Study on Concentration Fluctuations and Ordered Structure Formation Arising from Monomer Sequences in Binary Random Copolymers

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BACKGROUND AND OBJECTIVE

Random copolymers generally lack the long sequence blocks that drive conventional microphase separation. Nevertheless, local hydrophilic–hydrophobic interactions may generate concentration fluctuations and ordered nanostructures under selective environmental conditions. Here, a binary random copolymer of 2-hydroxyethyl acrylate (HEA) and 3-methacryloxypropyl tris(trimethylsiloxy)silane (TMSM) was investigated to determine whether hydration induces nanometer-scale ordering and to resolve the internal composition profile using contrast-variation small-angle neutron scattering (CV-SANS).

EXPERIMENTAL

P(HEA-co-TMSM) was synthesized by free-radical copolymerization using 2,2′-azobis(isobutyronitrile) as an initiator. The polymer was washed with water and hexane, dried, cast from a tetrahydrofuran solution, maintained at room temperature for 24 h, and subsequently vacuum-dried for 24 h. Five copolymers with different HEA/TMSM compositions were examined by SAXS in the dry and hydrated states. The near-equimolar composition exhibiting the highest degree of structural order was selected for CV-SANS measurements at SANS-U, JRR-3, using D_2O/H_2O mixtures with systematically varied solvent scattering length densities (SLDs).

RESULTS AND DISCUSSION

The hydrated samples exhibited a primary SAXS peak at $q^*\approx1.0$–1.1 nm^{-1} and a second-order reflection at $2q^*$, corresponding to a lamellar repeat distance of approximately 5.7–6.3 nm. In contrast, the SANS profile measured in D_2O was dominated by the first-order reflection. As the H_2O fraction increased, the first-order peak intensity decreased, whereas the second-order peak became increasingly prominent. This systematic redistribution of the diffraction intensities indicates that the repeat unit cannot be described by a simple two-layer lamellar model.

The contrast dependence was analyzed using a one-dimensional three-layer SLD profile, ρ(x), comprising a water-rich layer (3.0 nm), a thin main-chain-rich layer (0.5 nm), and a hydrophobic-side-chain-rich layer (2.0 nm). The experimental ratio of the second- to first-order peak intensities was evaluated by $I_2/I_1=\int I_1(q)q^2\mathrm{d}q/[\int I_2(q)q^2\mathrm{d}q$. The neutron scattering amplitude was calculated as $F(q)\propto\int\rho(x)\exp(-iqx)\mathrm{d}x$, with $I(q)\propto|F(q)|^2$. The calculated variation in I_2/I_1 reproduced the experimentally observed dependence of the peak-intensity ratio on the H_2O/D_2O composition.

CONCLUSION

Hydration induces an ordered lamellar nanostructure in near-equimolar P(HEA-co-TMSM). The CV-SANS results support a repeat unit consisting of water-rich, polymer-backbone-rich, and hydrophobic-side-chain-rich regions. These findings demonstrate that monomer-scale hydrophilic–hydrophobic heterogeneity in a random copolymer can generate an ordered structure under aqueous conditions.

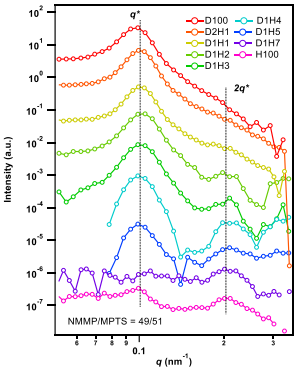

Figure 1. CV-SANS profiles and the dependence of the second-to-first-order peak intensity ratio on the H_2O content of the H_2O/D_2O mixtures.