2130 *J. Am. Chem. Soc.* **2000,** *122,* 2130−2131

Enhanced Fluorescence of Macrocyclic Polystyrene

Yaodong Gan, Dahai Dong, Stephane Carlotti, and
Thieo E. Hogen-Esch*

Loker Hydrocarbon Institute and Department of Chemistry
University of Southern California
Los Angeles, California 90089-1661

Received August 16, 1999

Compared with the corresponding linear polymers the presence of topological restraints in low MW macrocyclic polymers[1] is expected to result in profound differences in chain conformation and in chain dynamics. These differences may be expressed in their hydrodynamic,[2] rheological,[3] thermal,[4,5] and other[6] properties.

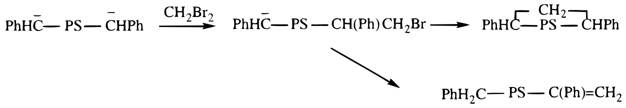
Here we report that the excimer emission intensity of narrow molecular weight distribution (MWD) macrocyclic polystyrenes[2a,7−9] is significantly increased compared with that of the matched linear polymers of the same MW distribution and tacticity as the degree of polymerization (DP) decreases. In particular, the apparent near UV absolute luminescence intensities of macrocyclic polystyrenes with number averaged DPs of 85, 34, and 22 are enhanced by factors of 1.5, 2.3, and 5.0, compared with that of the matching linear PS precursors.

We have prepared PS macrocycles by the lithium naphthalenide-initiated polymerization of styrene in THF at −78 °C giving the PS dianion.[1] This dianion in a separate end-to-end cyclization step is reacted with suitable bifunctional electrophiles (methylene bromide or 1,4-bis (bromomethyl)-benzene (DBX)) in highly dilute solution ([anion] $< 10^{-4}$ M) to give the PS macrocycles.[5,7−10] A small portion of the matching linear PS is obtained by protonation of a small portion of the common dianion precursor. Thus, at least in principle, matching linear and cyclic PS samples are obtained with the same MW and MW distribution.

The size exclusion chromatograms (SECs) carried out with well-defined PS standards typically show cyclization products having generally bimodal MW distributions with only 5−30% dimeric or higher MW coupling products being observed. More of the higher MW coupling products were observed for the cases where the anion concentrations were kept higher than 10^{-4} M or where the precursor MWs were in excess of 40 000. The apparent MWs of the cycles determined by SEC are between 21 and 27% lower than that of the matching linear precursors, indicating that the hydrodynamic volumes of the cycles have decreased, compared with the matching linear polystyrenes in accord with predictions.

After precipitation in methanol of the cyclization products, the higher MW intermolecular coupling products were removed by fractional precipitation monitored by SEC to give the cycles having MW distributions that were nearly identical to that of the matching linear precursors, differing only with respect to the mass of the coupling agent. Particular care was taken to make sure that the SEC mass of the cycles were not altered by the fractionation procedure. Number-average DPs and MW distributions (D) obtained by SEC of the linear (L) and cyclic (C) precursors were: $DP^L_n = 22.0$ ($D = 1.17$), $DP^C_n = 17.4$ ($D = 1.20$); $DP^L_n = 34$ ($D = 1.16$), $DP^C_n = 25.5$ ($D = 1.16$); $DP^L_n = 85$ ($D = 1.06$), $DP^C_n = 62$ ($D = 1.11$); $DP^L_n = 220$ ($D = 1.04$), $DP^C_n = 170$ ($D = 1.10$); $DP^L_n = 430$ ($D = 1.20$), $DP^C_n = 331$ ($D = 1.24$). The use of dibromomethane as coupling reagent results in a structurally more regular macrocycle without introduction of additional chromophores, and this coupling agent was used for the two lowest MW samples.[10]

At this time we do not report MALDI-MS data as have others in support of the structure of polystyrene macrocycles.[4b] However, it should be pointed out that, in this case, MALDI data per se do not indicate the presence of cycles. For instance the potentially competing intramolecular dehydrobromination of the initially formed $PSCH(Ph)CH_2Br$ end group by the remaining anion would give rise to a linear polystyrene that is protonated at one end and contains a terminal $PSC(Ph){=}CH_2$ olefin at the other. Such a polymer would have the same mass as the cycle formed by intramolecular coupling as illustrated below.



