Investigation of the water localization in the block copolymer-based elastomers containing hydrophilic aggregates

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So far, we have studied bond exchangeable network polymers with phase-separated structure.[1] The key feature is the use of quaternized pyridines as the cross-link units, which exhibited the bond exchange nature via trans-*N*-alkylation. In addition, quaternized pyridines were self-assembled to form nano-domains due to the hydrophilic nature, causing repulsive force against the network strand composed of polyacrylates. For this network, we have studied the effects of humidity on the relaxation dynamics. Assuming water molecules are locally segregated into the hydrophilic nano-domains of quaternized pyridines, the plasticity effect in the bond exchangeable domains is expected. In this study, we expand this concept into a block copolymer system in which one block component is cross-linked via quaternized pyridines, forming self-assembled nano domains in the corresponding block phase.

For this purpose, we synthesized a block copolymer composed of poly(methyl methacrylate) and poly(ethyl acrylate)-based random copolymer with pyridine side groups (Fig. 1a). The total molecular weight is 40k, and the weight fraction of poly(ethyl acrylate)-based random copolymer block is 0.44. The cross-linking was performed by pyridine quaternization reaction with diiodohexane. The cross-linked samples were immersed in deuterium oxide (D_2O) for 24 h, after which the water content was ca. 5 weight%. The SANS was conducted using a sample holder in which the water-containing sample was surrounded with sufficient amounts of D_2O.

Fig. 1b first provides the SAXS profile performed for the bulk sample (photon factory, BL-6A). The peak at $q \sim 0.22$ nm^{-1} and $q \sim 2.5$ nm^{-1} (q : scattering vector) originates from the periodic lamellar-like structure and the self-assembly of quaternized pyridines, respectively. The SANS spectrum for the sample swollen by D_2O provides the peaks at similar peak positions (Fig. 1c). The results indicate that D_2O molecules were incorporated in the domains of quaternized pyridines, as designed.

[1] M. Hayashi *et al*., ACS Macro Letter. **14**, 182 (2025).

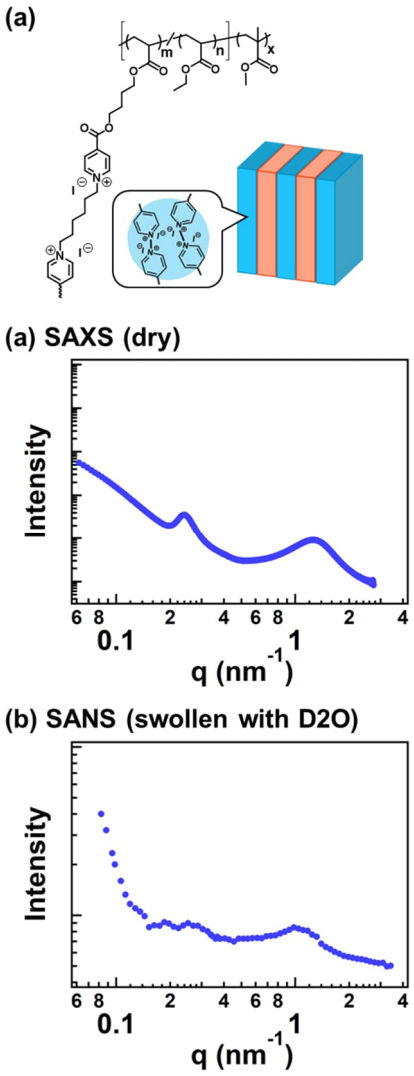

Fig. 1 (a) Molecular design of the present study. (b) SAXS data for the dry sample and (c) SANS data for the sample immersed in D_2O.