Ultraviolet Absorption and Fluorescence Emission Spectroscopic Studies of Macrocyclic and Linear Poly(9,9-dimethyl-2-vinylfluorene). Evidence for Ground-State Chromophore Interactions

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ABSTRACT: UV absorptivities of macrocyclic and matching linear poly(9,9-dimethyl-2-vinylfluorene) prepared from the same precursors show decreases of 30 and 15%, respectively, as degrees of polymerization (DP_n's) increase from 12 to 142. The strong increase in hypochromism with molecular weight for the macrocycles indicates an increase in ordering of the large pendent aromatic chromophores. The emission intensities of the low-DP_n macrocycles were found to be enhanced up to 20% compared to the matching linear polymers. This is attributed to both decreased excimer formation and lower rates of radiation-less decay especially in the smaller rings.

Introduction

Polyfluorenes have been studied for applications in light-emitting diodes and conducting materials.[1−7] For instance, they show interesting luminescent properties that are due to partial conjugation along the chain. On the other hand, poly(vinylfluorenes) lacking this conjugation may be of interest as a comparison system in the study of energy transfer[8−10] and light harvesting[11,12] in vinyl aromatic polymers. The molar absorptivity of fluorene in the near-UV region is on the order of 1.1×10^4 L mol^{-1} cm^{-1}, and its fluorescence quantum efficiency is as high as 80%.[8] Furthermore, the Förster radius is 23 Å, approximately double that of naphthalene and comparable to that of carbazole and methylanthracene.[8]

The synthesis and properties of macrocyclic polymers have seen a resurgence in recent years.[13] Macrocyclic vinyl polymers exhibit interesting differences with linear polymers in their hydrodynamic,[14] thermal,[15−21] and spectroscopic[22,23] properties. For instance, low molecular weight (MW) macrocyclic polystyrene (PS),[13a,15,19,24] poly(2-vinylpyridine) (P2VP),[19,25] poly(2-vinylnaphthalene) (P2VN),[20] and poly(9,9-dimethyl-2-vinylfluorene)[21] have higher glass transition temperatures (as much as 45 °C) compared with those of the matching linear polymers presumably due to bond angle and/or torsional constraints.

In turn, these appear to affect the photoluminescence and absorption properties. Thus, low MW macrocyclic PS exhibits a significantly greater (up to 3-fold) monomer emission than the matching linear polymer.[22] Similar emission enhancements have been observed for poly(2-vinylnaphthalene) (P2VN) macrocycles.[26]

Here we report the UV−vis absorption and steady-state fluorescence of macrocyclic poly(9,9-dimethyl-2-vinylfluorene) (PDMVF). The macrocyclic PDMVF is prepared by the potassium naphthalide-initiated polymerization of 9,9-dimethyl-2-vinylfluorene (DMVF) followed by end-to-end coupling with 1,4-bis(bromomethyl)benzene (DBX) under high dilution conditions (Scheme 1).[21] The methylation at both the 9-fluorenyl positions avoids deprotonation during anionic polymerization and also gives better solubility in hydrocarbon solvents.[27]

Experimental Section

The PDMVF macrocycles were prepared by the potassium naphthalide-initiated anionic polymerization of DMVF and the subsequent end-to-end coupling of PDMVF dianion with bifunctional electrophile under high dilution conditions, as reported elsewhere.[21] The polymers were characterized by size exclusion chromatography (SEC), NMR, and MALDI−TOF.

The 9,9-dimethyl-2-ethylfluorene model compound was synthesized by palladium (Aldrich, 10 wt % on activated carbon)-catalyzed hydrogenation of DMVF in toluene at room temperature for 16 h. ^{1}H NMR: δ (ppm) 7.70−7.14 (m, 7H), 2.77−2.68 (q, 2H), 1.48 (s, 6H), 1.32−1.26 (t, 3H).

