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Electrochemically Controlled Self-Assembly of an Organometallic Block Copolymer

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Abstract: A new means of controlling the order−disorder transition of block copolymers is presented. By applying small electrical potentials (2 V/cm) to disordered solutions of an organometallic block copolymer, oriented ordered grains were obtained near the positive electrode. After reversing the electrical bias on the system, the ordered grains disappeared, and new, oriented, ordered regions were formed at the opposite electrode. Our work establishes the concept of electrochemical self-assembly for controlling order formation in block copolymers.

Introduction

There is considerable interest in the development of new methodologies for controlling the self-assembly of nanostructures formed by amphiphilic molecules such as surfactants, phospholipids, and block copolymers.[1,2] The use of variables such as temperature, pressure, and solvent concentration to switch between different equilibrium morphologies is now well-established.[3] In contrast, our knowledge of self-assembly in systems that are driven out of equilibrium is limited. Both shear flow and electric fields have been used to align lamellar and hexagonal phases formed by block copolymers.[4,5] Electric fields have also been used to align other systems such as micellar structures adhered to surfaces.[6,7] The imposition of shear flow can induce a disorder-to-order transition,[8] but similar effects have not yet been demonstrated using electric fields. Electric field studies thus far, which are limited to conventional organic block copolymers, show that the application of fields of order 10^5 V/cm are needed to induce alignment in bulk materials.[9]

In this paper we report on the effect of electric fields on the self-assembly of an organometallic block copolymer. We demonstrate that the application of fields as low as 2 V/cm, when coupled with electrochemical reactions, leads to the formation of a partially aligned, ordered phase in a sample that is initially disordered. The order is localized to a region extending 1 mm into the sample near the positive electrode. When the bias on the electrodes is switched, the ordered phase returns to the disordered state, and a new ordered region appears at the other electrode. Our work establishes a fundamentally new mechanism for controlling the self-assembly of block copolymers.

Our ability to explore the electrochemical self-assembly of block copolymers rests on three important developments: (1) the work of Manners and co-workers who established the methodology for synthesizing the ferrocene (Fc)-containing block copolymers,[10] (2) the demonstration that the self-assembly of small-molecule Fc-containing surfactants can be controlled by electrochemical means by Abbott and co-workers,[11] and (3) the work of Vancso, Thomas, and co-workers who first accessed order−disorder transitions in Fc-containing block copolymers.[12]

Experimental Section

A polyisoprene-*block*-poly(ferrocenyldimethylsilane) (IF) copolymer (polydispersity index = 1.03), labeled IF(92-69), was synthesized and characterized by methods described previously.[13] The number-averaged molecular weights of the polyisoprene (PI) and poly(ferrocenyldimethylsilane) (PF) blocks were 92×10^3 and 69×10^3 g/mol, respectively, and the volume fraction of the PF block, ϕ_F, was 0.35. Based on previously

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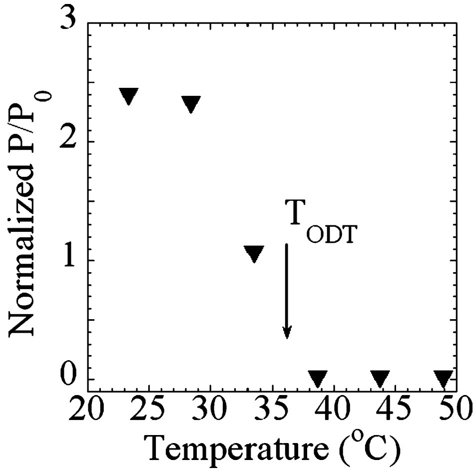

Figure 1. Birefringence detection of the bulk T_{ODT} of a 17 wt % solution of IF(92-69) in *o*-dichlorobenzene. Normalized P/P_0, $[(P/P_0)/(P/P_0)_{49\,°C} - 1]$, the normalized fraction of transmitted light through a 1-mm thick sample held between crossed polarizers versus temperature.

published thermodynamic data,[13] the copolymer melt is strongly segregated and well removed from the order−disorder transition ($\chi N \approx 120$ at 25 °C). SAXS measurements on the pure block copolymer (not shown for brevity) indicate the presence of a hexagonally packed cylindrical morphology, as expected for a $\phi_F = 0.35$ block copolymer.

