Comparison of Critical Micelle Concentrations of Gradient Copolymer and Block Copolymer in Homopolymer: Novel Characterization by Intrinsic Fluorescence

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Introduction. Controlled radical polymerization (CRP)[1−3] has resulted in relatively facile synthesis of numerous complex and/or novel polymeric architectures. Among the novel polymers synthesized via CRP are gradient copolymers which possess a gradual change in comonomer composition along the whole chain length or a major fraction of the chain length.[4] Gradient copolymers have been made by batch or semibatch reactions using all major forms of CRP, including nitroxide-mediated CRP,[5−15] atom transfer radical polymerization (ATRP),[16−18] and reversible addition−fragmentation transfer (RAFT)[19] as well as by ring-opening metathesis polymerization[20] and cationic polymerization.[21] Gradient copolymers have numerous potential applications. For example, they can exhibit unusually broad, single glass transition temperatures (T_gs), as large as 65−100 K, making them candidates for acoustic and vibration damping materials.[12,22] They can also be effective compatibilizers of immiscible polymer blends.[12,14,15]

One advantage that has been predicted for gradient copolymers over block copolymers as compatibilizers is related to the critical micelle concentration (cmc) in homopolymer. Copolymers located within micelles in one or the other phase of an immiscible blend are not available to serve as interfacial agents. Thus, copolymers with lower cmc values in the homopolymers constituting the blend may be less effective as blend compatibilizers.[23] Several years ago, Shull[24] used self-consistent mean-field theory to predict that gradient copolymers possess significantly larger cmc values in homopolymer than those associated with block copolymers[25−29] of similar overall composition and molecular weight (MW). At present, the only reported investigations of micelle formation involving gradient copolymers have been in low-MW solvent[18,21,30] rather than homopolymer.

Here, we provide the first experimental comparison of the cmc's of gradient copolymer and block copolymer in blends with homopolymer. Specifically, we investigate styrene (S)−methyl methacrylate (MMA) copolymers present at low levels in poly(methyl methacrylate) (PMMA). This system was chosen for two reasons. First, the polystyrene (PS)−PMMA system is weakly segregating (the Flory−Huggins interaction parameter, χ, is 0.037−0.038 at temperatures above T_g[31]), which should yield relatively large cmc's, eliminating issues with measurement sensitivity. Second, by selecting S-containing copolymers, we can employ intrinsic fluorescence to determine the cmc's of the copolymers in PMMA. Fluorescence is a powerful method for characterizing micellization of block copolymers.[32−41] However, most studies have been limited to determination of self-assembly of micelles in solvent rather than homopolymer and have employed polarity-sensitive fluorescence or fluorescence resonance energy transfer (FRET) (sometimes called nonradiative energy transfer (NRET)) to detect micelles. Such studies require the addition of free fluorescence dye or covalent attachment of dyes to the copolymers under study. In contrast, intrinsic styrene fluorescence has been rarely used for cmc determinations of block copolymer in solvent[40,41] and never for block or gradient copolymer in homopolymer. In the present study, we show not only that the determination of cmc's by intrinsic fluorescence is particularly simple for S-containing copolymers in a nonfluorescent homopolymer but also that the cmc of a gradient copolymer is substantially larger than that of a related block copolymer, in agreement with theory.

Experimental Section. The S-*block*-MMA copolymer (S-*b*-MMA) was from Polymer Laboratories Ltd. (M_n = 110 000 g/mol, M_w/M_n = 1.10, and S mole fraction (F_S) = 0.50, reported by the supplier); PMMA was from Polymer Source (M_n = 106 000 g/mol and M_w/M_n = 1.04, reported by the supplier). The S-*gradient*-MMA copolymer (S-*g*-MMA) was the same as that in ref 15. Its synthesis and characterization were reported previously[15] (M_n = 102 000 g/mol and M_w/M_n = 1.58, by gel permeation chromatography in tetrahydrofuran (THF) relative to PS standards; F_S = 0.55 by ^{1}H NMR), including the proof of the gradient structure. The block and gradient copolymers possess nearly identical apparent M_n and F_S values but very different sequence distributions.

