Electronic Supplementary Information for

Kinetically Controlled Morphology in Copolymer-based Hydrogels Crosslinked by Crystalline Nanodomains Determines Efficacy of Ice Inhibition

Pablo I. Sepulveda-Medina,[a] Chao Wang,[a,†] Ruipeng Li,[b] Masafumi Fukuto,[b] R.A. Weiss,[a] and Bryan D. Vogt [a,†]*

[a]Department of Polymer Engineering, University of Akron, Akron, OH 44325 USA

[b]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, USA

† Present address: Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, USA (C.W.); Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802 (B.D.V.)

* Corresponding author: bdv5051@psu.edu (B.D.V.)

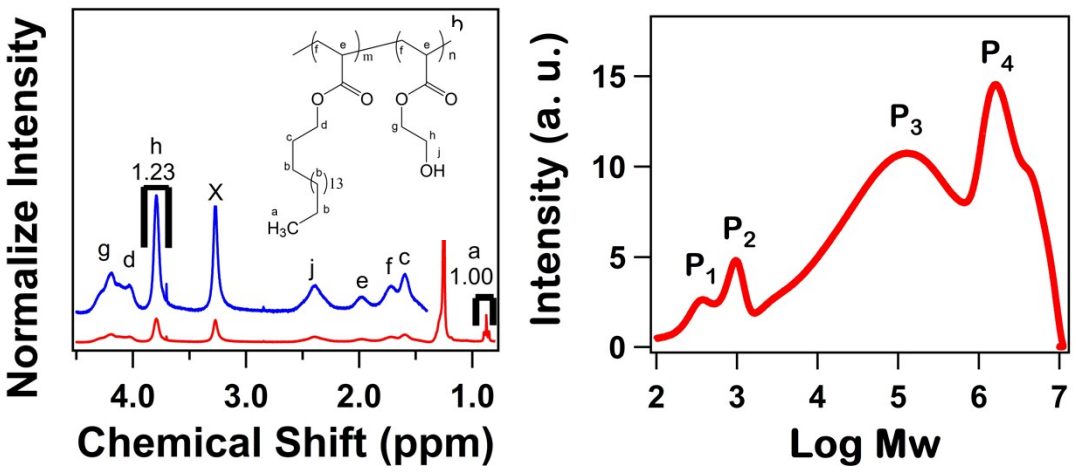

Figure S1. (left) ^{1}H NMR spectrum for the HEA-ODA copolymer in $CDCl_3$. The peak at the chemical shift at (X) arises from the -CH_2- proton of Diethyl Ether, which was used to precipitated the copolymer. (right) SEC trace for the HEA-ODA copolymer in DMF relative the polystyrene molecular mass. The multimodal trace is unexpected for free radical copolymerization of two acrylates and differs from those of copolymers used to make similar hydrogels that do not include a crystalline comonomer. We attribute the high molecular weight peak centered at 3.35 MDa (labeled as P_4) to crystallization to effectively branch the copolymer. Based on prior polymerizations of acrylates, the broad peak centered at 99 kDa (labeled as P_3) should be associated with the primary copolymer.

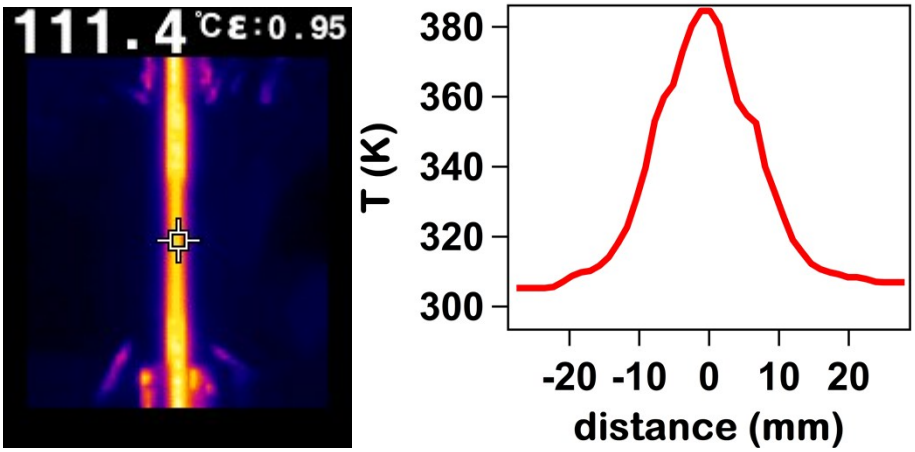

Figure S2. IR image illustrating the hot wire used for the zone annealing. The maximum temperature was 384 K. The temperature profile associated with the zone annealing is determined from the IR image.

