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Synthesis and Properties of Macrocyclic Vinylaromatic Polymers Containing a Single 1,4-Benzylidene or 9,10-Anthracenylidene Group

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Summary: The synthesis is reported of well-defined and narrow molecular weight distribution macrocyclic poly(2-vinylnaphthalene) (P2VN) and poly(9,9-dimethyl-2-vinylfluorene) (PDMVF) containing a single 1,4-benzylidene or 9,10-anthracenylidene unit. The synthesis involves the potassium naphthalide (K-Naph) initiated polymerization of 2VN or DMVF in THF at –78 °C followed by end-to-end coupling of the resulting P2VN dianions under high dilution conditions (10^{-6}–10^{-4} M) 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), NMR and MALDI-TOF.

Keywords: anionic polymerization; anthracene; macrocyclic polymers; polyvinylfluorene; polyvinylnaphthalene

Introduction

There has been a revival of interest in recent years in the synthesis of macrocyclic vinyl aromatic polymers.[1-17] We have successfully synthesized and characterized macrocyclic and matching linear polystyrene (PS),[11,12] poly(2-vinylpyridine) (P2VP),[3,12] poly(α-methylstyrene) (PAMS)[13] and poly(2-vinylnaphthalene) (P2VN),[14] and vinylaromatic block copolymers[15-17] by end-to-end cyclization of the corresponding dianions with bifunctional electrophiles, such as 1,4-bis(bromomethyl)benzene (DBX) and dibromomethane in highly dilute solutions

(10^{-4}-10^{-6} M). Vinyl aromatic polymers containing 2-naphthyl or 2-fluorenyl pendent groups have interesting photoluminescent properties and good chemical and thermal stabilities.[12,14,18-21] The molar absorptivity of fluorene in the near UV region is in the

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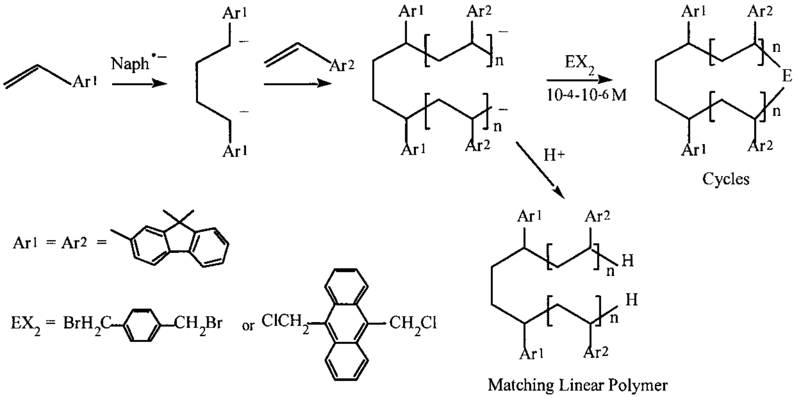
order of 10^4 and its fluorescence quantum efficiency is relatively high (about.80 percent).[20] Such polymers or copolymers are of interest in energy transfer studies in light harvesting polymers.[22-26]

Here we describe the synthesis, characterization, and properties of the potassium naphthalide mediated electron transfer initiated polymerization of 2-vinylnaphthalene (2VN) and 9,9-dimethyl-2-vinylfluorene [(DMVF) and the intramolecular cyclization of the resulting polymer dianion precursors in THF with DBX or 9,10-bis(chloromethyl)anthracene (BCMA) under high dilution conditions to give the corresponding macrocyclic P2VN and PDMVF (Scheme 1). The incorporation of anthracene in such polymers is of interest as this is a useful fluorescent acceptor probe in the study of energy migration.[25,26]



Scheme 1. Synthesis of macrocyclic and matching linear vinylaromatic polymers.