Films were prepared by solvent-casting 8−9 wt % solutions of copolymer and PMMA in toluene (Aldrich) onto quartz slides. The films were dried in a solvent-saturated environment for 48 h and then placed in a vacuum oven. The oven temperature was gradually increased to 115 °C over 120 h. The copolymers then achieved equilibrium dispersion in PMMA by annealing for 5 h at 170 °C; after this procedure, there was no change in the intrinsic fluorescence spectra upon further annealing.[42] The solution sample was prepared by dissolving copolymer in spectroscopic quality THF and adding to a quartz cuvette.

Steady-state fluorescence was measured at 20−21 °C using a Photon Technology International fluorimeter. The excitation wavelength was 260 nm, and emission and excitation slits had band-passes of 2 and 4 nm, respectively. For further details on measuring fluorescence from films, see refs 42 and 44.

Results and Discussion. Figure 1 compares the fluorescence emission spectrum of S-*b*-MMA present at 0.005 wt % in PMMA to that of S-*b*-MMA present at 1.0 g/L in THF solution (micelles are absent in both systems). The fluorescence spectrum for the dilute copolymer solution in THF is very similar to those reported previously for dilute solutions of PS[43,44] or S-containing block copolymer,[40,41] with one peak centered at ∼330 nm and a second, lesser peak centered at 280−285 nm. The lower wavelength peak, called monomer fluorescence, is due to emission from single, excited-state phenyl rings; the higher wavelength peak is due to emission from excited-state dimers formed when a single excited-state phenyl ring comes into a sandwich-like arrangement with a second phenyl ring with 3−4 Å separation distance.[45] This latter emission is called excimer fluorescence and in dilute solution results essentially exclusively from excimer formation involving S−S dyads (resulting in nearest-neighbor phenyl rings) along the chain backbone.[43]

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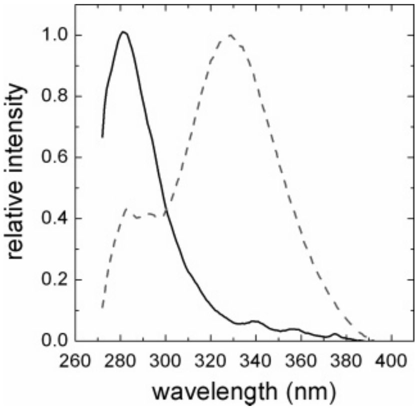

Figure 1. Fluorescence emission spectra for 0.005 wt % S-*b*-MMA in PMMA (solid curve) and 1.0 g/L S-*b*-MMA in THF (dashed curve). Spectral intensities are normalized to unity at the peak intensity.[49] The emission consists almost exclusively of monomer fluorescence when S-*b*-MMA is present at trace levels in PMMA;[50] in dilute THF solution, excimer fluorescence intensity, centered at 330 nm, exceeds monomer fluorescence intensity, centered at 280−285 nm. (Neither system contains micelles; the S-*b*-MMA is well solvated in both cases.)

In contrast to the presence of both monomer and excimer fluorescence when copolymer is dissolved in THF, excimer fluorescence is virtually absent when copolymer is present at trace levels in PMMA. The absence of excimer fluorescence has been reported previously in neat-state or solution-state random copolymer containing very low S mole fractions,[44,46] presumably due to the absence of nearest-neighbor S units along the chain backbone. However, such a result has never before been reported for PS or S-containing copolymers with high levels of S−S dyads. This effect must result from two factors. First, when trace copolymer is present in a glassy PMMA matrix, there is insufficient conformational mobility to achieve sandwich-like conformations of nearest-neighbor phenyl rings during the several nanosecond lifetime of an excited-state phenyl ring. Second, a negligibly small population of conformations leading to direct excitation of excimer is present when S-*b*-MMA is at trace concentration in PMMA.