UV−vis and steady-state fluorescence emission (excited at 307 nm) measurements were made using a Varian Cary 50 spectrometer and a PTI Quanta Master TM model C-60SE spectrofluorimeter (using a 3 nm band-pass), respectively. Spectra were recorded at a concentration of 5 mg/L in distilled cyclohexane. Extinction coefficients were calculated on the basis of concentration of fluorenyl units; the mass difference between linear and cyclic PDMVF due to the presence of 1,4-benzylidene linkage unit was accounted for, although this is a small correction (at most 4% for the macrocycle with $DP_n = 12$).

Results and Discussion

Synthesis. Narrow distribution macrocyclic PDMVF with number-average degrees of polymerization (DP_n) ranging from 12 to 142 were synthesized via the potassium naphthalide-initiated anionic polymerization of DMVF to give the living dianion PDMVF precursor. A portion of this precursor was then cyclized by high dilution end-to-end coupling with 1,4-bis(bromomethyl)benzene (DBX), the remainder being protonated to give the corresponding matching linear polymers with the same degree of polymerization (DP_n) (Table 1).[21] The crude cyclization product containing higher DP_n "polycondensates" formed by intermolecular coupling was

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Scheme 1

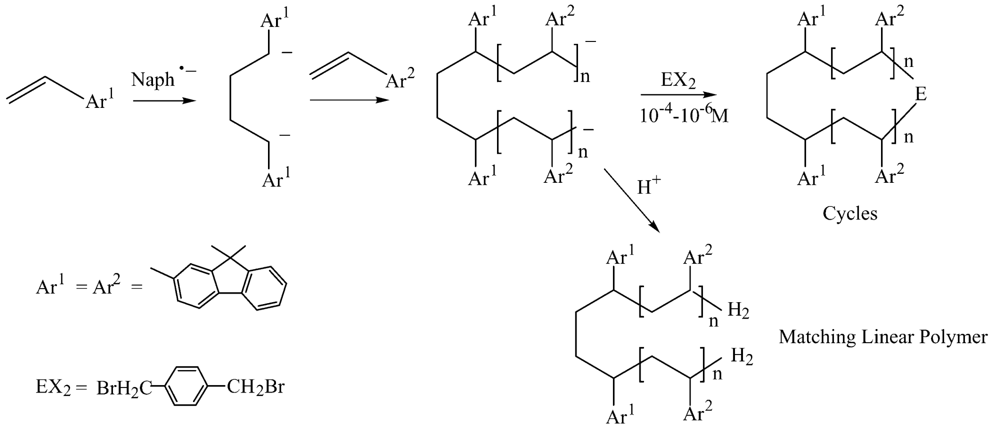

Table 1. Molecular Properties of Macrocyclic PDMVF[a,b]

		linear PDMVF			fractionated cyclic PDMVF			
no.	DP_n	M_n	M_p	PDI	M_n	M_p[c]	PDI	$\langle G\rangle$[d]
1	12	2600	2900	1.12	2600	2600	1.16	0.91
2	18	3900	4400	1.12	3500	3900	1.09	0.89
3[e]	19	4200	5000	1.13				0.89
4	30	6600	7800	1.12	5900	6600	1.14	0.84
5	47	10300	12000	1.09	7900	8800	1.09	0.73
6	142	31200	34400	1.07	20800	24700	1.08	0.71

[a] The coupling reagent was DBX, 1,4-bis(bromomethyl)benzene. [Monomer] = 0.15 M; cyclization reaction carried out over about 20 min at anion concentration of $\sim 10^{-5}-10^{-6}$ M. [b] Molecular weights were determined by SEC using polystyrene standards. [c] The values in parentheses are M_p's of unfractionated cyclic PDMVF. [d] $\langle G\rangle = M_{p(\text{crude cyclic})}/M_{p(\text{linear})}$. [e] Cyclization carried out under high anion concentration ($\sim 10^{-3}$ M).

then purified by incremental addition of methanol that precipitated this high DP_n fraction. This fractionation process was monitored by size exclusion chromatography (SEC). The rings, due to their smaller size, have lower apparent MW's but essentially identical MW distributions. The ring formation was confirmed by NMR, SEC, and MALDI−TOF spectrometry.[21]

