Supporting Information

Lee et al. 10.1073/pnas.1408678111

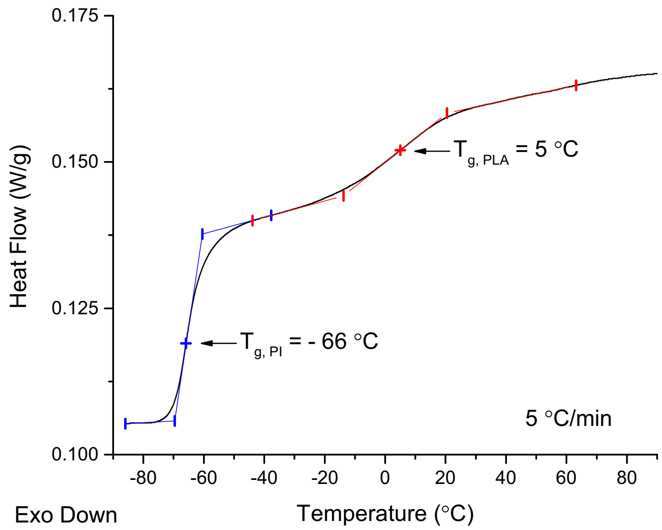

Fig. S1. DSC thermogram obtained from IL-15 heated at a rate of 5 °C/min. The glass transition temperatures of the polyisoprene-rich corona region, $T_{g,PI} = -66$ °C and the poly(lactide)-rich particle cores, $T_{g,PLA} = 5$ °C, are identified. The broad glass transition of the particle cores is consistent with a relatively broad interfacial composition profile (Fig. 6*D*).

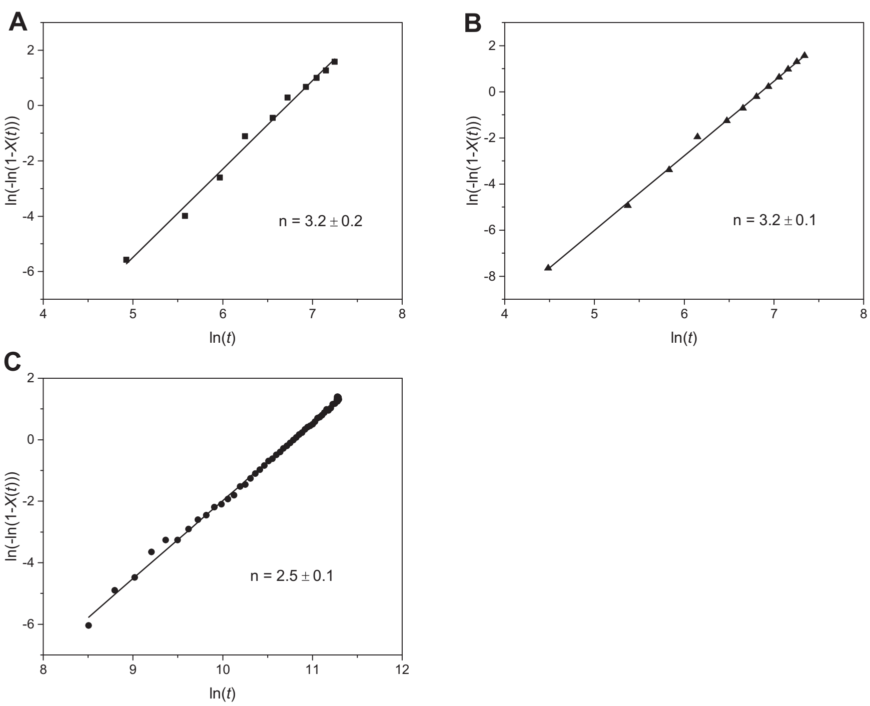

Fig. S2. Avrami plots derived from the development of the elastic modulus G' obtained following a rapid change in temperature of IL-15 from the disordered state ($T > T_{ODT}$) to (Fig. 3*A*) (*A*) 40 °C, (*B*) 25 °C (short times), and (*C*) 25 °C (long times). BCC order develops at 40 and 25 °C in about 30 min and the growth of the Frank–Kasper σ-phase requires approximately one day. The Avrami exponent n is identified in each case.

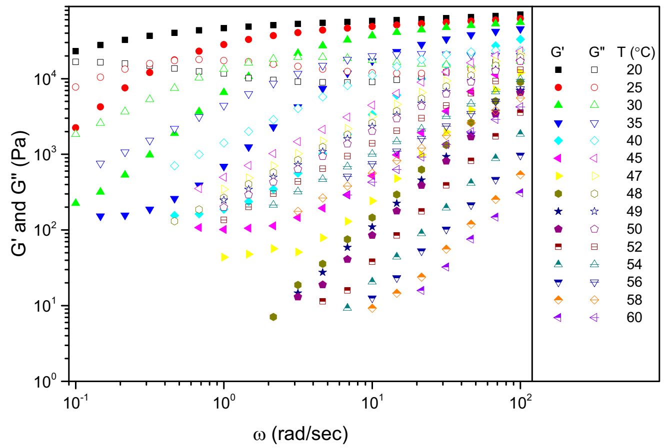

Fig. S3. Linear dynamic elastic (G') and loss (G'') moduli obtained as a function of frequency from IL-15 following rapid jumps in temperature from 60 °C to $T \leq T_{ODT} = 48 \pm 1$ °C, and under equilibrium conditions ($T > 48$ °C). These results have been time–temperature superposed as shown in Fig. 4.

