ACS Macro Letters

Letter

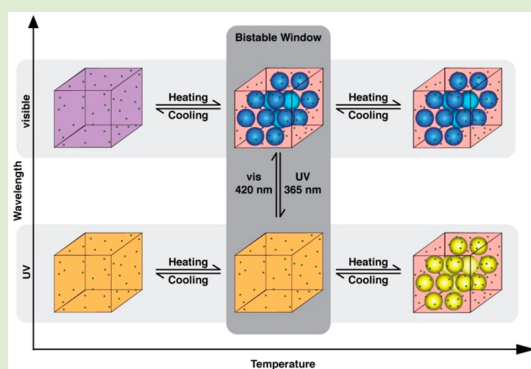# Photoreversible Order−Disorder Transition in an Ionic Liquid Solvated Block Polymer

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S *Supporting Information*

ABSTRACT: The structure of a solution of poly(methyl methacrylate)-*block*-poly(benzyl methacrylate-*stat*-(4-phenylazophenyl methacrylate)) in the ionic liquid 1-ethyl-3-methyl imidazolium bis-(trifluoromethanesulfonylimide) can be controlled with light. We explored the phase behavior of this block polymer at a concentration of 30 wt % as a function of temperature. Remarkably, this solution shows ordering into hexagonally closed packed spheres (HCP) upon heating under visible light, as confirmed by small-angle X-ray scattering. Small amplitude oscillatory shear rheology was used to demonstrate that the system could readily be converted between HCP and disorder by switching between visible and UV light wavelengths at 100 °C. This switching was cycled six times, without any noticeable change in the ordered or disordered state. The dependence on illuminating wavelength arises from the changes in polarity of the azobenzene moiety, which modulates its solubility in this ionic liquid to a significant extent. This is the first example of reversible light-triggered ordering of a "coil−coil" block polymer, a phenomenon that has been previously observed only in liquid crystalline systems.

Control over the nanoscale ordering of block polymers has been extensively studied, both in the bulk[1,2] and in solution.[3−7] The morphology of a bulk block polymer can be altered by changing the relative sizes of the blocks, the identity of the blocks themselves, or temperature. The addition of solvent can enable greater changes in the available morphologies for a block polymer of a given composition, and structure can also be tuned by choosing a neutral versus a selective solvent.[3−7] In all cases, to access an order−disorder transition (ODT) or order−order phase transition (OOT), the system must be chemically or physically altered. The incorporation of a light-responsive moiety in the block polymer, such as azobenzene, introduces a method by which the system can undergo OOTs or ODTs in response to a contactless stimulus.

Azobenzene is a well-studied photochromic molecule.[8,9] Under visible light, the *trans* ground state of the molecule is relatively nonpolar. Irradiation with UV light causes isomerization to the more polar *cis* state. This *cis* isomer can revert to the ground state either via thermal relaxation or under visible light. This switching is fully reversible, allowing extensive cycling of polarity without significant degradation.[10,11] The use of azobenzene to control the ordering of liquid crystals (LC) has been extensively studied. Incorporation of azobenzene into LCs, polymeric or otherwise, has been shown to enable photoinduced optical anisotropy.[12−15] This moiety can also be used to induce LC alignment,[16,17] as applied for use in optical switching and image storage.[18−21] The reversible isomerization makes azobenzene ideal for applications; the absence of a facile

degradation pathway allows for reversible writing of images, as well as cycling for use in switches. The used of polarized light can also induce macroscopic flow of polymer films to generate surface relief gratings.[22] This work has recently been extended to the use of azobenzene-containing LCs in block polymers. The ability of the azobenzene moiety to drive alignment in the liquid crystal phase allows for macroscopic alignment of the block polymer as a whole.[23−26] In some cases, irradiation of these block polymers with UV light can induce a transition from an LC phase, such as nematic, to a disordered phase.[27−29]

Although there have been studies of light-induced ODTs in azobenzene-containing LC block polymers,[30,31] the exploration of azobenzene-containing amorphous "coil−coil" block polymers has not been as extensive. The use of azobenzene in the end blocks of an ABA triblock as a Langmuir−Blodgett layer has been able to produce an OOT.[32,33] However, this transition is not fully reversible and requires high humidity. It is likely that water swells the film, and the isomerization induces a change in the ordered morphology by either taking up water in the polar *cis* state or excluding it in the nonpolar *trans* state. Another study incorporated azobenzene in the poly(*n*-butyl methacrylate) block of a polystyrene-*block*-poly(*n*-butyl methacrylate) polymer;[34] the phase behavior included a lower critical ordering transition, LCOT, analogous

to the lower critical solution temperature (LCST) phase behavior observed in homopolymer solutions or blends, where phase separation occurs on heating. The authors observed that they could bring the system close to the LCOT, but they did not reach it. They also observed that the degree of ordering was light-dependent, as expected with the incorporation of azobenzene. Some work has also been done on blending polymers with additives to achieve ordering with light.[35]

