Supplemental Information for Ordered and foam structures of semifluorinated block copolymers in supercritical carbon dioxide

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We estimated the swelling ration of the block copolymer in this study from the swelling ratio of similar polymers. We assume that the swelling ratio of each copolymer domain is identical to the corresponding homopolymer.[1] Li *et al.*[2,3] have reported swelling ratio of polystyrene, poly(1,1'-dihydroperfluorooctyl methacrylate) (PDHFOMA), and poly(1,1',2,2'-tetrahydroperfluorooctyl methacrylate) (PTHFOMA). Using the results of their study, we estimated swelling ratios of PS and PFMA at 60 °C, and at 15 MPa to 10 and 120 % , respectively. Furthermore, densities of PS and PFMA (ρ_{PS}, ρ_{PFMA}) are also necessary to calculate volume fractions. ρ_{PS} is 1.05 g/cm^3 (from MSDS of PS). The density of PFMA can be estimated by

$$\rho_{\mathrm{PFMA}} = \rho_{\mathrm{FMA}} \times \frac{\rho_{\mathrm{PTHFOMA}}}{\rho_{\mathrm{THFOMA}}}. \tag{1}$$

Here, FMA and THFOMA represent monomers of PFMA and PTHFOMA, respectively. ρ_{FMA} and ρ_{THFOMA} are 1.496 and 1.590 g/cm^3 respectively, available from online catalog of ABCR. ρ_{PTHFOMA} is 1.53 g/cm^3, provided by Li *et al.*[3] From these values, ρ_{PFMA} is estimated to 1.63 g/cm^3. Since the weight fractions of PS and PFMA are 0.740 and 0.260, volume fractions of two domains are estimated to 0.815 and 0.185. Considering the swelling ratio, apparent volume fraction of PFMA at 60 °C, and at 15 MPa is estimated to 0.31, close to 1/3.

In the same way, we estimated the swelling ratio of PFMA at 60 °C, and at 10 MPa to 60 %, and calculated the apparent volume fraction of PFMA to 0.25. Appearance of lamellar structure with such an asymmetric volume ratio is probably due to comb-like architecture of PFMA, in which bulky fluoroalkyl chains are attached onto short backbones. Namely, the fluoroalkyl side chains stack as smectic layer to stabilize lamellae, as previously reported.[4] Here, thickness of PFMA and PS layer ($d_{\mathrm{PFMA}}, d_{\mathrm{PS}}$) can be calculated from interdomain spacing of lamellae (d) and the composition ratio. At 10 MPa, d, d_{PFMA} and d_{PS} are 23.0, 5.8 and 17.2 nm, respectively. Those at 15 MPa are 23.5, 7.3 and 16.2 nm, respectively. d and d_{PFMA} at 15 MPa are thinner than expected values assuming uniaxial (perpendicular to the layers) swelling. Furthermore, d_{PS} surprisingly decreased to 16.2 nm. Such decreasing d_{PS} suggests that CO_2 swells PFMA and reduces the number of bcp chains per unit area of lamellae. In order to maintain certain volume fraction of PS domains, PS chains need to shrink to compensate the reduction of number density of PS chains per unit area of lamellae.

It is noteworthy that FMA monomers have bulky side chains so that each PFMA has only 11.7 units. From the number of C-C bonds, the bond length and angle, contour length of PFMA is roughly estimated to 3.0 nm. However, PFMA domain of 7.3 nm at 15 MPa means that PFMA chains are length of at least 3.7 nm, which is significantly larger than the contour length. The gap can be bridged by side chains ($1 \sim 2$ nm) attached to the end of the main chains. While inner side chains stack parallel to the layers as previously mentioned, it is possible that the topmost ones slightly point upward to accommodate large amount of CO_2. At any rate, PFMA chains appear highly stretched, and further swelling maintaining lamellar structure is not feasible.

References

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