Highly reproducible steady-state emission spectra[11−14] were obtained at 25 °C in cyclohexane on a Perkin-Elmer LS-5 fluorescence spectrometer between 260 and 400 nm under nitrogen at an excitation wavelength of 253 nm.[15] Absorptivities and monomer and excimer emission intensities (I_m and I_e, respectively) determined at concentrations between 2×10^{-3} M and 8×10^{-5} M (styrene units) were found to be highly reproducible and were shown to increase linearly with concentration.

The emission spectra of all of the linear polymers and the high MW macrocycles (DP $>$ 200) show monomer emission at about 280 nm and a second more intense and broad structureless excimer band with a maximum at about 334 nm.[11−14] The spectra of these polymers were essentially identical and independent of molecular weight. In agreement with previous studies, the emission spectra of these polymers were found to be concentration independent below 2.0×10^{-3} M in styrene units indicating intramolecular excimer formation only.[12−14,16−21]

---

(1) Keul, H.; Hoecker, H. In *Large Ring Molecules*; Semlyen, J. A., Ed.; John Wiley & Sons: New York, 1996; Chapter 10 and references therein.

(2) (a) Hoecker, 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.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 493.

(3) (a) Dodgson, K.; Semlyen, J. A. *Polymer* **1977**, *18*, 1265. (b) Rempp, P.; Lutz, P. and Strazielle, C. *Makromol. Chem*. **1986**, *7*, 599. (c) Roovers, J.; *Macromolecules* **1985,** *18*, 1359. (d) McKenna, G. B.; Hadziioanou, G.; Lutz, P.; Hild, G.; Strazielle, C.; Straupe, C.; Rempp, P.; Kovacs, A. J. *Macromolecules* **1987**, *20*, 498. (e) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22*, 1834.

(4) (a) Rique-Lurbet, L.; Schappacher, M.; A.Deffieux, A. *Macromolecules* **1994**, *27,* 6318. (b) *Pasch, H.; Deffieux, A.; Ghahary R.; Schappacher, M.; Rique-Lurbet, L.; Macromolecules* **1997**, *30,* 98. (c) Ishizu, K.; Kanno, H. *Polymer* **1996**, *37,* 1487. (d) Kubo, M.; Hayashi, T.; Kobayashi, H.; Tsubo, K.; Itoh, T. *Macromolecules* **1997**, *30,* 2805.

(5) Gan, Y.; Dong, D.; Hogen-Esch, T. E. *Macromolecules* **1995**, *28,* 383.

(6) Yerushalmi, R.; Hostetter, B. J.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 2984.

(7) Rempp, P.; Hild, G.; Kohler, A. *Eur. Polym. J.* **1980**, 16, 525. Hoecker, H.; Geiser, D. *Macromolecules* **1980,** *13*, 653.

(8) Vollmert B.; Huang, J. X. *Makromol. Chem., Rapid Commun.* **1981**, *2,* 467.

(9) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.

(10) Dong D.; Hogen-Esch, T. E. *ACS Polym. Prepr.* **1996**, *37 (1),* 589.

(11) Atik, S. S.; Nam, M.; Singer, L. A. *Chem. Phys. Lett*. **1979**, *67*, 75.

(12) (a) Ishii, T.; Handa, T.; Matsunaga, S. *Makromol. Chem.* **1976**, *177*, 283. (b) Ishii, T. Handa, T.; Matsunaga, S. *Makromol. Chem.* **1977**, *178*, 2351. (c) Ishii, T.; Handa, T.; Matsunaga, S. *Macromolecules* **1978**, *11*, 40.

(13) (a) Vala, M.; Rice, S. J. *J. Chem. Phys*. **1983**, *39*, 2348. (b) Vala, M. T.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886.