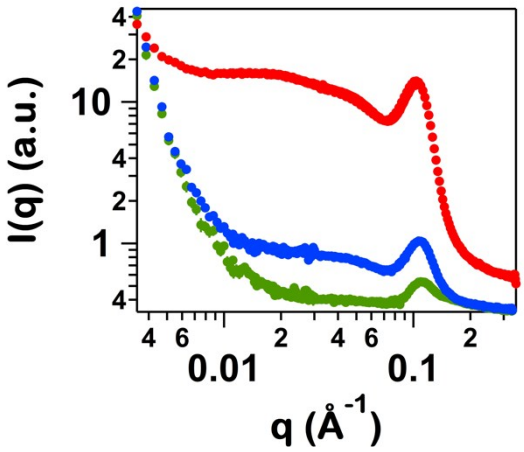

Figure S3. SANS 1D scattering profiles for hydrogel that was fabricated from copolymer was compression molded at 383K using different scattering contrasts based on the D_2O/H_2O composition in the hydrogel: red (D_2O), blue (91.37/8.62 v/v D_2O/H_2O mixture that matches the SLD of HEA) and green (72.49/27.5 v/v D_2O/H_2O mixture that matches the SLD of ODA). A correlation peak is observed for all contracts.

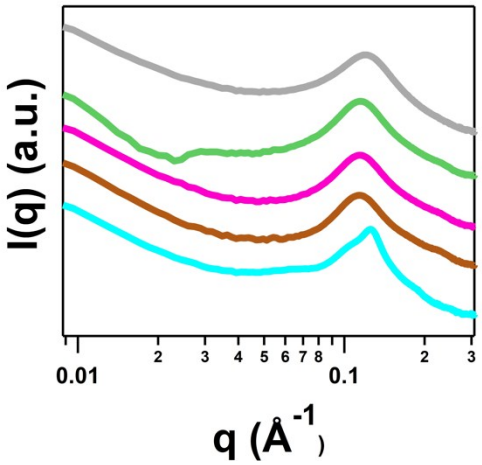

Figure S4. SAXS pattern of HEA-ODA hydrogel at 295K for different rotational zone annealing locations corresponding to zone annealing velocities of (from top to bottom) 46.5$\mu m/s$ (grey), 68.0$\mu m/s$ (green), 94.9 $\mu m/s$ (pink), 121.8 $\mu m/s$ (brown), and 162.1 $\mu m/s$ (light blue).

