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Polar Aprotic Solvents Disrupt Interblock Hydrogen Bonding and Induce Microphase Separation in Double Hydrophilic Block Copolymers of PEGMA and PAAMPSA

Tracy L. Bucholz[†] **and Yueh-Lin (Lynn) Loo***[,‡]

Department of Chemical Engineering, the University of
Texas at Austin, 1 University Station C0400, Austin,
Texas 78712, and Department of Chemical Engineering,
Princeton University, A217 Engineering Quadrangle,
Princeton, New Jersey 08544

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Many double hydrophilic block copolymers (DHBCs)[1] are biocompatible[2] and stimuli-responsive,[3] have adjustable amphilicity,[4] and can self-assemble in solution.[5] The combination of these properties renders these materials attractive as templates for growing inorganic crystals with unusual polymorphs[6] and assembling organic−inorganic colloids[7] as well as for the development of drug- and protein-delivery systems.[8,9] That DHBCs can spontaneously assemble in solution and act as templates for the subsequent growth and assembly of other materials relies on their specific intermolecular interactions with the templated species. In many cases, the very nature of the intermolecular interactions also results in intramolecular interactions between the two segments within DHBCs. For example, the ability for poly(acrylic acid), PAA, to hydrogen bond with silica precursors[10] and other hydrophilic polymers[11] is also responsible for its complexation[12] with poly(ethylene oxide), PEO, in PAA/PEO DHBCs.

While the extent of interblock hydrogen bonding of DHBCs in solutions can be manipulated and adjusted through solvent choice, the attractive nature of this specific interaction in the solid state is so strong that DHBCs typically form single-phase, homogeneous melts, regardless of their molecular weights. Until now, there thus has not been any evidence of microphase separation in DHBCs, though disruption of similar hydrogen bond interactions has been reported for blends of PAA and PEO. Specifically, PAA was neutralized to induce macroscopic phase separation[13] of these polymer blends. While this approach effectively disrupts the hydrogen bonding between the two polymer constituents, it necessitates the removal of the acid functionality of PAA. The introduction of dioxane has also been noted to decrease, but not completely eliminate, complexation in blends of PAA and PEO.[14]

By solvent casting a DHBC with polar aprotic solvents, we demonstrate that we can effectively disrupt interblock hydrogen bonding to induce microphase separation of the block copolymer in the solid state. The DHBC of interest was made by atom transfer radical polymerization (ATRP)[15,16] and contains poly(oligoethylene oxide methyl ether methacrylate), PEGMA, a methacrylate-based polymer with PEO pendant chains 8−9 units long, and poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA, a strong polymer acid that can be used to protonate polyaniline.[17,18] The block copolymer is hereafter referred to as PEGMA/PAAMPSA 23/26 ($M_n = 49.3$ kg/mol; PDI = 1.37) where the numbers represent the PEO-equivalent number-average molecular weight of the respective blocks in kg/mol.

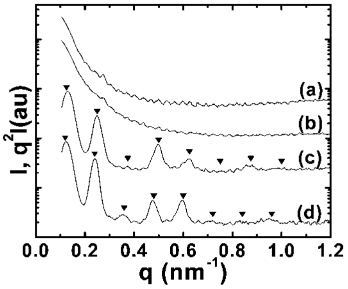

Figure 1. Small-angle X-ray scattering profiles of PEGMA/PAAMPSA 23/26 cast from (a) methanol, (b) water, (c) DMF, and (d) DMSO. The traces have been shifted along the *y*-axis for clarity. PEGMA/PAAMPSA 23/26 cast from methanol and water are plotted as I vs q. PEGMA/PAAMPSA 23/26 cast from DMSO and DMF are plotted as q^2I vs q. PEGMA/PAAMPSA 23/26 cast from both methanol and water is disordered. PEGMA/PAAMPSA 23/26 cast from both DMSO and DMF adopts a lamellar morphology with expected reflections at q/q^* ratios of 1, 2, 3, 4, etc. (indicated with the triangles).

Figure 1 contains the SAXS profiles acquired on films of PEGMA/PAAMPSA 23/26 cast from four different solvents: methanol, water, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The SAXS profiles in Figure 1a,b are featureless, indicating that PEGMA/PAAMPSA 23/26 forms a single-phase, homogeneous melt when cast from methanol and water. This observation is not surprising, given that the ether oxygens on the PEO side chains of PEGMA can complex with the sulfonic acid groups of PAAMPSA through hydrogen bonding. The SAXS profiles of PEGMA/PAAMPSA 23/26 cast from DMSO and DMF, however, are drastically different. Specifically, the SAXS profiles exhibit a narrow and intense primary peak at $q^* = 0.12$ nm^{-1} and higher-order reflections at q/q^* ratios of 2, 3, 4, 5, 6, 7, and 8. Figure 1c,d thus indicates that PEGMA/PAAMPSA 23/26 is microphase separated when cast from DMSO and DMF. And given the positions of the higher-order reflections, PEGMA/PAAMPSA 23/26 readily adopts an alternating lamellar morphology in the solid state when cast from either DMSO or DMF. The fact that eight orders of reflections are observed is atypical, especially for block copolymers with polydispersity indices greater than 1.1, and points to the high degree of order of the lamellar microdomains. To our knowledge, this is the first evidence of microphase separation in a DHBC that is capable of interblock hydrogen bonding. We attribute this phenomenon to DMSO and DMF disrupting the interblock hydrogen bonding between PEGMA and PAAMPSA. That we have effectively increased the chemical incompatibility between PEGMA and PAAMPSA is also suggested by the large number of reflections observed in the SAXS profiles in Figure 1c,d.