To circumvent the reversibility issues, such as those reported in refs 32 and 33, the light-responsive block polymer could be combined with a nonvolatile solvent rather than relying on humidity. This would allow the isomerization of azobenzene to control the selectivity of the solvent and, thus, drive OOTs or ODTs in solution. A related idea has been explored in dilute solution, through controlling the micellization and demicellization of an azobenzene-containing block polymer in ionic liquid using light.[36] This work has also been extended to an ABA system, where gelation can be triggered with visible light[37] and the gel undergoes self-healing when irradiated with UV light.[38] These studies have not explored polymers at higher concentrations to access the traditional block polymer ordered morphologies.

In this work we use a block polymer composed of poly(methyl methacrylate) (PMMA, M) and poly(benzyl methacrylate-*stat*-(4-phenylazophenyl methacrylate)) (P-(BzMA-*stat*-AzoMA), BsA). The PMMA block is fully soluble in the ionic liquid 1-ethyl-3-methyl imidazolium bis-(trifluoromethanesulfonylimide) (EMI TFSI). The structures of the polymer and the ionic liquid are shown in Scheme 1. As

Scheme 1. Chemical Structures of the Light-Responsive Block Polymer PMMA-*b*-P(BzMA-*stat*-AzoMA) and the Ionic Liquid EMI TFSI

previously explored,[39−41] BsA shows light-dependent LCST phase behavior. At low temperatures, EMI TFSI will act as a virtually neutral solvent, dissolving both blocks. Increasing the temperature induces an LCOT, driving the EMI TFSI preferentially out of the BsA blocks. The ordering upon heating is due to a change in the solubility of the polymer in the solvent, which can be modified by changing the isomerization state of azobenzene. The *cis* state under UV light is more polar, increasing its solubility in EMI TFSI. Thus, the ordered structure formed under visible light can be dissolved under UV light.

The structure of 30 wt % MBsA(22−24(5)) without exposure to UV light was characterized using small-angle X-ray scattering; here, 22 and 24 refer to the block molecular weights in kDa, respectively, and 5 refers to the mole percent of the azo monomer in the second block. Under ambient light, the *trans* ground state of azobenzene dominates,[8] leading to a lower T_{ODT} than would be expected with the more polar *cis*

isomer. At low temperatures, the sample displayed a scattering pattern characteristic of the disordered state (see Figure S1). Upon heating, sharp Bragg peaks appear starting at 100 °C, indicating the ODT (Figure S1). Heating the sample to 150 °C did not produce any further changes in the scattering; a representative pattern from 150 °C is shown in Figure 1.
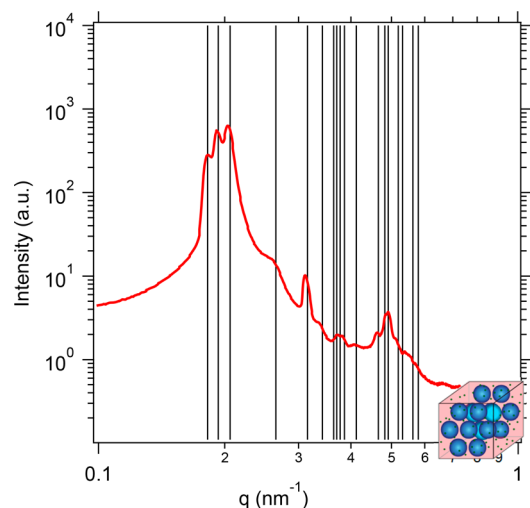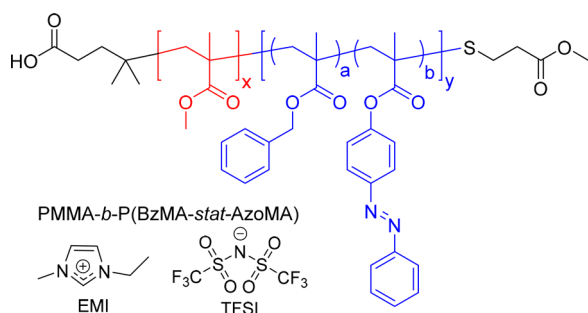
Figure 1. Structure of 30 wt % M(BsA) (22−24(5)) in EMI TFSI at 150 °C from small-angle X-ray scattering. The red line is the scattering data, and the vertical black lines indicate the expected reflections for hexagonally close-packed spheres, HCP. The position of the principal scattering peak, $q*$, is 0.182 nm^{-1}. The expected peak positions for HCP are tabulated in the SI, in terms of multiples of $q*$ and the allowed Miller indices. The distance between spheres, a, was calculated to be 39.9 nm, and the interlayer spacing, c, was calculated to be 65.2 nm. A cartoon illustration inset of the graph shows the packing structure for HCP.

