Communication

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Effect of Chemical Oxidation on the Self-Assembly of Organometallic Block Copolymers

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Controlling the spontaneous formation of ordered domains in soft materials such as block copolymers is a subject of considerable current interest.[1–3] These systems may enable the development of stimuli-responsive materials for applications such as actuators[4] and photonics[5] due to the reversible nature of order formation. However, the stimuli that are typically used to control the morphology of block copolymers, e.g., temperature, pressure, solvent concentration, etc., are not well-suited for applications that require repeated switching between morphologies. In this communication we demonstrate that the oxidation state of redox-active species incorporated in block copolymer chains can be used to control order formation. Since the state of redox active species can be controlled electrochemically,[6,7] this study lays the groundwork for using electrochemical potential to control the self-assembly of block copolymers.

Poly(isoprene-*block*-ferrocenyldimethylsilane) (IF) and poly-(styrene-*block*-ferrocenyldimethylsilane) (SF) copolymers, with total molecular weights of 18 and 23 kg/mol respectively, were synthesized following the procedure of Manners et al.[8] The volume fraction of the F block was 0.48 and 0.56 for the IF and SF polymers, respectively, and the ordered phases were lamellar. The order−disorder transition temperatures (T_{ODT}) of both polymers in the neat state was determined by small-angle X-ray scattering (SAXS) to be 164 ± 3 °C.

Oxidation of the ferrocene moiety to the ferrocenium cation was accomplished by reaction with silver nitrate. On the basis of the large difference in reduction potentials of Ag^+ and ferrocenium, we expect quantitative reduction of the silver nitrate. Figure 1 shows the UV−visible spectra of a series of 0.1 wt % solutions of oxidized IF samples in benzene. The molar ratio of added silver nitrate to ferrocenyldimethylsilane moieties, x, was varied from 0.0 to 0.10. The absorbance peaks seen at 458 and 638 nm in Figure 1 are characteristic of ferrocene and the ferrocenium cation, respectively. The inset of Figure 1 shows that the dependence of the measured absorbance at 638 nm is proportional to x. It is clear that the parameter x is proportional to the fraction of ferrocenium cations per chain and is a measure of the extent of oxidation of our polymers. The UV−visible spectra of the SF system were similar. We thus report our results in terms of percent oxidation, which we assume to be $100x$.

Typical SAXS profiles obtained from the oxidized samples are shown in Figure 2a (inset) where SAXS intensity I is plotted versus q ($q = 4\pi \sin(\theta/2)/\lambda$ where θ is the scattering angle and λ is the X-ray wavelength) for the SF sample with $x = 0.04$ at temperatures near the order−disorder transition. We assume the primary scattering peak at $q \approx 0.35$ nm^{-1} is of the form $I(q) = C \exp[-(q - q_{peak})^2/\sigma^2] + I_{bgd}(q)$, where $1/I_{bgd}(q)$, assumed to be
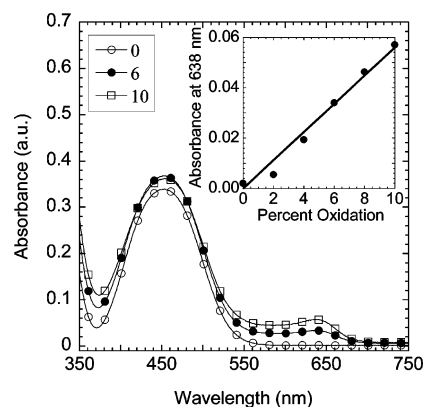

Figure 1. UV−visible spectra of the IF copolymers for different oxidation percentages ($100x$). The inset shows the absorbance at 638 nm, the wavelength of the ferrocenium cation absorption peak, versus percent oxidation.

a quadratic function of q, accounts primarily for the low-q scattering upturn.[9] In Figure 2a, we plot the peak width, σ, versus temperature obtained from the SF sample with $x = 0.04$. A discontinuous increase in the peak width is seen when the temperature is changed from 136 to 141 °C during both heating and cooling runs (see Figure 2a). We also observed a discontinuity in the temperature dependence of the peak intensity at the same temperature step. These are standard SAXS signatures of the order−disorder transition in block copolymers.[10] We thus conclude that the T_{ODT} of SF with $x = 0.04$ is 138 ± 3 °C. This is substantially lower than T_{ODT} of unoxidized SF which was 164 ± 3 °C.