Experimental Section

Materials. The procedures for the preparation and characterization of macrocyclic vinylaromatic polymers using break-seal techniques have been reported.[11a,14] The DMVF was prepared by bis-methylation of 2-vinylfluorene[27] (2VF) at the 9-position using a modified procedure.[28] UV-Vis absorption on the P2VN samples was run on a Varian Cary 50 spectrometer with a baseline correction using 50 mg/L P2VN solutions in cyclohexane/THF (90/10 v/v) mixtures and 1 mm quartz cells. UV-Vis measurements of the PDMVF samples were carried out in cyclohexane at 5 mg/L on a Varian Cary 50 spectrometer using a 1 cm quartz cell with a baseline set using solvent. Fluorescence experiments were run in cyclohexane at 5 mg/L in a 1 cm fluorescence cell on a PTI Quanta Master TM Model C-60SE spectrofluorimeter with a 3 nm bandpass.

Results and Discussion

A number of narrow MW distribution macrocyclic P2VN and PDMVF with DP_n's from 7 to 142 were synthesized in THF at –78 °C through the potassium naphthalide initiated polymerization and coupling at anion concentrations that fluctuated typically between 10^{-4} and 10^{-6}M using 1,4-bis(bromomethyl)benzene (DBX) or 9,10-bis(chloromethyl)anthracene (BCMA) (Tables 1 and 2).

Table 1. Formation of macrocyclic P2VN by coupling of P2VN-K_2 and DBX or BCMA in THF at –78 °C[a]

#	$M_n^{calc}.10^{-3}$ (g/mole) [f]	P2VN linear [b,d]			P2VN cyclic [b,d]			
		M_p[b] 10^{-3} (g/mole)	$M_n.10^{-3}$ (g/mole)	PDI	M_p[b] 10^{-3} (g/mole)	$M_n.10^{-3}$ (g/mole)	PDI	<G> [c]
1	5.70	6.50	5.60	1.12	5.24	11.5	3.86	0.80
2	5.70	7.00	6.00	1.12	5.45	11.7	5.22	0.78
3	0.55	0.95	0.74	1.34	0.91	0.94	2.65	0.95
4[e]	0.85	1.10	1.00	1.18	0.98	1.15	2.70	0.89
5	1.10	1.25	1.15 (1.25)	1.16	1.07	1.15 (1.00)	1.13	0.86
6	1.50	1.80	1.60 (1.75)	1.16	1.53	1.67 (1.58)	1.12	0.85
7[e]	2.30	2.89	2.50	1.15	15.0	4.70	-	-
8	3.40	4.40	3.80 (4.05)	1.12	3.35	4.00 (2.90)	1.11	0.76
9[e]	3.70	4.43	4.00 (4.00)	1.11	3.48	4.40 (3.15)	1.13	0.79
10	11.0	14.8	13.2 (12.3)	1.16	10.6	15.0 (11.1)	1.12	0.71

a. Coupling agent was DBX except as indicated. *b.* MW's determined by SEC using polystyrene standards Apparent peak molecular weight. *c.* Ratio of apparent peak molecular weights of macrocyclic and linear P2VN. *d.* The values in parentheses are Mn's of fractionated P2VN. *e.* BCMA was used as coupling reagent. *f.* Calculated MW's

The first reaction (Table 1, #2) was carried out at a relatively high anion concentration of 5.10^{-3}M in order to determine the coupling efficiency (Table 1, #2, Figure 1a). The SEC of the unfractionated product shows a peak at 12 mL that corresponds to the expected high MW "polycondensation"[29-31] product (M_p=112,000) (Figure 1a). The presence of a significant fraction of the intended P2VN macrocycle at 15.5 mL with an apparent peak MW ($M_{p,}$) of about 5,500 macrocyclic polymer at high anion concentrations is consistent with predictions.[32]

The apparent MW corresponding to the peak at 14.5 mL (M_p=11,200) is almost exactly double of that of the primary macrocycle, and is attributed to the macrocyclic dimer formed by one inter- and one intramolecular coupling. The linear P2VN (M_p =7000) is shown for comparison. At the typically much lower anion concentrations the SEC yields of the cycles are much higher (Table 1, # 6, Figure 1b).