Samples for the electrochemical studies were obtained by chemical oxidation of the polymer using $AgNO_3$ as the oxidant. Solutions of the block copolymer in degassed benzene and $AgNO_3$ in degassed methanol were mixed in an argon-filled glovebox and stirred for 12 h. Stoichiometric amounts of the oxidant were used, resulting in oxidation of 1% of the Fc to $FcNO_3$. The solutions were centrifuged in sealed tubes, and the supernatant, while under an argon atmosphere, was passed through 0.2-μm filters to remove silver aggregates. Samples were then vacuum freeze-dried from methanol/benzene solutions. The dried 1% oxidized block copolymer was then placed in a quartz optical cell. Degassed *o*-dichlorobenzene was pipetted into the cell, resulting in approximately 17 wt % polymer solutions. A Chemglass Airfree valve with a nonrotating Teflon barrel was attached to the cell to maintain an inert atmosphere above the sample. Two platinum electrodes entered the cell through the barrel, and the gaps between the electrodes and barrel were sealed using an epoxy sealant. The solutions were homogenized by centrifugation and annealing at 70 °C.

Results and Discussion

The solutions of oxidized block copolymer were placed between crossed polarizers, and the fraction of the incident light power from a white light, transmitted through the polarizers and sample, P/P_0, was monitored using a CCD camera as a function of temperature. The P values were determined by averaging the 8-bit pixel intensity over the sample image. The P_0 value was obtained by removing the sample cell and uncrossing the polarizers. A CCD camera was used rather than a simple photodiode to allow for spatial resolution over the entire sample during application of electrochemical potential. Figure 1 shows the normalized P/P_0 data during heating with 30-min hold times at each temperature. The discontinuous decrease of the optical signal at 39 °C is a standard signature of an order−disorder transition and reveals the bulk order−disorder transition temperature of the sample, T_{ODT}.[14] All of the work described in this paper is based on approximately 17 ± 3 wt % of 1.0 ± 0.2% oxidized IF(92-69) *o*-dichlorobenzene solutions. The T_{ODT} of the solutions varied between 36 and 40 °C due to unavoidable variability in the polymer concentration and percent oxidation between samples. By tilting the cell, we observed that the sample was fluid above T_{ODT} and solidlike below T_{ODT}. We assumed that the morphology of the solution is the same as that of the bulk block copolymer because *o*-dichlorobenzene is a common solvent for both PI and PF blocks.[15] We were unable to use small-angle X-ray scattering (a tool routinely used to characterize the ordered state of block copolymer solutions) due to the absorption of X-rays by the solvent, and higher-order scattering peaks were not observed in small-angle neutron scattering experiments. In bulk block copolymers, the disordered phase can contain micelles if the minor block volume fraction is about 0.20.[16] Since ϕ_F is well-removed from this value, we expect a nonmicellar disordered phase in our system.

Once the T_{ODT} of a sample had been determined to within 1 °C, electrochemical experiments were performed at a temperature 2−7 °C below the T_{ODT} after first disordering the sample. In this temperature range, no evidence for order formation was found in quiescent samples for about 4 days. This is not surprising; finite undercooling is almost always necessary for overcoming nucleation barriers during disorder-to-order transitions.[17] The sample shown in Figure 2, which had an T_{ODT} of 36 °C, was heated to 37 °C to disorder the sample and was then cooled to 34 °C. We define $t = 0$ as the time at which the temperature controller setting was changed from 37 to 34 °C. A potential of 2 V was applied to the sample at $t = 0$. It took about 5 min for the sample temperature to reach the final temperature of 34 °C. The birefringence signal in the vicinity of each electrode was obtained by averaging the pixel intensity in a 1 mm × 4 mm thin vertical box. The intensity thus obtained, normalized by the value obtained at $t = 0$ (prior to turning on the field) and by the time-dependent intensity obtained from an identical box drawn in the middle of the cell, is plotted versus time in Figure 2a. The first sign of order formation is seen at $t = 40$ h, after which the signal increases monotonically with time. The bias was switched at $t = 80$ h. This results in a relatively rapid decay in the birefringence at the right electrode followed by a slow buildup of birefringence at the opposite electrode. Images of the sample cell acquired at selected times marked by (b), (c), (d), and (e) in Figure 2a are shown in panels b−e of Figure 2. The ordered regions near the electrodes are approximately 1-mm wide (panels c and e of Figure 2). The data in Figure 2 establish the ability of the system to undergo an electrochemically controlled reversible order−disorder transition. We repeated the experiments on several independent samples and found that undercoolings between 2 and 7 °C were needed to observe electrochemically induced order formation within 80 h. We turned off the electric field after completion of the electrochemical ordering experiment and observed the sample for 24 h. No changes were observed at either electrode during this time.