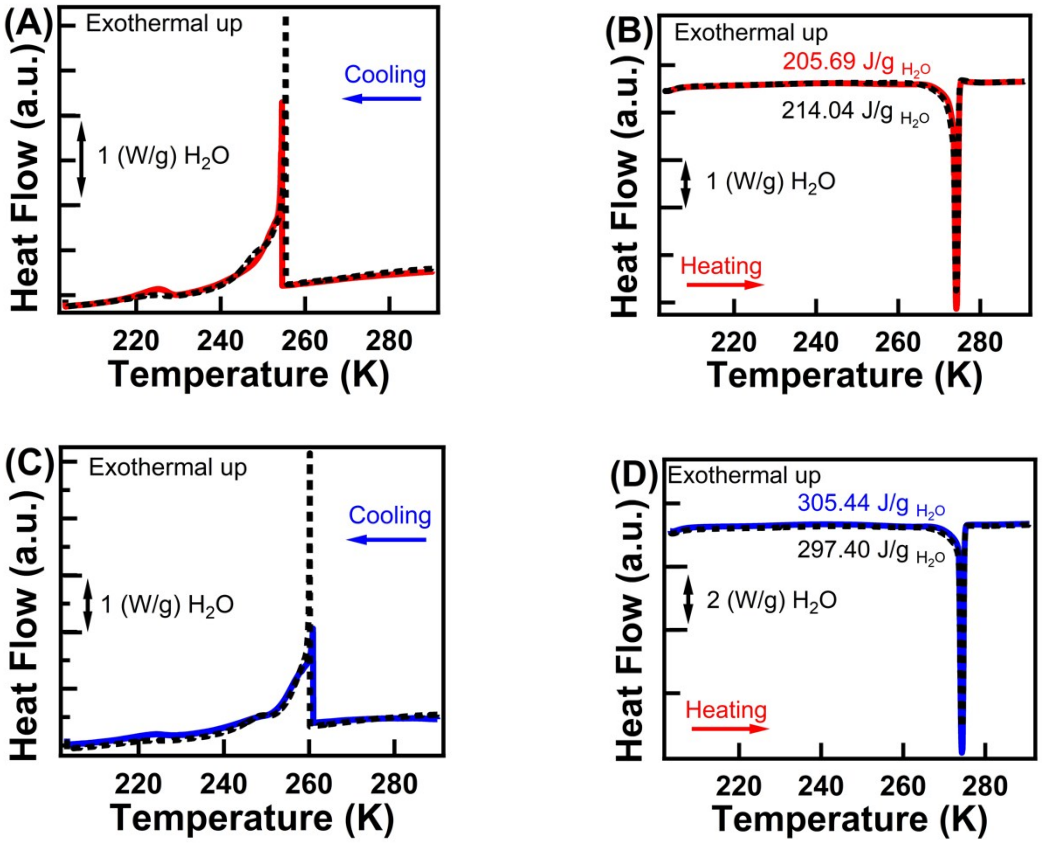

Figure S5. DSC thermograms at 2K/min for HEA-ODA hydrogels zone annealed at (A,B) 68.0 $\mu m/s$ and (C,D) 121.8 $\mu m/s$ on (A,C) cooling and (B,D) heating. Thermograms for 1st cycle (solid line) and 2nd cycle (black dashed line) are shown. For these hydrogels, the unfrozen water fraction is 0.36 at 68.0$\mu m/s$ and 0.16 at 121.8 $\mu m/s$.

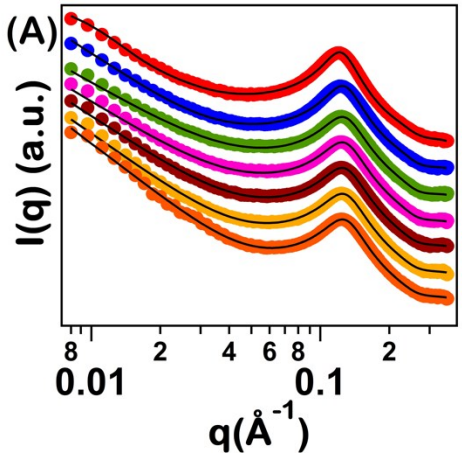

Figure S6. Azimuthally averaged 1D SAXS profiles for the HEA-ODA hydrogels that was zone annealed at 46.5 μm/s at (red) 290 K, (blue) 270 K, (green) 241 K, (pink) 211 K, (brown) 185 K, (yellow) 152 K, and (orange) 131 K. The solid black line is the best fit of the scattering data.

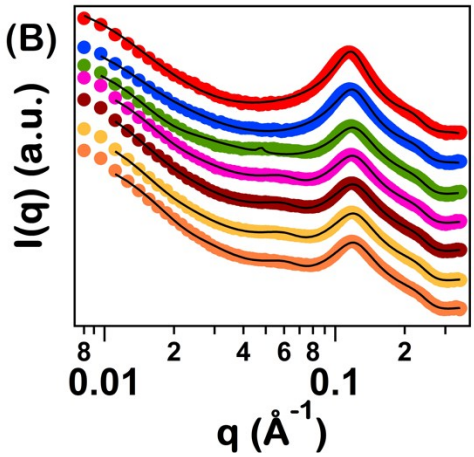

Figure S7. Azimuthally averaged 1D SAXS profiles for the HEA-ODA hydrogels that was zone annealed at 94.9 μm/s at (red) 289 K, (blue) 268 K, (green) 239 K, (pink) 209 K, (brown) 179 K, (yellow) 150 K, and (orange) 129 K. The solid black line is the best fit of the scattering data.