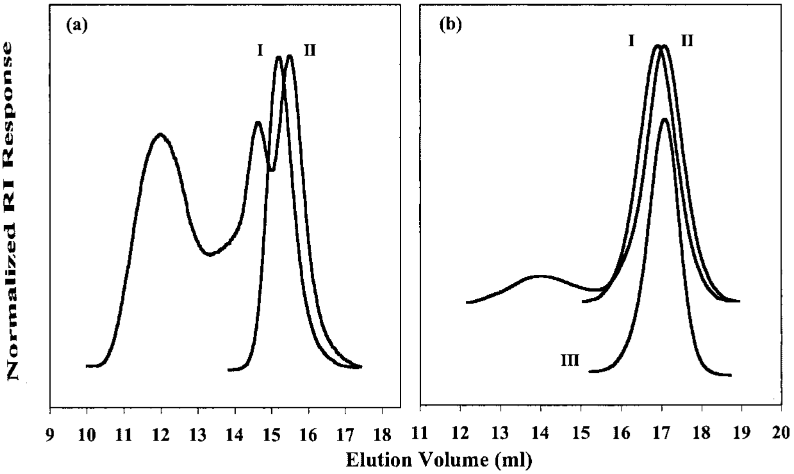


Figure 1. SEC (RI) traces of (a) linear P2VN (I) and (DBX) cyclization (Table 1, # 2) and (b) precursor P2VN (I), product of coupling with DBX under high dilution (II) (Table 1, # 6). and fractionated macrocyclic P2VN (III).

The M_n of the highest MW fraction in Figure 1a indicates a high coupling efficiency as it is 17 times that of the linear precursor giving an effective degree of step polymerization of 34. The corresponding apparent average functionality of the corresponding P2VN-K_2 calculated from the SEC data, at least at 5.10^{-3}M, is equal to 1.94 indicating that approximately three percent of total anion might have been inadvertently terminated.[33] Thus, the expected fraction of P2VN chains terminated at *both* chain-ends is negligible (about 0.001) at least at this concentration.

The linear analogues with the same MW were prepared by protonation of the P2VN dianion using methanol. Although the presence of a 1,4-benzylidene unit in macrocyclic PS affects its spectroscopic properties,[11a] this should not be the case for P2VN as absorption and emission of 1,4-benzylidene is negligible in this case.[20]

Table 2. Cyclization of DMVF Coupled with DBX or BCMA at –78 °C in THF[a]

#	Mn^{calc} (g/mole)	Linear PDMVF Mn^b (g/mole)	Linear PDMVF Mp^b (g/mole)	Linear PDMVF PDI	Cyclic PDMVF Mn^b (g/mole)	Cyclic PDMVF $Mp^{b,c}$ (g/mole)	Cyclic PDMVF PDI^b	SEC Yield[d]	<G>[e]
1	2200	2620	2920	1.12	2560	2600	1.16	72%	0.91
2	3300	3930	4420	1.12	3470	3930	1.09	65%	0.89
3^f	3530	4210	4970	1.13		4420		50%	0.89
4	6180	6560	7810	1.12	5860	6600	1.14	50%	0.84
5^g	8820	9710	11420	1.10	8080	8930	1.12	66%	0.77
6	9240	10320	11990	1.09	7910	8820	1.09	70%	0.73
7	26440	31240	34420	1.07	20840	24670	1.08	38%	0.71

a. [Monomer] = 0.15 M; cyclization carried out over about 20 minutes at anion concentration of ~ 10^{-5}-10^{-6} M. *b*. determined by SEC using polystyrene standards.. *c*. SEC maxima of unfractionated cyclic PDMVF. *d*. estimated from SEC. *e*. <G>: see text. *f*. Cyclization carried out at [anion] =10^{-2} M. *g*. BCMA was used as coupling reagent.

The apparent functionality for the PDMVF under comparable conditions (Table 2, #3) is 1.90, indicating about 5 percent anion termination at each chain end and thus the presence of about 0.25 percent PDMVF inadvertently terminated at both ends. However the presence of somewhat higher amounts of linear impurities at the much lower anion concentrations employed during most coupling reactions can not be excluded.

The efficient formation of P2VN and PDMVF macrocycles is confirmed by decreases in the values of <G> (= M_{cyclic}/M_{linear}) with increasing DP's from 0.95 to 0.71 for P2VN[14] and from 0.91 to 0.71 for PDMVF (Tables 1 and 2). We have observed such trends for all macrocyclic polymers we have studied.[3,11-16] This may be due to the severe conformational restraints in the cycles as the number of monomer units decreases.