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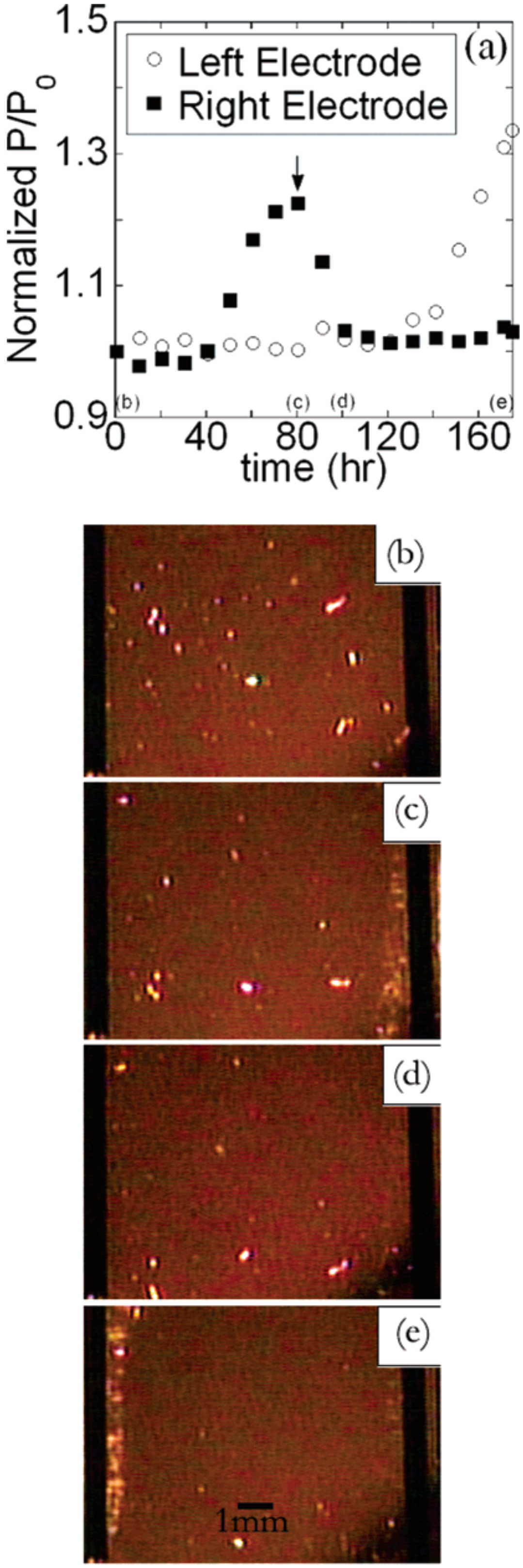

Figure 2. (a) Normalized P/P_0, $(P/P_0)/[(P/P_0)_{t=0}(P/P_0)_{\text{sample center}}]$, for 1-mm wide regions near the electrodes versus time. The arrow indicates the bias reversal time ($t = 80$ h). Labels (b−e) indicate the image capture times. Images of the electrochemical cell thermostated at 34 °C held between crossed polarizers (b) before application of 2 V at $t = 0$, (c) after application of 2 V at $t = 80$ h (positive electrode is on the right side), (d) after bias reversal at $t = 100$ h (positive electrode is on the left side), and (e) at $t = 175$ h (positive electrode is on the left side). The dark vertical strips in the images are the platinum electrodes.

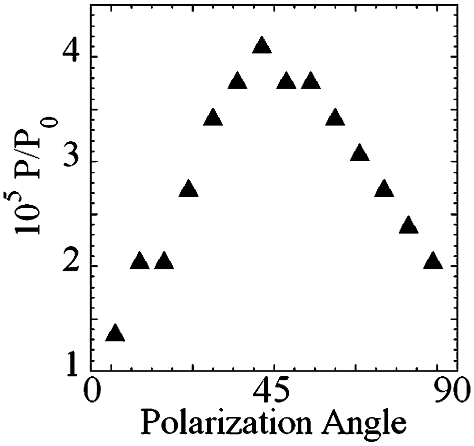

Figure 3. Angular dependence of the birefringence signal P/P_0 of the region next to the positive electrode in Figure 2e. An angle of 0° corresponds to the orientation of the electrode.