In addition to the primary peak, the SAXS profiles of oxidized SF and IF samples exhibited a significant up-turn at low q ($q < 0.25$ nm^{-1}). The low-q scattering was insensitive to changes in temperature as shown for the $x = 0.04$ sample in Figure 2a (inset), but increased systematically with x. The up-turn was not seen in the neat, unoxidized SF and IF samples. At this early stage, we are not certain about the origin of the low-q scattering. Similar low-q upturns are seen in other charged systems such as ionomers and polyelectrolytes.[11] It is worth noting, perhaps, that the SAXS profiles from partially oxidized block copolymers are not constrained to approach zero as q approaches zero due to randomness in the location of the ferrocenium moieties.[12]

The order−disorder transition temperatures of a series of SF and IF samples with x values ranging from 0 to 0.08 were determined by SAXS as described above. The results of our analysis are summarized in Figure 2b where T_{ODT} is plotted versus $100x$ for both the SF and IF copolymers. It is evident that T_{ODT} decreases systematically with increasing levels of oxidation in both cases. Figure 2b shows that altering the redox state of organometallic block copolymers can change T_{ODT} by as much as 40 °C.

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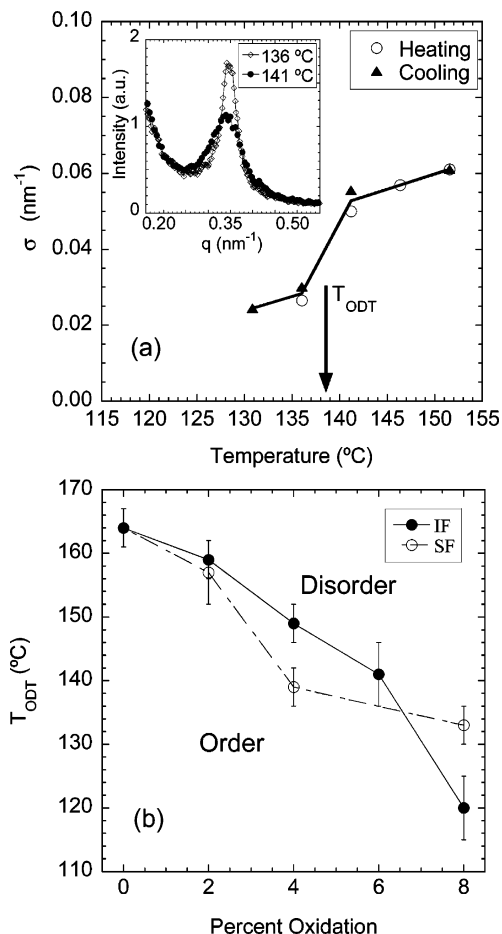§ Environmental Energies and Technologies Division.

Figure 2. SAXS results. (a) Peak width, σ, of the SF sample with $x = 0.04$ as a function of temperature for both heating and cooling of the sample. The inset shows typical SAXS profiles at 136 and 141 °C. (b) Phase diagram of SF and IF polymers as a function of percent oxidation ($100x$).

Simple arguments based on polarizibility of the blocks would indicate that the repulsion between the organic and organometallic blocks would increase with oxidation. The Flory–Huggins parameter, χ, that is used to quantify interactions between polymer chains is assumed to be proportional to the difference in the polarizibility of the blocks.[13] The polarizibility of polyferrocenyldimethylsilane, which is larger than that of either polystyrene or polyisoprene,[14] must increase upon oxidation due to the presence of the NO_3^- ions. This will cause an increase in χ upon oxidation. Arguments based on polarizibility thus lead to the conclusion that oxidation would stabilize the ordered phase. It is clear from Figure 2b, however, that oxidation stabilizes the disordered phase.