While solvent casting PEGMA/PAAMPSA 23/26 from DMSO and DMF yielded highly ordered microphase-separated structures, solvent casting the same diblock copolymer from methanol and water consistently yielded disordered melts. DMSO and DMF are polar aprotic solvents; they are known to be strong hydrogen-bond acceptors (HBA), with the highest HBA basicities among most common organic solvents (0.710 for DMF and 0.752 for DMSO).[19] In contrast, water and methanol are both protic solvents with lower HBA basicities (∼0.2 for water and ∼0.6 for methanol; these values are less

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[*] To whom correspondence should be addressed. E-mail: lloo@princeton.edu.

[†] The University of Texas at Austin.

[‡] The University of Princeton.

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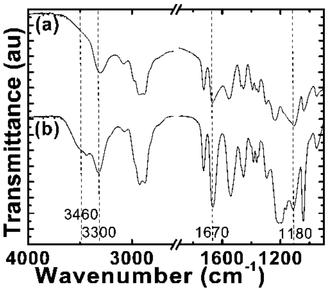

Figure 2. Fourier transform infrared spectroscopy spectra of PEGMA/PAAMPSA 23/26 cast from (a) methanol and (b) DMSO. The spectra have been shifted along the *y*-axis for clarity. The dotted lines indicate peaks that denote differences between the two spectra.

precise and more difficult to determine given that these solvents can hydrogen bond to themselves).[19] Given the higher HBA basicities, DMSO and DMF can more readily accept hydrogen bonds from the sulfonic acid groups of PAAMPSA. As opposed to hydrogen bonding with the ether oxygens in PEGMA (HBA basicity of about 0.4; estimated based on alkyl ethers),[19] the introduction of DMSO and DMF provides more favorable hydrogen-bonding sites for the sulfonic acid groups in PAAMPSA.[20] Using DMSO and DMF as casting solvents thus enabled the disruption of interblock hydrogen bonding that would otherwise be present in PEGMA/PAAMPSA 23/26. On the other hand, methanol and water are not capable of disrupting the interblock hydrogen bonding between PEGMA and PAAMPSA because their HBA basicities are not sufficiently high. This observation is consistent with a recent study that revealed that small-molecule organic sulfonic acids readily form hydrogen bonds with both DMF and DMSO, but they merely protonate methanol and water.[21]

FTIR spectra acquired on PEGMA/PAAMPSA 23/26 films cast from methanol and DMSO are shown in Figure 2. There is no evidence of residual solvents in any of the FTIR spectra. The dotted lines in this figure highlight key peaks in the spectra. The broad shoulder at 3460 cm^{-1} and the peak at 3300 cm^{-1} are associated with the free OH and the acrylamide groups of PAAMPSA, respectively. The peak at 1670 cm^{-1} is attributed to the carbonyl stretch of PAAMPSA while the broad absorbance at 1180 cm^{-1} is associated with the sulfonic acid group of PAAMPSA.[22] We observe considerable differences between the FTIR spectrum of PEGMA/PAAMPSA 23/26 cast from methanol compared to that of the same diblock copolymer cast from DMSO. For instance, the FTIR spectrum of PEGMA/PAAMPSA 23/26 cast from methanol at 3460 cm^{-1} is suppressed compared to that of the block copolymer cast from DMSO. This comparison indicates a reduction in free OH groups PEGMA/PAAMPSA 23/26 cast from methanol, suggestive that these groups are hydrogen bonded.[23] Additionally, the peak at 3300 cm^{-1} is broader and shifted to lower wavenumbers for PEGMA/PAAMPSA 23/26 cast from methanol compared to that cast from DMSO. The broadening and shift of this NH stretch indicate that the acrylamide protons in the methanol-cast film are hydrogen bonded.[22,23] The same broadening is observed for the peak at 1670 cm^{-1} in the methanol-cast PEGMA/PAAMPSA 23/26 film, suggesting multiple bonding environments for the carbonyl, presumably due to hydrogen bonding.[10] Finally, we also observe an increase in intensity of the sulfonic acid peak (1180 cm^{-1}) relative to the carbonyl peak in the methanol-cast film compared to the DMSO-cast film. This increased intensity is attributed to molecular associations of the sulfonic acid groups,[22] presumably with the ether atoms of the PEO side chains of PEGMA. Together, these differences in the FTIR spectra between the two cast PEGMA/PAAMPSA 23/26 films suggest the presence of interblock hydrogen bonding in the methanol-cast film but not the DMSO-cast film.

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Supporting Information Available: Complete synthetic and characterization details of PEGMA/PAAMPSA 23/26; SAXS profiles and physical characteristics of other PEGMA/PAAMPSA diblock copolymers examined in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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