Further investigation of the birefringent region in Figure 2e revealed that the ordered morphology possessed long-range alignment. A 0.5-mm diameter laser beam of wavelength $\lambda = 633$ nm was passed through the birefringent region, and the polarization of the incident light was swept through a 90° angular range. In these experiments, the birefringence signal, P/P_0, was monitored using a photodiode. In Figure 3 we plot P/P_0 versus the polarization angle measured relative to the orientation of the electrode. The data are peaked at 45°, indicating that the microphase-separated cylinders of the PF block lie either parallel or perpendicular to the applied field.[18] Because application of the electrochemical potential resulted in a steady-state current, it is likely that the cylinders orient parallel to the field to more easily enable transport of the Fc^+ ions in solution.

Time- and spatially resolved in situ SANS experiments were conducted to investigate the effect of electrochemical potential on molecular-length scales. The same quartz cells pictured in Figure 2 were used in the SANS experiments. We used a small-diameter neutron beam obtained from a 1/16 in. sample aperture to probe three different positions in the sample, two near the electrodes and one in the center of the sample. Data for a representative sample are shown in Figure 4. The T_{ODT} of the solution was 40 °C. The sample was first disordered at 43 °C and then cooled to 33 °C in the SANS beamline; 2 V was then applied across the platinum electrodes at time $t = 0$. Two-dimensional SANS profiles were recorded as a function of time at the three positions. Figure 4 shows the azimuthally averaged scattering profiles for the three positions within the sample at early ($t = 0$) and late ($t = 73$ h) times. All of the scattering profiles contain a single scattering peak, indicating the presence of periodic structures with a spacing of 87 nm. At early times, the scattering profiles obtained from all three positions were within experimental error, and the scattering peak arises from disordered concentration fluctuations. With the passage of time, the SANS peak obtained from the region near the positive electrode increased substantially in intensity, while that obtained near the negative electrode remained unchanged (Figure 4). The changes in the scattering profile obtained from the middle position lay between these two extremes, suggesting that the electrochemical driving force for self-assembly decreases

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[18] The absolute value of P/P_0 is low due to optical absorption.

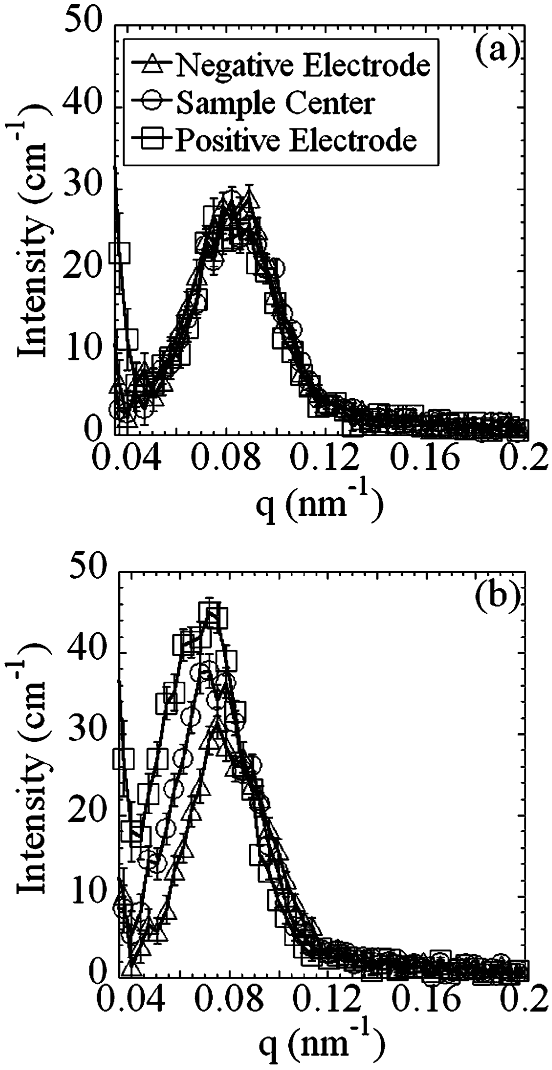

Figure 4. Small angle neutron scattering profiles of three positions in the electrochemical cell at 33 °C at (a) $t = 0$ and (b) $t = 73$ h.

linearly as the distance from the positive electrode increases. The data in Figure 4 clearly establish that microphase separation in our sample is responsive to relatively small changes in electrochemical potential.[19] The nonuniform distribution of charged species under the applied electric field may be a reason for the increase in low-*q* scattering seen in Figure 4.