Figure 2 compares the fluorescence spectra of S-*g*-MMA and S-*b*-MMA copolymers in PMMA matrix at different copolymer concentrations. Like the block copolymer, the gradient copolymer exhibits monomer fluorescence nearly exclusively when present at trace levels in PMMA. However, when the copolymer exceeds a certain concentration, there is a measurable level of excimer fluorescence relative to monomer fluorescence. This increase in the ratio of excimer to monomer fluorescence is an indication of the formation of micelles in which there is a high local concentration of S units within the micelle cores. Other studies have used the ratio of excimer to monomer fluorescence in blends of PS with other polymers to characterize phase separation into PS-rich and PS-lean phases.[47,48] It should also be noted that when intrinsic fluorescence was used to characterize micellization in S-containing block copolymer solutions, the sensitivity was associated with the concentration dependence of excimer emission band energy[40,41] and not the ratio of excimer to monomer fluorescence.

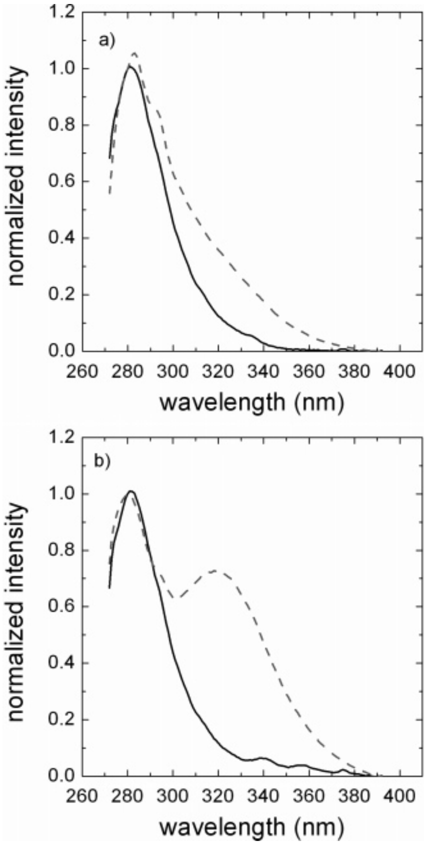

Figure 2. Fluorescence spectra for copolymer in PMMA: (a) 0.005 wt % S-*g*-MMA (solid curve) and 3.5 wt % S-*g*-MMA (dashed curve) and (b) 0.005 wt % S-*b*-MMA (solid curve) and 3.5 wt % S-*b*-MMA (dashed curve). Intensities are normalized to unity at 280 nm.[49]

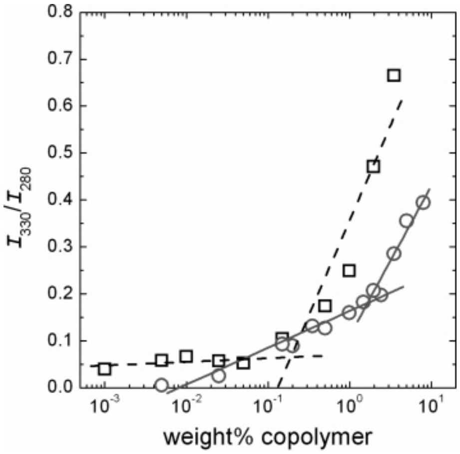

Figure 3. Concentration dependence of I_{330}/I_{280} for copolymer present in PMMA: S-*b*-MMA (squares, dashed lines): S-*g*-MMA (circles, solid lines). Critical micelle concentrations are estimated from the intersections of the fits to low and high concentration data; block copolymer cmc = 0.2 wt %, and gradient copolymer cmc = 2 wt %.

Figure 3 quantifies the copolymer cmc's via plots of the ratio of fluorescence intensity at 330 nm to that at 280 nm (I_{330}/I_{280}) as a function of logarithmic copolymer concentration in PMMA. At block copolymer concentrations below 0.2 wt %, I_{330}/I_{280} is close to zero and nearly independent of concentration. At block copolymer concentrations exceeding 0.2 wt %, I_{330}/I_{280} rises sharply with concentration. An intersection of the linear fits to the low and high concentration data leads to an estimated cmc of 0.2 wt % for S-*b*-MMA in PMMA. At gradient copolymer concentrations below 2 wt %, I_{330}/I_{280} is also near zero but exhibits a slight concentration dependence. The slight concentration dependence may result from the polydisperse nature of the gradient copolymer, with very small levels of micelles forming from the highest MW and F_S fractions of the gradient copolymer. However, for concentrations above 2 wt %, I_{330}/I_{280} also increases dramatically with logarithmic concentration as in the higher concentration regime for the block copolymer. Ignoring polydispersity effects, an intersection of the linear fits to low and high concentration data leads to an estimated gradient copolymer cmc of 2 wt %, an order of magnitude larger than the block copolymer cmc.