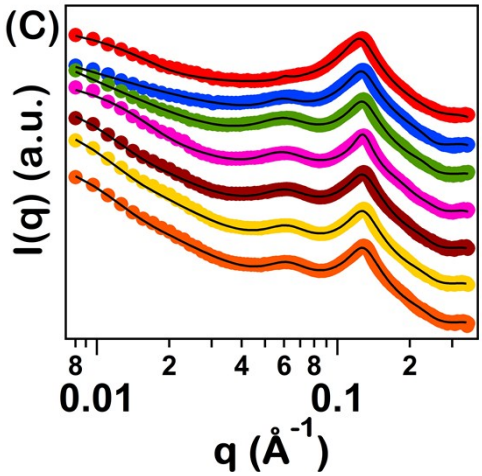

Figure S8. Azimuthally averaged 1D SAXS profiles for the HEA-ODA hydrogels that was zone annealed at 162.1 μm/s at (red) 288 K, (blue) 265 K, (green) 236 K, (pink) 206 K, (brown) 177 K, (yellow) 129 K, (orange) 128 K. The solid black line is the best fit of the scattering data.

Figure S9. Photograph of HEA-ODA hydrogel that is contained within Kapton pouch after removal from Linkam TST350 strain stage following a cooling and heating experiment. The red circles indicate the location of water droplets on the outside surface of the Kapton pouch. This water is a result of condensation from the atmosphere when the sample was at low temperature.

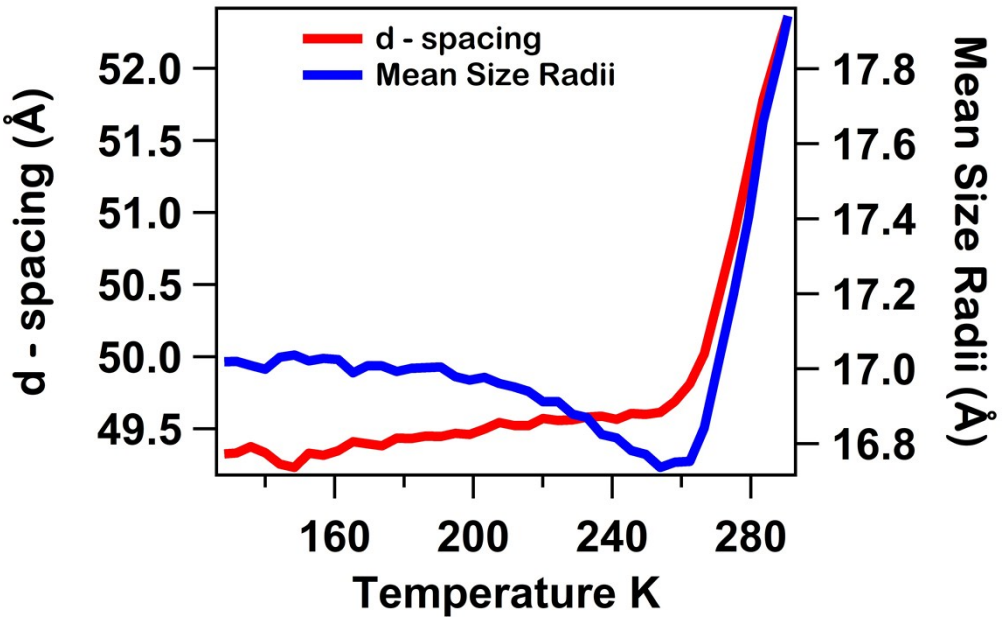

Figure S10. Temperature dependence of the interdomain spacing (blue) and mean size of the ODA nanodomains (red) for HEA-ODA hydrogel that was zone annealed at 46.5 $\mu m/s$.