(14) Kloepffer, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, Chapter 7.

(15) The reproducibility of the emission spectra in purified spectrophotometric grade cyclohexane was checked using by using two instruments (a Perkin-Elmer 650-10S and a Perkin-Elmer LS-5 fluorescence spectrophotometers) using a 3.0 nm emission slit width. This always gave the same results. Both fluorimeters were calibrated with a standard ovalene block (no. 2, Perkin-Elmer) and a 1,2:5,6-dibenzanthracene solution in heptane.

(16) Nishihara, T.; Kaneko, M. *Makromol. Chem.* **1969**, *124*, 84.

(17) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.

(18) Semarak, S. N.; Franck, C. W. *Adv. Polym. Sci.* **1983**, *54*, 33.

10.1021/ja9929638 CCC: $19.00

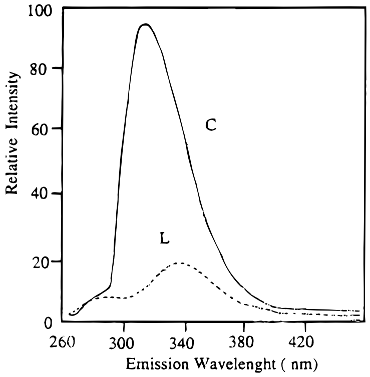


Figure 1. Emission of linear (L) and macrocyclic (C) PS.

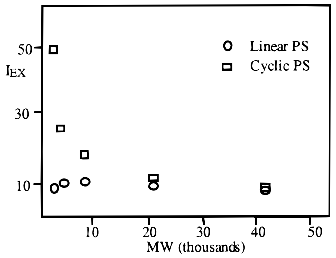


Figure 2. Effect of PS molecular weight on relative fluorescence intensity.

However, the emission intensities of the macrocycles compared with those of the matching linear precursors show significant enhancements as the molecular weight decreased. Thus, at a DP of 8500, the excimer emission intensity increased by about 50% relative to that of the isobaric linear PS. At a DP of 34 the emission intensity approximately doubled, and at a DP of 22 the enhancement is more than a factor of 5. (Figures 1 and 2). Also, the emission maxima of the macrocycles with DP_n's of 220, 85, 34, and 22 are blue-shifted by 3, 10, 17, and 21 nm, respectively, with respect to that of the matching linear PS. The overall emission is the sum of that of a *distribution* of macrocycles so that the emissions of the smaller cycles in the distribution contribute disproportionately. Thus, the bands are skewed and broadened (Figure 1). The apparent intensities (I_m) of the monomer emissions at 280 nm did not change much, thus giving corresponding sharp increases in I_e/I_m with decreasing DP_n's.

In contrast to the linear PS[20] and the high molecular weight cycles the absorbances of the DP = 34 cycle and DP = 22 cycles are increased by about 15 and 150% respectively compared with those of the linear homologues. As in all of the other cases, compliance with Beer's law was observed.

The enhanced excimer emission of the cycles, is surprising and appears to be unprecedented. Corrected for the increased absorptivities, there is an approximately 2-fold excimer emission enhancement, and monomer emission at 280 nm is reduced. However the exact reasons for the above emission and absorptivity enhancements are not altogether clear. Although the SEC chromatograms indicate cycle formation, the occurrence of side reactions, such as illustrated above, could result in the formation of some chains containing olefinic or other impurities, but these were not indicated by NMR and chemical analysis. Furthermore, the effects are not consistent with the expected increased phenyl group concentrations within the macrocyclic polymer domains that are contracted between 15 and 30% relative to that of the linear polymers.[1] Moreover, such small increases should not be strongly MW dependent and cannot account for the enhanced apparent emission quantum yields and for the hyperchromicity of the smallest cycle.