We propose that the effect observed in Figure 2b is due to the ionic nature of the oxidized ferrocenium nitrate moieties. Rabin and co-workers have shown that the introduction of dissociated charges on one of the blocks of a diblock copolymer leads to stabilization of the disordered phase.[15] They also quantified the increase in χ at the ODT, χ_{ODT}, due to the entropic contribution of the dissociated counterions. Using the known temperature dependence of χ for the SF system,[16] we conclude that χ_{ODT} in the oxidized SF block copolymer with $x = 0.08$ is 0.0321, while χ_{ODT} for the unoxidized SF copolymer is 0.0314. The number of dissociated charges per chain required to obtain this increase in

χ_{ODT}, according to the theory of Rabin et al., is 0.064. The average number of ferrocenium moieties in each SF chain is 4.6. This implies that the fraction of NO_3^- ions in the oxidized SF polymer that are dissociated is 0.014. The relatively little dissociation needed to obtain the observed stabilization of the disordered phase is consistent with the low dielectric constant of our polymers.[14]

In conclusion, we have demonstrated that chemical oxidation of SF and IF copolymers leads to stabilization of the disordered state. Changing the redox state of 8% of the ferrocene moieties results in a reduction of the order–disorder transition temperature by as much as 40 °C. We suggest that this stabilization is due to the entropy of a very small fraction of dissociated counterions that are introduced during the oxidation step. An interesting property of ferrocene is the fact that its oxidation state can be altered reversibly by the application of small electric fields (e.g., ± 2 V/cm). Pioneering work by Abbott and co-workers used this to control the self-assembly of small-molecule amphiphiles containing ferrocene.[7] Our results suggest that the self-assembly of ferrocene-containing block copolymers may be controlled by the application of electrochemical potential in a suitable electrolyte.

Supporting Information Available: Sample preparation, experimental details, auxiliary data, stability of oxidized chains, and calculation of dissociation constant. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401–1404.
(2) Segalman, R. A.; Yokoyama, H.; Kramer, E. J. *Adv. Mater.* **2001**, *13*, 1152–1155.
(3) Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126–2129.
(4) Liu, Z.; Calvert, P. *Adv. Mater.* **2000**, *12*, 288–291.
(5) Bockstaller, M. R.; Thomas, E. L. *J. Phys. Chem. B* **2003**, *107*, 10017–10024.
(6) Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709–1711.
(7) Gallardo, B. S.; Gupta, V. K.; Eagerton, F. D.; Jong, L. I.; Craig, V. S.; Shah, R. R.; Abbott, N. L. *Science* **1999**, *283*, 57–60.
(8) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102–4114.
(9) Lee, J. H.; Ruegg, M. L.; Balsara, N. P.; Zhu, Y.; Gido, S. P.; Krishnamoorti, R.; Kim, M. H. *Macromolecules* **2003**, *36*, 6537–6548.
(10) Perahia, D.; Vacca, G.; Patel, S. S.; Dai, H. J.; Balsara, N. P. *Macromolecules* **1994**, *27*, 7645–7649.
(11) Ermi, B. D.; Amis, E. J. *Macromolecules* **1998**, *31*, 7378–7384.
(12) Fredrickson, G. H.; Milner, S. T.; Leibler, L. *Macromolecules* **1992**, *25*, 6341–6354.
(13) Graessley, W. W. *Polymeric Liquids and Networks: Structure and Properties*; Garland Science: New York, NY, 2004.
(14) Paquet, C.; Cyr, P. W.; Kumacheva, E.; Manners, I. *Chem. Commun.* **2004**, *2*, 234–235.
(15) Marko, J. F.; Rabin, Y. *Macromolecules* **1992**, *25*, 1503–1509.
(16) Eitouni, H. B.; Balsara, N. P.; Hahn, H.; Pople, J. A.; Hempenius, M. A. *Macromolecules* **2002**, *35*, 7765–7772.

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