These approaches will be extended to other copolymer/homopolymer systems in order to investigate how segregation strength, associated with χ and copolymer and homopolymer MWs, and strength of the composition gradient affect the relative difference in gradient copolymer and block copolymer cmc's. It will also be useful to determine how measurement temperature relative to homopolymer T_g affects the excimer to monomer fluorescence intensity ratio in S-containing gradient and block copolymers below and above the cmc in homopolymer. Studies are underway.

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References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987−2988.

(2) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.

(3) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(4) The definition of gradient copolymer employed in this study states that a composition gradient is present over the whole chain or a major part of the copolymer. As a result, tapered block copolymers (Cigana, P.; Favis, B. D.; Jerome, R. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1691−1700), which have a composition gradient over a small fraction of the chain, are expected to exhibit behavior much more like that of block copolymers than gradient copolymers and are considered distinct from gradient copolymers. Recently, Ruzette, Leibler, and co-workers (Jouenne, S.; Gonzalez-Leon, J. A.; Ruzette, A. V.; Lodefier, P.; Tence-Girault, S.; Leibler, L. *Macromolecules* **2007**, *40*, 2432−2442) studied triblock copolymers in which the mid-block has the structure of a gradient copolymer. In their case, the two ends of the mid-block have similar comonomer compositions (rich in one monomer) with a composition gradient going to the middle of the mid-block (rich in the other monomer). When the mid-block and the composition gradient are sufficiently large, these copolymers are expected to possess characteristics more similar to the gradient copolymers defined in this study than to block copolymers.

(5) Gray, M. K.; Zhou, H. Y.; Nguyen, S. T.; Torkelson, J. M. *Macromolecules* **2004**, *37*, 5586−5595.

(6) Gray, M. K.; Zhou, H. Y.; Nguyen, S. T.; Torkelson, J. M. *Polymer* **2004**, *45*, 4777−4786.

(7) Woo, D.; Kim, J.; Suh, M. H.; Zhou, H. Y.; Nguyen, S. T.; Lee, S. H.; Torkelson, J. M. *Polymer* **2006**, *47*, 3287−3291.

(8) Karaky, K.; Billon, L.; Pouchan, C.; Desbrieres, J. *Macromolecules* **2007**, *40*, 458−464.

(9) Karaky, K.; Pere, E.; Pouchan, C.; Garay, H.; Khoukh, A.; Francois, J.; Desbrieres, J.; Billon, J. *New J. Chem.* **2006**, *30*, 698−705.

(10) Farcet, C.; Charleux, B. *Macromol. Symp.* **2002**, *182*, 249−260.

(11) Lefay, C.; Save, M.; Charleux, B.; Magnet, S. *Aust. J. Chem.* **2006**, *59*, 544−548.

(12) Kim, J.; Zhou, H. Y.; Nguyen, S. T.; Torkelson, J. M. *Polymer* **2006**, *47*, 5799−5809.

(13) Kim, J.; Mok, M. M.; Sandoval, R. W.; Woo, D. J.; Torkelson, J. M. *Macromolecules* **2006**, *39*, 6152−6160.

(14) Kim, J.; Gray, M. K.; Zhou, H. Y.; Nguyen, S. T.; Torkelson, J. M. *Macromolecules* **2005**, *38*, 1037−1040.

(15) Tao, Y.; Kim, J.; Torkelson, J. M. *Polymer* **2006**, *47*, 6773−6781.

(16) Matyjaszewski, K.; Ziegler, M. J.; Arehart, S. V.; Greszta, D.; Pakula, T. *J. Phys. Org. Chem.* **2000**, *13*, 775−786.