The mechanism of PS excimer formation was studied extensively[13,14,16−22] and appears to involve parallel rings with a separation distance of about 3.7 Å or less. However, the actual distance between phenyl groups, apparently, is strongly affected by conformational effects of the chain backbone. For instance, excimer emission in isotactic PS was found to be more than twice as large as in atactic PS, and this was ascribed to more numerous excimer "trapping sites" in 3:1 isotactic PS helices, with exciton migration ("energy hopping") occurring intramolecularly between the approximately parallel phenyl rings.[12,18,22,23]

We and others have reported that PS cycles below a MW of 10 000 have glass transition temperatures that are as much as 20 °C above that of the matching linear polystyrenes.[4,5] This and the above suggests that the detailed molecular conformation of the low DP macrocycles is associated with the emission enhancements and hyperchromicities. Thus, force field modeling (Sybyl, AM1, MM2) of atactic PS cycles with DPs between 12 and 30 show optimized elliptical disklike structures that are approximately planar with most phenyls being deployed equatorially.[24] Many of the pendent phenyl groups are roughly parallel, giving typical interchromophore (C1−C′1) distances of between about 3.0 and 5.0 Å. These short distances would account for the increased excimer formation compared to the case of linear polymers.

However, the phenyl groups tend not to be completely parallel due to torsional and bond angle strains as well a lack of stereoregularity and this results in partial overlap of adjacent phenyls. This would be consistent with the formation of higher energy (partial overlap) excimers emitting at a lower wavelengths.[18,25−28] These features tend to be more pronounced with the smaller cycles (DP < 20). The larger cycles generally show similar but increasingly less pronounced features as molecular weights increase.

The detailed reason(s) for the observed hyperchromism of low DP (DP = 22) macrocyclic PS is not clear at present. Calculations using the Rhodes−Tinoco model[29,30] on planar cyclic arrays of 20 radially positioned phenyl rings predict absorptivity increases of about 200% or less.[24] Similar but smaller hyperchromicity effects were reported for bridged cyclic diphenyldiacetylenes compared with the absorption intensities of the corresponding linear analogues.[31]

Acknowledgment. This work was supported by NSF-DMR Polymers Program. We wish to thank A. Adamson, S. Bradforth and L. Singer for helpful discussions and A. Adamson for the use of the fluorescence equipment. We wish to thank Mr. Tim La and Ms. Rosalie Richards for their technical assistance.

JA9929638

---

(19) (a) David, C.; Piens, M.; Geuskens, G. *Eur. Polym. J.* **1973**, *9*, 533. (b) David, C.; Lavoreille, N. P.; Geuskens, G. *Eur. Polym. J.* **1974**, *10*, 617. (c) Polacki, Z. *Polym. Photochem.* **1986**, *7*, 325−336.

(20) Torkelson, J. M.; Lipsky, S.; Tirrell, M.; Tirrell, D. A. *Macromolecules* **1983**, *16*, 326.

(21) Nakahira, T.; Sakuma, T.; Iwabuchi, S.; Kojima, K. *Makromol. Chem., Rapid Commun.* **1980**, *1*(7), 413.

(22) Ishii, T.; Handa, T.; Matsunaga, S. *J. Polym Sci., Polym. Phys. Ed.* **1979**, *17*, 811.

(23) Longworth, J. W. *Biopolymers* **1966**, *4*, 1131.

(24) Casanova, J.; Dong, D.; Gan, Y.; Hogen-Esch T. E.; Vala, M., manuscript in preparation.

(25) (a) Kuehnle, W.; Zachariasse, K. *J. Photochem.* **1976**, *5*, 165. (b) Kuehnle, W.; Zachariasse, K. *Z. Phys. Chem.* **1976**, *101*, 267.

(26) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 1091.

(27) Guillet, J. E. *Trends Polym. Sci.* **1996**, *4*(2), 41.

(28) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.

(29) (a) Tinoco, I. *J. Am. Chem. Soc.* **1960**, *82*, 4785. (b) Tinoco, I. *J. Chem. Phys.* **1961**, *34*, 1067.

(30) Rhodes, W. *J. Am. Chem. Soc.* **1961**, *83*, 3609.

(31) Toda, F.; et al. *Bull. Chem. Soc. Jpn.* **1971**, *44*(*7*), 1914.