UV−vis Absorption Spectra. PDMVF exhibits a complicated UV spectrum that resembles that of free fluorene (except for a 6 nm red shift observed for the substituted fluorene), for which a relatively complete assignment has been proposed.[28] Following Sudipati et al.'s assignments, there are two types of transitions, corresponding to polarization along the long (B_2 symmetry excited state) and short (A_1 symmetry excited state) axes. There is a strong UV absorption at 307 nm (1^1B_2 band origin) with vibronic fine structure at 300 and 296 nm and bands at 268 and 274 nm (2^1B_2 band), including vibronic and substructure of other states of A_1 symmetry. Two higher lying, weaker structured bands at 229 and 235 nm are assigned as transitions from ground to 4^1A_1 and 3^1B_2 states, respectively. Finally, between 210 and 220 nm two intense transitions are attributed to the overlapping 5^1A_1 and 5^1B_2 states. Compared to the absorption spectrum of the 9,9-dimethyl-2-ethylfluorene (DMEF) model compound, the polymer 1^1B_2 band is red-shifted by 1 nm and the 3^1B_2 and 4^1A_1 bands are red-shifted by 5 and 7 nm, respectively (to 235 and 230 nm).

Compared to the model compound, both linear and cyclic polymers have lower molar absorptivities with some bands being affected more than others. Furthermore, at equal fluorenyl concentrations, the cycles have lower UV absorptivities than the matching linear polymers at almost all wavelengths, except that at 229 nm (4^1A_1 band) and 235 nm (3^1B_2 band) where the absorptivities are higher (Figure 1).

For instance, at 307 nm the $DP_n = 30$ macrocycle has an approximately 9% lower UV absorptivity than the matching linear polymer (Figure 1, bottom). For the macrocycle with a DP_n of 142, the absorptivity at 307 nm is 22% lower than the matching linear polymer. These differences are not due to the 1,4-benzylidene coupling unit as the absorption of this group is too low to affect the spectra and does not contribute any absorbance above 285 nm. As shown more clearly in Figure 1 (top), the ratio of cyclic to linear extinction coefficients, ϵ_c/ϵ_l, indicates a clearly structured progression of bands that appear to correspond to distinct fluorene transitions (to the 4^1A_1 and 3^1B_2 electronic states[28]). A similar ϵ_c/ϵ_l spectrum is observed for each molecular weight, the 225−235 nm region having a distinct ratio compared to the remainder of the spectrum. Figure 1 indicates that the intensity increases at 229 and 235 nm for the rings relative to the linear polymers are due to "borrowing" from the other transitions. A similar phenomenon has been found for macrocyclic poly(2-vinylnaphthalenes) (P2VN's) that have slightly higher absorptivities than the corresponding linear polymers at the S_1 band (~324 nm) but a lower absorptivities at the S_2 band (~270−300 nm).[26]

As number-average degrees of polymerization (DP_n's) increase from 12 to 142, the UV absorptivities of the linear and cyclic polymers at 307 nm decrease by 15 and 30%, respectively, the absorptivities of the linear polymers being 4−22% higher than those of the matching macrocycles depending on MW (Figure 2). The absorptivity of the lowest MW linear PDMVF ($DP_n = 12$, $\epsilon \sim$ 13 900) is nearly the same as that of the 9,9-dimethyl-2-ethylfluorene (DMEF) model compound ($\epsilon \sim$ 13 900) (Figure 2). The absorptivity of linear PDMVF (ϵ_l) decreases about 12% when the DP_n increases from 12 to 18 but decreases little at higher DP_n's. In contrast,