Remarkably, the observed scattering pattern matches the expected peak positions for hexagonally close packed spheres (HCP). Ordered spherical morphologies are expected for relatively low concentrations of block polymers in selective solvents, but typically either body-centered cubic (BCC) or face-centered cubic (FCC) structures are observed.[3−7] Both HCP and FCC result from close-packed spheres, where the HCP lattice has ordered layers stacked in a repeating AB pattern, whereas FCC is a repeating ABC pattern. While it is unusual to observe HCP for block polymer solutions, FCC close packing has been observed for "crew-cut" micelles, when the corona block is relatively short compared to the core-forming block.[4,42] Lower concentrations (20 and 25 wt %) of MBsA (22−24(5)) also show HCP packing at elevated temperatures. SAXS additionally confirmed that the ordering upon heating is fully reversible upon cycling the temperature between 150 and 30 °C.

Due to current limitations of the experimental geometry, it was not possible to achieve in situ light exposure during SAXS measurements. On the other hand, small amplitude oscillatory shear rheology offers a method of in situ light exposure while measuring the mechanical properties of a sample, and it is well established that the low frequency viscoelastic properties of block polymer samples are very sensitive to the state of order. Temperature sweeps shown in Figure 2a give the response of the sample upon heating from 30 to 150 °C, both in the dark and under UV light irradiation. At low temperatures, $G'' > G'$, indicating liquid-like behavior. As the temperature is increased,
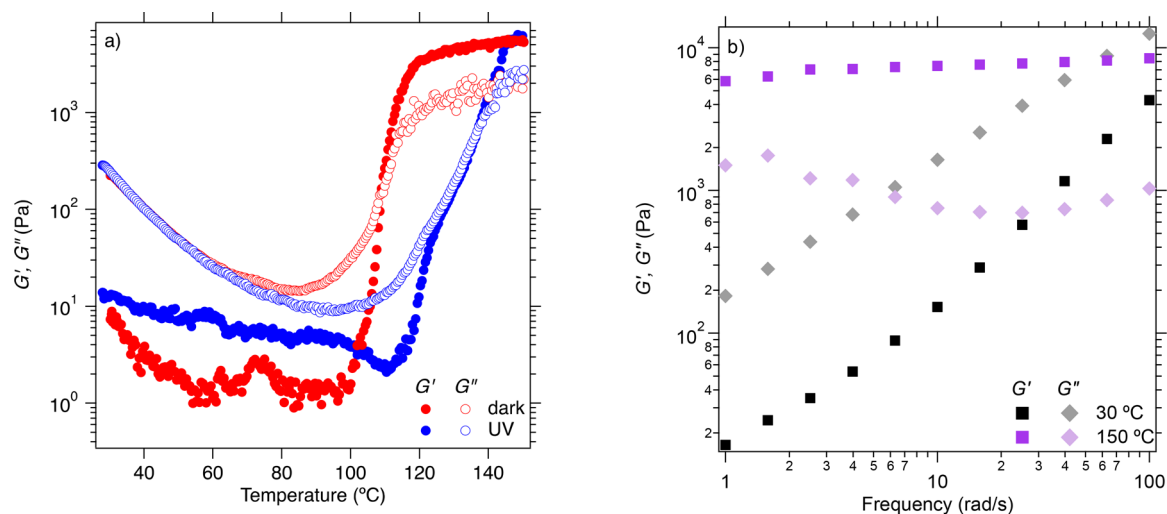
Figure 2. (a) Temperature sweep of 30 wt % M(BsA) (22−24(5)) in EMI TFSI. Closed symbols correspond to G', open symbols correspond to G''. Data colored in red were obtained in the ground *trans* state of azobenzene, the data shown in blue symbols were obtained by irradiating the sample with UV light at a power of 50 mW/cm^2. The sample was measured at a frequency of 1 rad/s, 1% strain, a heating rate of 3 °C/min, and a gap of 200 μm. (b) Frequency sweeps of 30 wt % M(BsA) (22−24(5)) in EMI TFSI at 30 °C (black squares for G', gray diamonds for G'') and 150 °C (purple squares for G', light purple diamonds for G''). Measurements were performed in the dark, with 1% strain, and a gap of 200 μm.
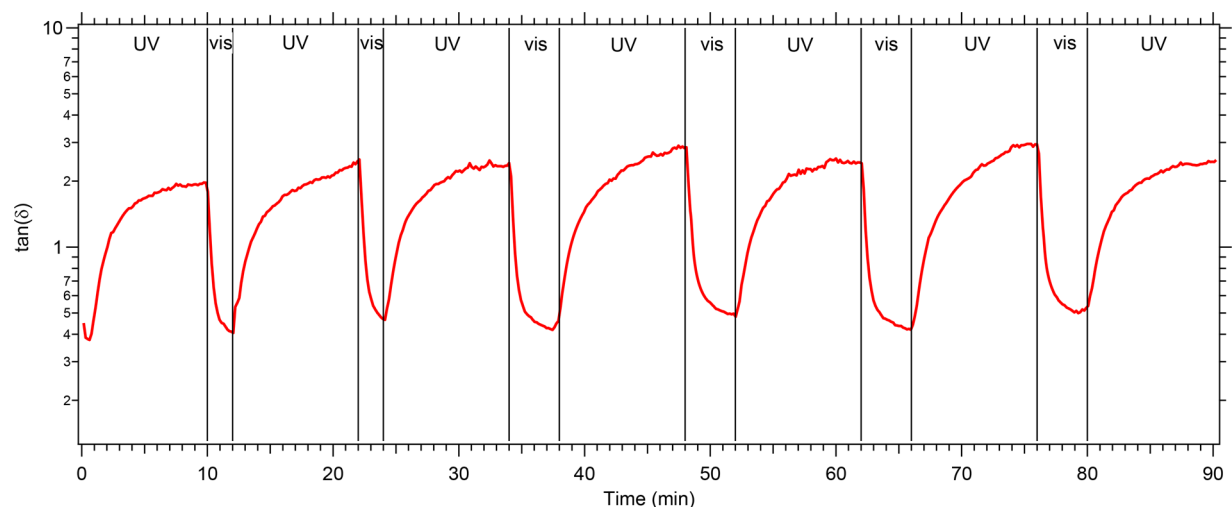