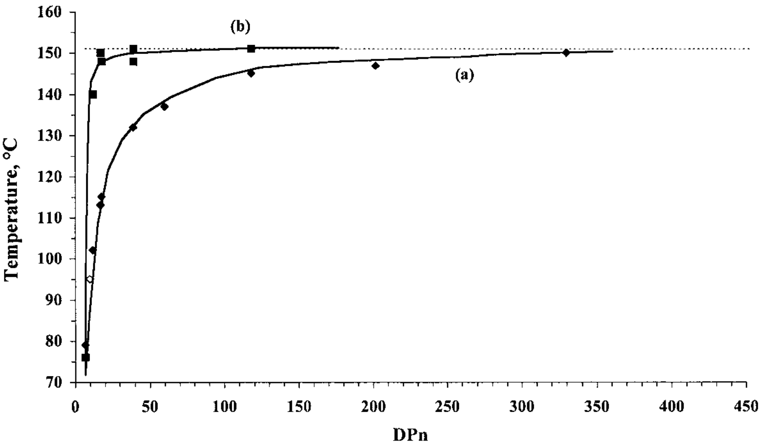


Figure 2. Relationship between glass transition temperature (T_g) and degree of polymerization (DP_n) of linear (a) and macrocyclic (b) PDMVF.

The PDMVF cyclization yields estimated from the SEC chromatograms varied from 38 to 72 percent and generally decreased with increasing DP_n, consistent with predictions.[32] For the case of the PDMVF cycles MALDI-TOF measurements of the fractionated macrocyclic PDMVF and the matching linear polymer (Table 1, # 1) showed convincing evidence for ring formation. Thus the interval between the peaks, corresponding to the molar mass of DMVF unit, is 220 Da in both cases and the masses of the cycles were 102 Da higher than the matching linear polymers due to the 1,4-benzylidene linkages.

Glass transitions. The dependence of the glass transition temperature (T_g) of linear and cyclic P2VN on DP_n is similar to that observed for PS[12] and PAMS.[13] Thus, as shown in Figure 2, the T_g's of the P2VN macrocycles above a DP_n of about 20 are equal to that of the highest MW linear P2VN (about 150 °C) and independent of MW.[14] Below a DP_n of 20, the P2VN cycles decrease sharply with decreasing MW. However, as shown in Figure 3, the glass transition temperatures of the macrocyclic PDMVF did not follow this trend. Thus, the T_g values of the cycles actually *increased* with decreasing DP_n and the differences with the linear PDMVF were larger than for any other vinylaromatic macrocycle (as large as 45 °C, Table 2, # 1). Furthermore, the T_g values of the linear and cyclic PDMVF's at high MW's did not converge at the highest MW, indicating that the T_g's of the cycles did not yet approach their high MW limit. These differences are tentatively attributed to the increasing rigidity of the conformationally encumbered PDMVF macrocycles (see below).

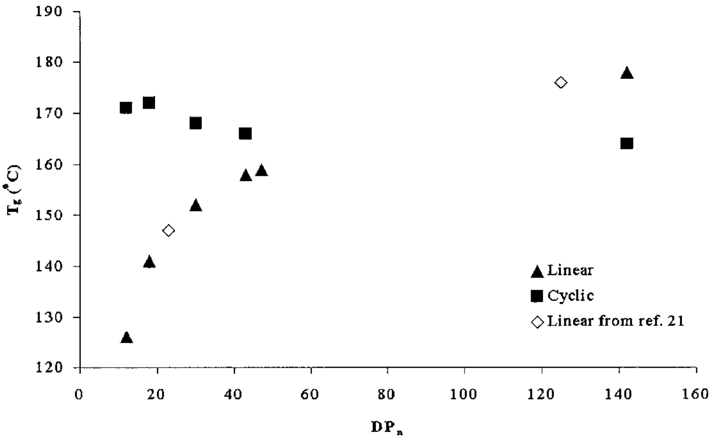


Figure 3. Relationship between glass transition temperature (T_g) and degree of polymerization (DP_n) of macrocyclic and linear PDMVF.