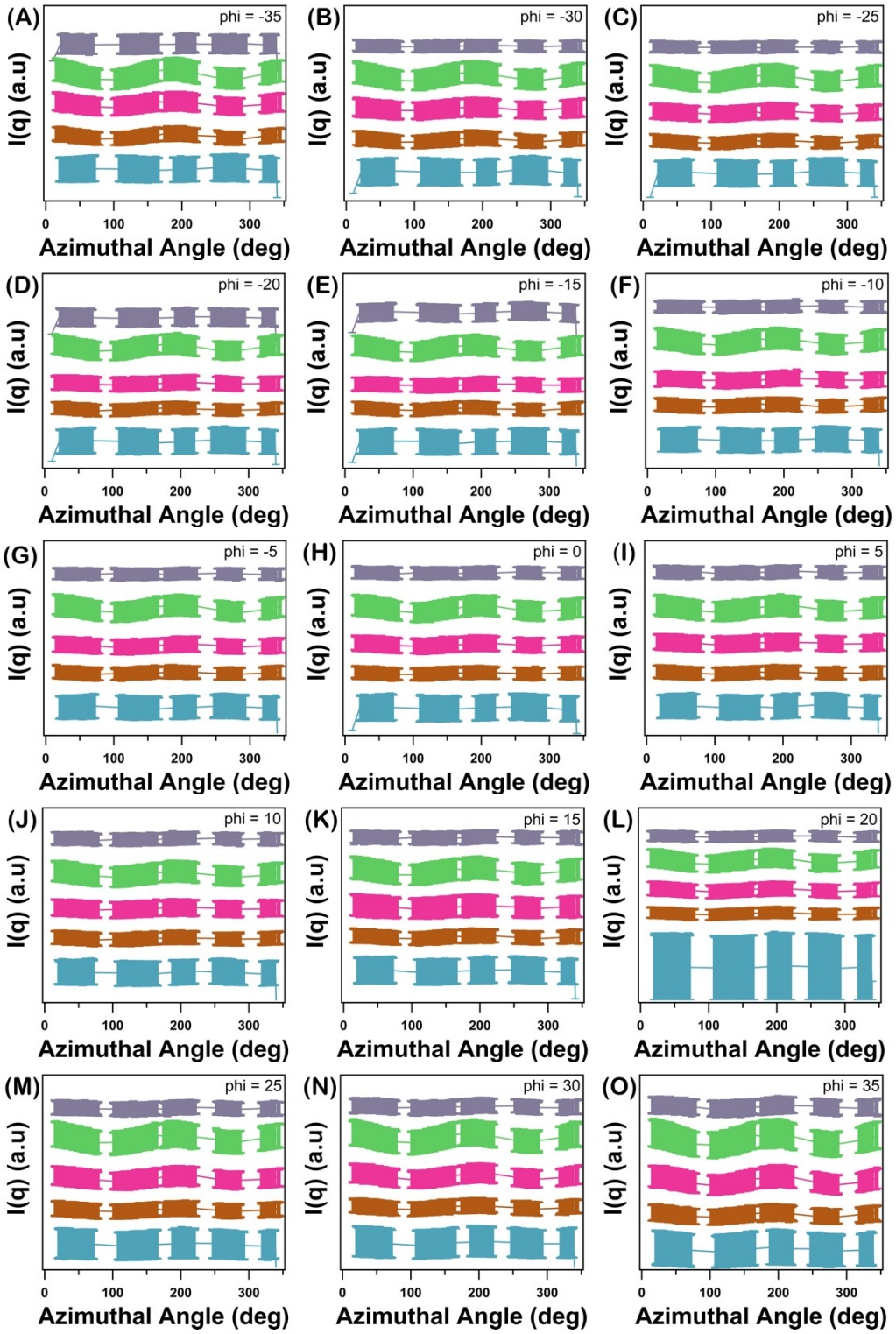

Figure S11. Azimuthal dependence of the scattered intensity at the peak location ($0.0589 < q < 0.1332$) 298 K for the hydrogels that were zone annealed at 46.5$\mu m/s$ (grey), 68.0$\mu m/s$ (green), pink 94.9 $\mu m/s$ (pink), 121.8 $\mu m/s$ (brown), and 162.1 $\mu m/s$ (blue). These transmission measurements where performed at different incident angles to face of the hydrogel. Φ indicates the incident angle of the beam relative to the normal of the hydrogel surface (Φ = 0^0 indicates perpendicular beam). The azimuthal angle is relative to the zone annealing direction where 90^0 is the zone annealing direction.