Figure 3. Light-triggered ordering and disordering of 30 wt % M(BsA) (22−24(5)) in EMI TFSI under UV and visible light. The sample was equilibrated at 100 °C in the dark for 60 min, then at the start of the experiment, the UV light was turned on. Each black line indicates the time at which the light filter was changed. The red data are the tan(δ) measured from a time sweep in rheology, with a frequency of 1 rad/s, 1% strain, and a constant temperature of 100 °C. The lamp power was held at 50 mW/cm^2 of UV light.

G'' and G' cross over and reach a plateau at high temperatures, where $G' > G''$. Overall, the storage modulus increases by ~3 orders of magnitude, starting at ~100 °C, consistent with the disorder to HCP transition observed in SAXS. When the sample is irradiated with UV light, the temperature at which G' and G'' crossover increases. Notably, the storage modulus under UV light achieves the same maximum value as in the dark, suggesting that the ordered structure formed may also be HCP, although determination of the structure via future in situ UV exposure during SAXS will be required to confirm this assignment. The shift in T_{ODT} gives a range of temperatures at which the system is bistable, and an ODT between disorder and HCP can be triggered with light.

Figure 2b shows frequency sweep measurements performed in the dark at 30 and 150 °C. At 30 °C, $G'' > G'$ and the moduli scale with frequency as expected for terminal behavior of a viscoelastic fluid. At 150 °C, the storage modulus is invariant with respect to frequency. This response is typical of cubic ordered structures, consistent with the HCP structure observed in SAXS.

The bistable window mapped by the temperature sweep data gave a range of temperatures, 108−123 °C, where photo-triggering between disorder and HCP should be possible. The SAXS patterns show a clear transition from liquid-like packing at 90 °C to HCP at 100 °C, indicating that the ordering begins at a lower temperature than suggested in Figure 2a; this is primarily due to the long annealing times in SAXS versus the significant heating rate in rheology. Therefore, 100 °C was chosen as a suitable temperature for triggering, to ensure that the difference between the states under visible and UV light was as large as possible. To monitor this behavior, a time sweep experiment was performed. The samples were equilibrated at 100 °C for 1 h in the dark, after which the light source was turned on with the UV light filter in place.