UV 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 (Figure 4).[37] 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 and 235 nm where the absorptivities are higher. As shown more clearly in the figure (top), the ratio of extinction coefficients of cyclic and linear PDMVF ($\varepsilon_c/\varepsilon_l$) indicate a clearly structured progression of bands that correspond to distinct fluorene transitions with similar $\varepsilon_c/\varepsilon_l$ spectra being observed for each MW. The intensity increases at 229 and

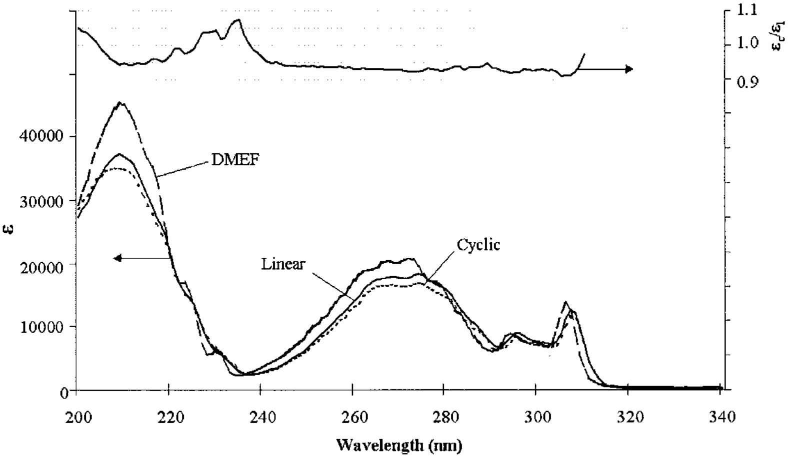


Figure 4. Extinction coefficients of cyclic (ε_C) and linear (ε_L) PDMVF (DP_n = 30). and their ratio ($\varepsilon_C/\varepsilon_L$) and that of 9,9-dimethyl-2-ethylfluorene; concentration = 5 mg/L in cyclohexane.

235 nm for the rings relative to the linear polymers are due to "borrowing" from the other transitions.[38]

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 dramatically, by 15 and 30 percent respectively, the absorptivities of the linear polymers being 4-22 percent higher than those of the matching macrocycles depending on MW (Figure 5).

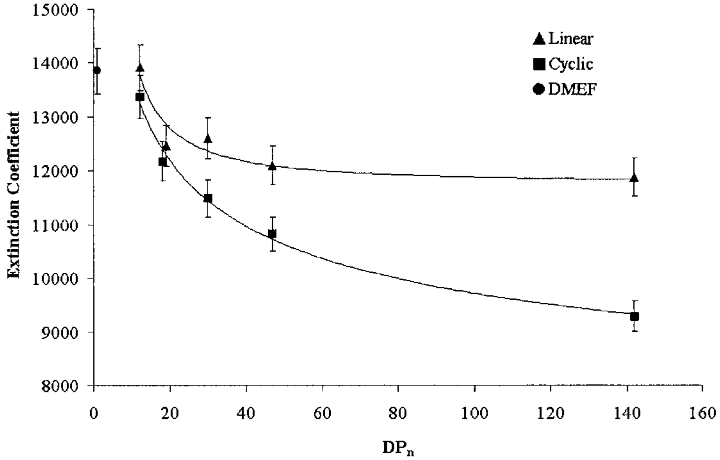


Figure 5. Extinction coefficients of 9,9-dimethyl-2-ethylfluorene (DMEF) model compound (at 306 nm), cyclic(■) and linear (▲) PDMVF (at 307 nm) as a function of degree of polymerization (DP$_n$) (trend-lines added).