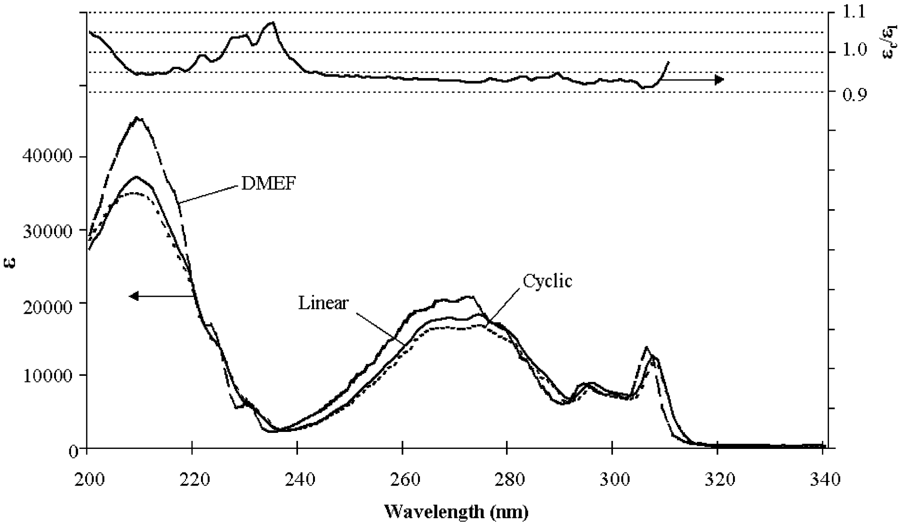

Figure 1. UV extinction coefficients ϵ_C and ϵ_L of cyclic (dotted line) and linear (solid line) PDMVF (DP_n = 30) ϵ_C/ϵ_L (top). DMEF model compound (dashed line) is shown for comparison. Concentrations (5 mg/L) in cyclohexane are corrected for the mass differences due to the presence of linking unit (see text).

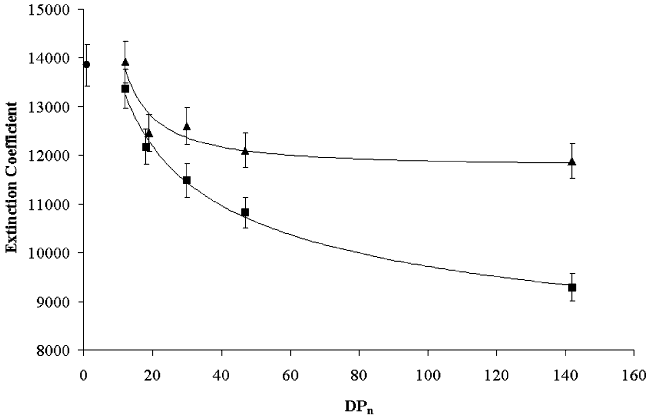

Figure 2. Extinction coefficients of DMEF model compound (at 306 nm) and cyclic and linear PDMVF (at 307 nm) as a function of degree of polymerization (DP_n) (trend-lines added to guide the readers' eyes).

the absorptivities of the cycles show greater decreases (30%) that persist even at higher DP_n's.

Intensity borrowing by a higher electronic transition of one chromophore from a lower electronic transition of a different chromophore is often described as hypochromism.[29] For vinyl aromatic polymers this is indicative of aromatic ring stacking and ordering which leads to weak electronic interactions between π-chromophores. For example, isotactic polystyrene shows a well-known hypochromism; however, relatively modest hypochromic effects (about 10%) were observed.[30] Larger hypochromic effects (50% or more) have been observed especially for high MW linear vinyl polymers with large pendent π-chromophores such as poly(*N*-vinylcarbazole).[31] It has also been found that the hypochromism varies with solvent polarizability and to a lesser extent with addition of nonsolvent,[30] the latter leading to more π stacking of pendent chromophores. The large hypochromic effects we observed for cyclic PDMVF suggest the presence of stronger chromophore stacking in the more congested rings.[29]

The above observations indicate significant conformational changes with MW, in the PDMVF rings, and to a lesser extent in the linear polymers. This is also suggested by the much higher glass transition temperatures (T_g's) of the macrocycles compared with the matching linear polymers.[21] Since the early work of Vala and Rice,[30] attempts to interpret and quantify absorption band oscillator strength changes with conformation for polyvinyl aromatics from first principles have been relatively sparse. A recent simulation study suggests that conformation information is available.[32] However, the systems considered were of much larger molecular weight and did not focus on the short-range chromophore electronic interactions to which hypochromism was originally ascribed.[29,31]