(17) Paris, R.; De La Fuente, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5304−5315.

(18) Lee, S. B.; Russell, A. J.; Matyjaszewski, K. *Biomacromolecules* **2003**, *4*, 1386−1393.

(19) Luo, Y. W.; Liu, X. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6248−6258.

(20) Dettmer, C. M.; Gray, M. K.; Torkelson, J. M.; Nguyen, S. T. *Macromolecules* **2004**, *37*, 5504−5512.

(21) Okabe, S.; Seno, K.; Kanaoka, S.; Aoshima, S.; Shibayama, M. *Macromolecules* **2006**, *39*, 1592−1597.

(22) Mok, M. M.; Torkelson, J. M. *Polym. Prepr.* **2007**, *48* (1), 959−960.

(23) Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590−5598.

(24) Shull, K. R. *Macromolecules* **2002**, *35*, 8631−8639.

(25) Chang, K. H.; Morse, D. C. *Macromolecules* **2006**, *39*, 7746−7756.

(26) Cavallo, A.; Müller, M.; Binder, K. *Macromolecules* **2006**, *39*, 9539−9550.

(27) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482−492.

(28) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550−3557.

(29) Wang, Y.; Mattice, W. L.; Napper, D. H. *Langmuir* **1993**, *9*, 66−70.

(30) Okabe, S.; Fuse, C.; Sugihara, S.; Aoshima, S.; Shibayama, M. *Physica B* **2006**, *385*, 756−758.

(31) Russell, T. P.; Hjelm, R. P.; Seeger, P. A. *Macromolecules* **1990**, *23*, 890−893.

(32) Major, M. D.; Torkelson, J. M.; Brearley, A. M. *Macromolecules* **1990**, *23*, 1700−1710.

(33) Major, M. D.; Torkelson, J. M.; Brearley, A. M. *Macromolecules* **1990**, *23*, 1711−1717.

(34) Wilhelm, M.; Zhao, C. L.; Wang, Y. C.; Xu, R. L.; Winnik, M. A.; Mura, J. L.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 1033−1040.

(35) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7339−7352.

(36) Webber, S. E. *J. Phys. Chem. B* **1998**, *102*, 2618−2626.

(37) Tang, D. H.; Lin, J. P.; Lin, S. L.; Zhang, S. N.; Chen, T.; Tian, X. H. *Macromol. Rapid Commun.* **2004**, *25*, 1241−1246.

(38) Yusa, S.; Shimada, Y.; Mitsukami, Y.; Yamamoto, T.; Morishima, Y. *Macromolecules* **2004**, *37*, 7507−7513.

(39) Wang, Y. M.; Kausch, C. M.; Chun, M. S.; Quirk, R. P.; Mattice, W. L. *Macromolecules* **1995**, *28*, 904−911.

(40) Yeung, A. S.; Frank, C. W. *Polymer* **1990**, *31*, 2101−2111.

(41) Ylitalo, D. A.; Frank, C. W. *Polymer* **1996**, *37*, 4969−4978.

(42) Roth, C. B.; Torkelson, J. M. *Macromolecules* **2007**, *40*, 3328−3336.

(43) Torkelson, J. M.; Lipsky, S.; Tirrell, M. *Macromolecules* **1981**, *14*, 1601−1603.

(44) Mundra, M. K.; Ellison, C. J.; Behling, R. E.; Torkelson, J. M. *Polymer* **2006**, *47*, 7747−7759.

(45) Vala, M. T.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886−897.

(46) Reid, R. F.; Soutar, I. *J. Polym. Sci., Part B: Polym. Phys.* **1978**, *16*, 231−244.

(47) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 1486−1491.

(48) Tsai, F. J.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 1026−1033.

(49) The background intensity associated with noise from the fluorimeter photomultiplier tube was subtracted from all fluorescence spectra.

(50) The several very small peaks apparent at 335−380 nm in the block copolymer fluorescence spectrum in Figures 1 and 2b are not associated with excimer fluorescence but instead may be due to impurities or initiator fragments covalently attached to the copolymer during its commercial synthesis. Those very small peaks do not affect in any significant way the analysis described in this paper.

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