A likely mechanism for the electrochemical self-assembly process is pictured in Figure 5. The application of an electrochemical potential across the electrodes results in a steady-state current, which in turn sets up a steady-state concentration profile of $FcNO_3$ across the cell.[20] At steady state, the current density through the sample was measured to be about 10^{-4} A/m^2, irrespective of whether the sample was ordered or disordered. Figure 5 shows a diagram of the electrochemical cell with the expected concentration gradients of the charged species at steady state. Due to electric neutrality, the concentration profile of Fc^+ ions will be identical to that of the NO_3^- ions (we have shown a linear profile in Figure 5 for simplicity). The Fc moieties on polymer chains in contact with the positive electrode give up electrons and are thus oxidized, while the Fc^+ moieties on polymer chains in contact with the negative electrode are reduced (the half-wave potential between the reduction and oxidation peaks measured by cyclic voltammetry was 0.4 V; recall that the electric potential applied is 2 V). These electrochemical reactions will thus set up the $FcNO_3$ concentration gradient shown in Figure 5. Chains with excess Fc^+ ions will migrate toward the negative electrode due to both field-induced migration and diffusion (the relative importance of these transport mechanisms remains to be determined). Chains with excess Fc moieties, produced at the negative electrode, will migrate toward the positive electrode by diffusion. The applied potential provides the driving force for maintaining the proposed concentration gradients. Since the chemical oxidation step leads to random oxidation, we expect that the initial solution (prior to turning on the electric field) will contain IF copolymer chains with a distribution of oxidation levels. The electrochemical reactions described above will widen this distribution and preferentially locate chains with higher levels of oxidation at the positive electrode and the chains with lower levels of oxidation at the negative electrode. While this is undoubtedly the reason for the observed electrochemically induced ordering and disordering, the underpinnings of our observations remain to be established. In ref 13, we demonstrated that in the melt state chemical oxidation of IF polymers leads to stabilization of the disordered phase. In the present work, we find that electrochemical oxidation of IF polymers in *o*-dichlorobenzene results in stabilization of the ordered phase. The stability of the ordered and disordered phases near the positive and negative electrodes may be due electric field effects (e.g., current distribution) or changes in local polymer concentration induced by the electric field.

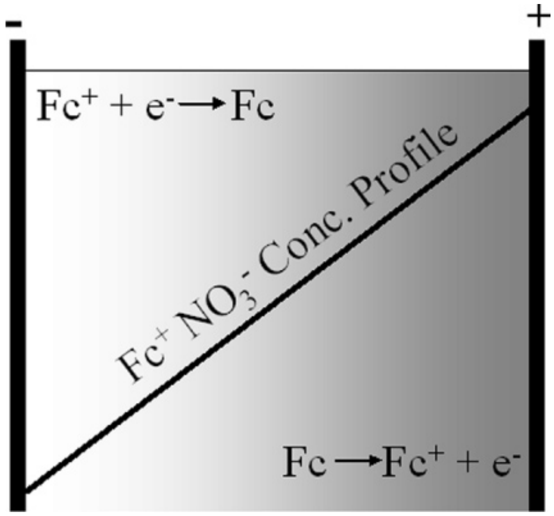

Figure 5. Schematic representation of the proposed electrode reactions and concentration gradients in the electrochemical cell with a 2 V potential across the electrodes.

Concluding Remarks

In conclusion, we have shown that the application of a 2 V/cm electric field across solutions of organometallic block copolymers, when coupled with electrochemical reactions, results in the stabilization of the ordered state near the positive electrode

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[19] The sample was examined visually after the SANS experiments between crossed polarizers, and we found that it was not birefringent. When we observed this in our optical experiments, we increased the undercooling and repeated the experiment (after disordering). However, limited access to the SANS instrument prevented us from repeating this experiment at different quench depths.

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and the disordered state near the negative electrode. The ordered regions were shown to possess significant long-range orientation and are localized near the positive electrode. After reversal of the electrical bias on the system, the ordered regions underwent order-to-disorder transitions, and new ordered regions were formed at the opposite electrode. We have thus established a technique for exerting localized reversible control over the formation of block copolymer microphases using electrical fields. One of the problems with the current system is that order formation takes a long time. It is conceivable, however, that this time may be decreased by replacing the inert platinum electrodes by active electrodes, decreasing the distance between electrodes, decreasing solution viscosity, etc. In future studies we will attempt to identify the parameters that control the electrochemical self-assembly process. Despite these limitations, our work represents an important first step in using electrochemical potential to control the structure and properties of block copolymers.

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