Fluorescence Emission Enhancements. As shown in Figure 3, cyclic and linear PDMVF's with a DP_n of 18 exhibit strong and characteristic fluorene ("monomer") emissions at 311 and 322 nm (λ_{ex} = 307 nm). There is a weaker tailed emission between 360 and 370 nm that is likely due to excimer formation, consistent with the absence of this tail in the DMEF model.[33] Like the absorption spectra, the shape and peak position of the monomer emission band of cyclic and linear PDMVF are the same. However, after correction for absorptivity differences, the emission intensities of the macrocycles at 311 and 322 nm are increased by 19 and 16%, respectively, compared to the matching linear polymers (Figure 3). The total emission quantum yield of the DP_n = 18 macrocycle is the same as the DMEF model, but all linear polymers have lower emission yields. We note that enhanced monomer emission of cyclic polymers has also been observed for PS[22,23] and P2VN.[26]

Compared to the linear polymer, the macrocycle shows a decrease in the excimer band, as shown in the inset of Figure 3. Although the excimer emission increases with increasing DP_n, the macrocycles always have lower excimer emission yields (Figure 4b). These variations are apparently not due to aggregation as the ratios of monomer and excimer emission are concentration independent. The formation of excimer sites on low MW macrocycles may be hindered due to bond angle and torsional strains that are expected to be especially severe for the low MW cyclic PDMVF, consistent with the much higher glass transition temperatures of the cyclic compared to matching linear PDMVF.

Low MW linear vinyl aromatic polymers have been shown to have smaller excimer site densities, presumably due to end-group effects that are consistent with

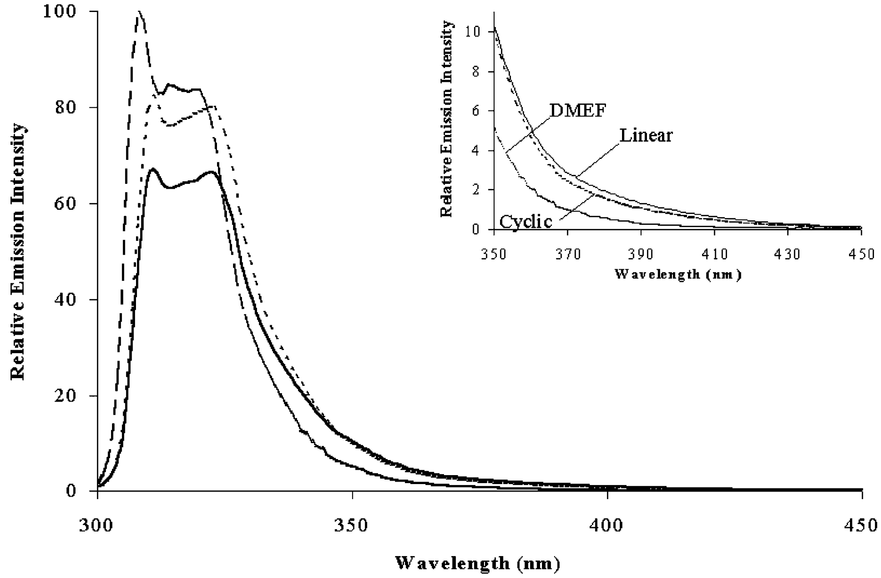

Figure 3. Emission spectra of DMEF (dashed line, $\lambda_{ex} = 306$ nm), cyclic (dotted line), and linear (solid line) PDMVF with $DP_n = 18$ ($\lambda_{ex} = 307$ nm). Concentrations: 5 mg/L in cyclohexane. Counts normalized by optical density at excitation wavelength.