Figure 3 shows how $\tan(\delta)$, the ratio G''/G', changes as the wavelength of light illuminating the sample is switched. Immediately after the sample is exposed to UV light, $\tan(\delta)$ is less than 1, corresponding to $G' > G''$ or the ordered HCP state. The UV light exposure drives the sample into a disordered, $\tan(\delta) > 1$ state. Once the signal plateaued, suggesting a fully disordered state, the filter was switched to irradiate the sample with visible light. Visible light irradiation quickly induced a drop in $\tan(\delta)$ as the ordered HCP morphology reformed. This cycle of UV-to-visible light was repeated six times to demonstrate reversibility and, as shown, there is no evidence of any loss of sample integrity after multiple cycles.

The first UV and visible light cycles were fit with exponential functions, shown in Figure 4. Both disordering and ordering
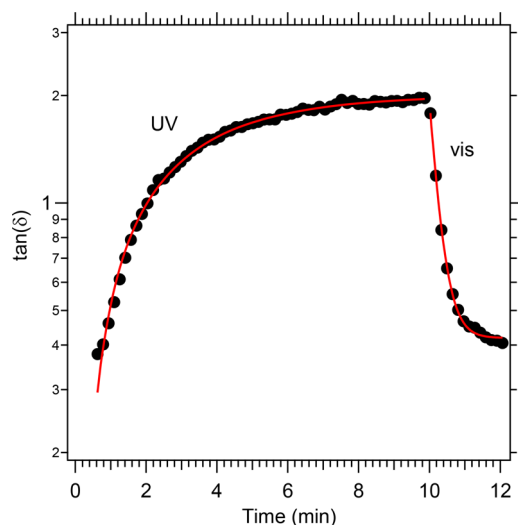

Figure 4. Fitting of the first disordering and ordering cycle shown with exponential growth and decay of $\tan(\delta)$, respectively. Black symbols represent the $\tan(\delta)$ data obtained from rheology, and red curves are fits of the data with exponential functions with the associated time constants of 0.38 min^{-1} for disordering and 3.7 min^{-1} for ordering.

kinetics are well-fit with single exponentials, suggesting an uncomplicated transition. The disordering process is slower than ordering, taking 2 min to achieve $\tan(\delta) > 1$, whereas it takes only 14 s for $\tan(\delta)$ to drop below 1 after visible light irradiation begins. This is consistent with observations of hysteresis in LCST phase behavior, where breaking apart the aggregated polymers requires cooling below the LCST observed upon heating. Under visible light illumination, thermal reversion is also driving isomerization back to the *trans* ground state. These two mechanisms work in parallel, which may accelerate the formation of HCP relative to the rate of disordering. The broader spectrum of wavelengths used to irradiate with visible light, 400−500 nm, may also yield a higher flux of visible light relative to UV light, with a single peak at 365 nm, at the same lamp output set to deliver 50 mW/cm^2 of UV light.

To our knowledge, this is the first example of a light-controlled reversible ODT in a coil−coil block polymer system. At low temperatures, the block polymer/ionic liquid solution is always disordered, as confirmed by rheology and SAXS. At 150 °C and in the absence of UV light, the system shows HCP ordering in SAXS. In the intermediate region (ca.

100−140 °C), a bistable window exists where the ordering of the system is dictated by the wavelength of light to which the sample is exposed.

The ability to trigger an ODT with light could enable the use of these ionic liquid/block polymer solutions as, for example, photoreversible adhesives. Homopolymers of azo-benzene-based monomers have been shown to act as adhesives under visible light and transition to a liquid-like state upon UV irradiation, allowing for easy removal of the adhesive.[43] The use of azobenzene in the hard block of a thermoplastic elastomer has been shown to enable control of the plasticity of the elastomer with light.[44] Combining these two concepts, the use of an azobenzene-containing block polymer as a thermoplastic elastomer could be used in adhesive applications. Alternatively, light could be used to pattern block copolymer thin films at the micron scale and above or as a means of contactless zone-refining of the state of order.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00153.

> Experimental details and indexing of HCP structure; Figure S1: SAXS scattering patterns of M(BsA) (22−24(5)) as a function of temperature; Figure S2: SEC traces of PMMA-CTA and M(BsA) (22−24(5)); Figure S3: ^{1}H NMR spectra of PMMA-CTA and M(BsA) (22−24(5)) (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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