamada, M.; Eguchi, S.; Danda, Y.; Tezuka, Y. *Macromolecules* **2001**, *34*, 2776.
(10) Lepoittevin, B.; Dourges, M. A.; Masure, M.; Hemery, P.; Baran, K.; Cramail, H. *Macromolecule* **1999**, *32*, 8218.
(11) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834.
(12) Gan, Y. D.; Dong, D. H.; Hogen-Esch, T. E. *Macromolecules* **2002**, *35*, 6799.

(13) Gan, Y.; Dong, D. H.; Hogen-Esch, T. E. *Macromolecules* **1995**, *28*, 383.
(14) Dong, D. H.; Hogen-Esch, T. E. *e-Polym*. **2001**, 007.
(15) Nossarev, G. G.; Hogen-Esch, T. E. *Macromolecules* **2002**, *35*, 1604.
(16) (a) Höecker, H.; Geiser, D. *Macromolecules* **1980**, *13*, 653. (b) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843. (c) Hadziioanou, G.; Cotts, P. M.; Ten Brinke, G.; Han, C. C.; Luta, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 493.
(17) Alberty, K. A.; Tillman, E.; Carlotti, S.; King, K.; Bradforth, S. E.; Hogen-Esch, T. E.; Parker, D.; Feast, W. J. *Macromolecules* **2002**, *35*, 3856.
(18) Yin, R.; Hogen-Esch, T. E. *Macromolecules* **1993**, *26*, 6952.
(19) Gan, Y.; Zoeller, J.; Yin, R.; Hogen-Esch, T. E. *Makromol. Chem., Makromol. Symp.* **1994**, *77*, 93.
(20) Lescanec, R. L.; Hajduk, D. A.; Kim, G. Y.; Gan, Y.; Yin, R.; Gruner, S. M.; Hogen-Esch, T. E.; Thomas, E. L. *Macromolecules* **1995**, *28*, 3485.
(21) Zhang, X.; Hogen-Esch, T. E. *Macromolecules* **2000**, *33*, 9176.
(22) Zhang, X.; Hogen-Esch, T. E. Manuscript submitted.
(23) (a) Birks, L. B. *Photophysics of Aromatic Molecules*; John Wiley: London, 1970. (b) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: London, 1971. (c) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.
(24) Semarak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 33.
(25) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985.
(26) (a) Guillet, J. E. *Trends Polym. Sci.* **1996**, *4*, 41. (b) Nowakowska, M.; Strorsberg, J.; Zapotoczny, S.; Guillet, J. E. *New J. Chem*. **1999**, *23*, 617.
(27) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.
(28) (a) Pokorno, V.; Vyprachticky, D.; Pecka, J.; Mikes, F. *J. Fluoresc.* **1999**, *9*, 59. (b) Tong, J.-D.; Ni, S.; Winnik, M. A. *Macromolecules* **2000**, *33*, 1482.
(29) Ushiki, H.; Horie, K.; Okamoto, A.; Mita, I. *Polym. J.* **1981**, *13*, 191.
(30) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854.
(31) Tillman, E. S.; Hogen-Esch, T. E. *J. Polym. Sci., Part A: Polym. Chem*. **2002**, *40*, 1081.
(32) Dong, D.; Hogen-Esch, T. E.; Shaffer, J. S. *Macromol. Chem. Phys.* **1996**, *197*, 3397.
(33) (a) Carothers, W. H. *Trans. Faraday Soc.* **1936**, *32*, 39. (b) Odian, G. *Principles of Polymerization*; John Wiely & Sons: New York, 1991; Chapter 5.
(34) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(35) Tillman, E. S.; Hogen-Esch, T. E. *Macromolecules* **2001**, *34*, 6616.
(36) Sterling, W. J.; Walline, K. S.; Mccoy, B. *J. Polym. Degrad. Stab.* **2001**, *73*, 75.

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