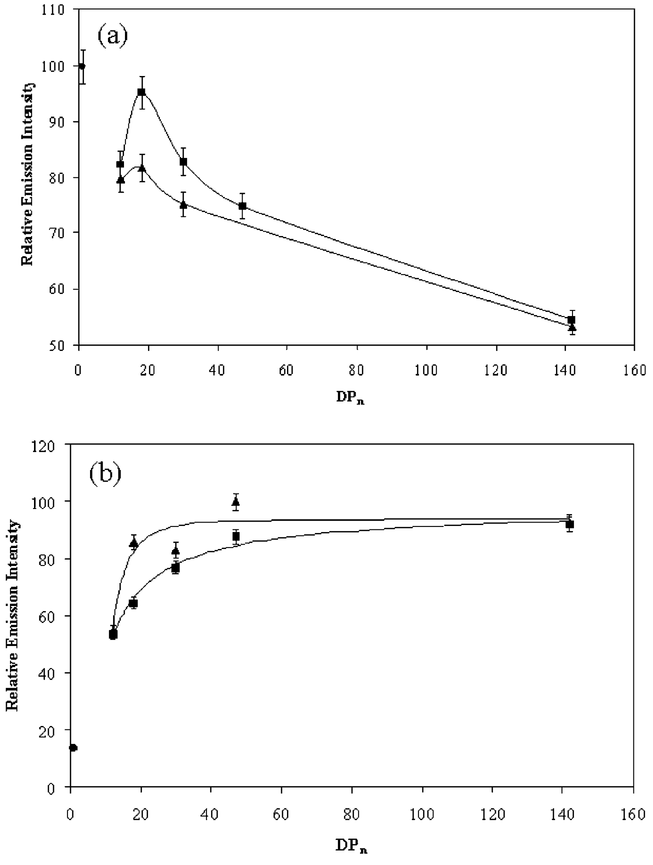

Figure 4. Monomer (a) and excimer (b) emission intensities of cyclic (square) and linear (triangle) PDMVF as a function of DP_n at 322 nm ($\lambda_{ex} = 307$ nm) and DMEF (at 318 nm, $\lambda_{ex} = 306$ nm) (solid circle). Emission intensities normalized by optical density at excitation wavelength (trend-lines added).

their lower glass transition temperatures.[34] The apparent correlation of enhanced monomer emission and increased glass transition temperatures for cyclic polymers has been documented for both PS and P2VN.[20,22,26] The decrease in monomer emission and concomitant increase in excimer emission observed for both cyclic and linear polymer with increasing MW are consistent with the increased number of excimer traps available on a given chain or cycle. If the exciton is mobile,[35,36] then the excitation has a greater probability of encountering an excimer trap site on the larger chains or cycles.

Compared with the matching linear chains, emission enhancements are observed for the cycles with both lower and higher DP_n than the $DP_n = 18$ cycle that has a maximum enhancement (Figure 4a). The emission intensities of the largest macrocyclic and linear polymers (DP_n's of 142), corrected for optical densities, are nearly the same within experimental error (±3%). The same is the case for the excimer intensities at the largest DP_n. The quantum yield maximum for the $DP_n = 18$ cycle is noteworthy in that a similar maximum was observed for PS macrocycles.[37] We have suggested that the occurrence of largest overall emission enhancement for small macrocycles can be discussed in terms of variation in the radiationless decay rate in macrocycles with changing rigidity of the backbone, the “loose bolt effect”.[8a,38,39] To further interrogate this idea, fluorescent lifetime measurements are in progress.

It is interesting that the significant effects described so far were observed for configurationally and conformationally disordered vinyl aromatic macrocycles. A larger effect would be expected for the stereoregular, especially isotactic, polymers.[40]

We close by comparing observations on the hypochromicity and fluorescence with polymer size for the macrocycles. The increase in hypochromicity in the macrocycles with increasing MW suggests the occurrence of local chromophore ordering, perhaps due to short helical sections or other forms of π stacking.[30,31b] The reduced fractions of sandwich-type excimer sites in the low molecular weight macrocycles, and their smaller radiationless decay rates, which we attribute to skeletal strain, together give rise to higher emission quantum yields.

As DP's get large, the photophysical properties of the linear and cyclic systems should converge. This is borne out in the emission properties, but the hypochromicity difference is largest in the high molecular weight polymers. This suggests rather different length scales for the chromophore ordering giving rise to these two effects. Detailed transient absorption anisotropy and exciton annihilation studies exploring energy transfer in the PDMVF system as a function of MW are the subject of separate papers.[35,36] Ongoing analysis of these time-resolved experiments should help unravel the complex and intriguing photophysics of these macrocyclic polymers.

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