The absorptivity of the lowest MW linear PDMVF (DP$_n$ = 12, $\varepsilon \sim 13900$) is nearly the same as that of the 9,9-dimethyl-2-ethylfluorene (DMEF) model compound ($\varepsilon \sim 13800$). Absorptivities of linear PDMVF decrease about 12 percent when the DP$_n$ increases from 12 to 18 but decreases little at higher DP$_n$'s. The large hypochromic effects for PDMVF cycles suggest the presence of stronger chromophore stacking in the more congested higher MW rings leading to weak electronic interactions between π-chromophores.[39,40] Similar decreases in absorptivity of the P2VN cycles compared to the linear P2VN chains were observed.[41]

9,10-Anthracenylidene macrocycles. The formation of macrocyclic P2VN and PDMVF containing a single 9,10-anthracenylidene unit by reaction of P2VN,K_2 or PDMVF,K_2 with 9,10-bis(chloromethyl)anthracene proceeded well under high dilution conditions as indicated by a symmetrical SEC peak and clear shifts to a higher elution volumes compared with the linear polymers and high SEC yields (50-70%). In addition, the <G> values follow the same trends obtained for the above DBX mediated P2VN cycles being slightly higher for the same MW's, most likely on account of the larger 9,10-anthracenylidene spacers.

The uniform incorporation of a single AN into macrocyclic P2VN was confirmed by identical RI and UV SEC traces of the fractionated macrocycles run at both 405 nm and 295 nm, the wavelength where only naphthalene absorbs (data not shown). The anthracene content in the fractionated macrocycles calculated using the DP_n from the linear precursor and absorption at 405 nm using the extinction coefficient for 9,10-dimethylanthracene[20] (ε =10,000) was about 90 percent, confirming a high degree of anthracene incorporation. Studies on the photophysics of these labeled macrocycles are being carried out.[36]

Fluorescence. As shown in Figure 6, 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 emission between 360 and 370 nm that is likely due to excimer formation, consistent with the absence of a long red-shifted tail in the fluorescence spectrum of the DMEF model.[41]

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 nm and 322 nm are increased by 19 and 16 percent respectively, compared to the matching linear polymers. 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.

Enhanced monomer emission polymers has also been observed for cyclic PS [11] and cyclic P2VN.[42]

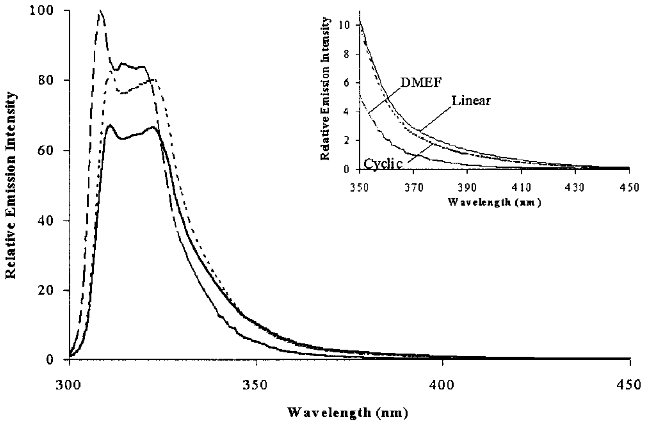


Figure 6. Fluorescence emission spectra of 9,9-dimethyl-2-ethylfluorene (DMEF) model compound (dashed line, l_{ex} = 306 nm), cyclic (dotted line) and linear (solid line) PDMVF with DP_n = 18 (l_{ex} = 307 nm). Concentration: 5 mg/L in cyclohexane. Counts normalized by optical density at excitation wavelength.

Compared to the linear PDMVF, the macrocycle shows a decrease in the excimer band at 360 – 400 nm, as shown in the inset of Figure 6, and although the excimer emission increases with increasing DP_n, the macrocycles always have lower excimer emission yields than the linear polymers. The decrease in monomer emission and concomitant increase in excimer emission observed for both cyclic and linear polymers with increasing MW is consistent with the increased number of excimer traps available on a given chain or cycle.

Compared to the linear PDMVF, the formation of excimer sites on the macrocycles may be hindered due to bond angle and torsional strains especially for the low MW cyclic PDMVF. This is consistent with the much higher glass transition temperatures of the cyclic- compared to matching linear PDMVF. Low MW linear polymers also have been shown to have smaller excimer site densities, presumably due to entropic effects that are consistent with their lower glass transition temperatures.[43]

Acknowledgements

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