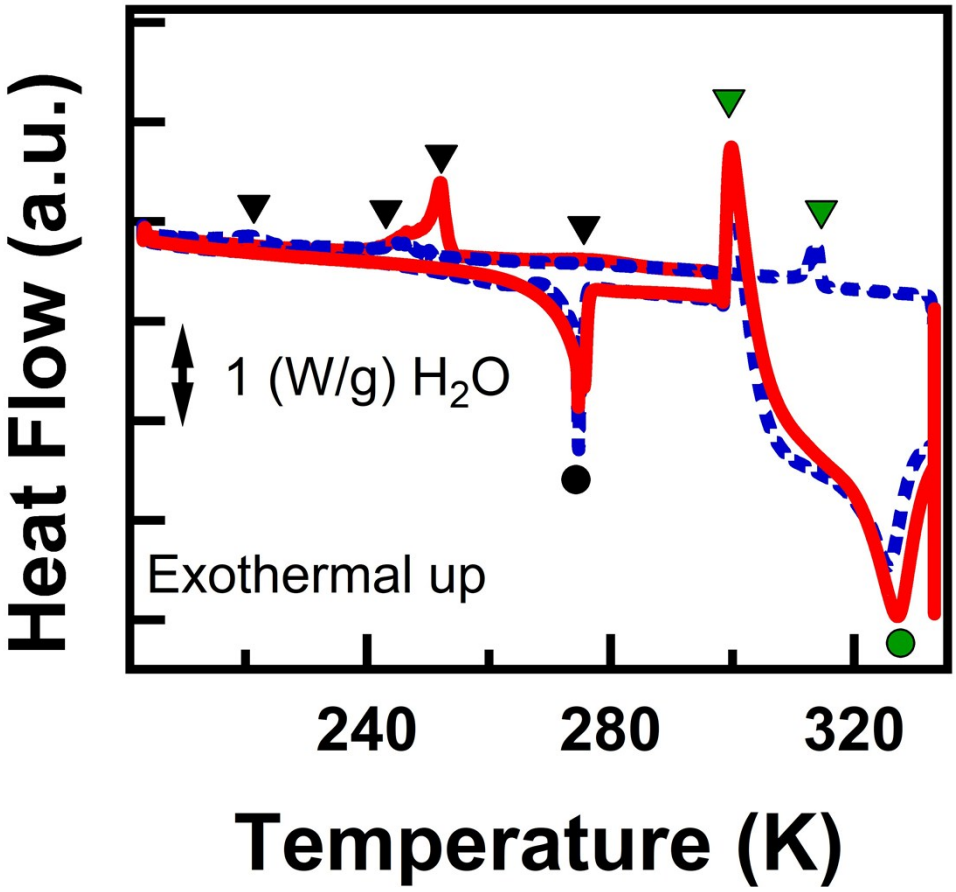

Figure S12. DSC thermograms at 2K/min for HEA-ODA that was melt processed at 383 K, where (red) the hydrogel was first cooled to 203.15 K and after remaining isothermal for 10min, the sample was heated up to 333.15 K. For the second cycle (blue), the hydrogel was cooled down from 333.15 to 203.15 K. After 10min of isothermal condition at 203.15 K, the sample was heated up to 333.15 K. Here the exotherms associated with the crystallization of water are denoted by (□) and ODA crystallization events (□). The melting event from water is denoted by (•) and the one from ODA domains is denoted by (•)