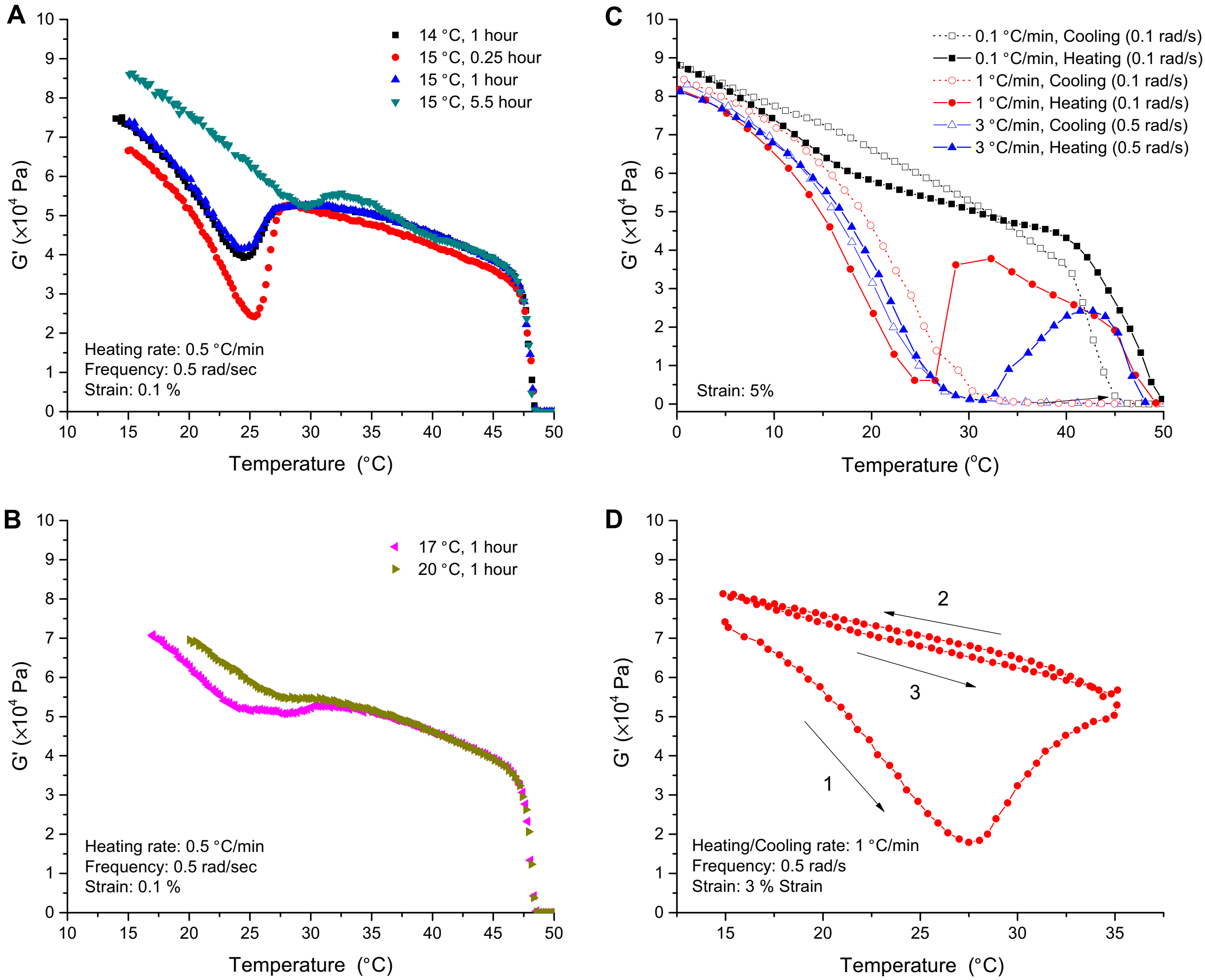

Fig. S4. Representative results obtained while monitoring dynamic elastic modulus G' at the indicated frequencies during experiments with IL-15 while cooling and heating at various rates. (*A, B*) Specimens in a disordered state at 60 °C ($>T_{ODT}$) were quenched to the specified temperatures from 60 °C (T_{ODT} = 48 °C) then annealed as noted, followed by acquisition of G' while heating at the indicated rates. (*C*) The specimen was heated and cooled at the same rate while monitoring G' at the indicated frequencies. These results demonstrate that the disordered state becomes trapped in a glassy state when cooled quickly enough to avoid nucleation and growth of an ordered phase. We estimate the particle glass transition temperature $T_{g,p} = 15 \pm 1$ °C. In each example the glassy solid orders upon heating above $T_{g,p}$ as indicated by a discontinuous increase in G'. The temperature at which this occurs is roughly anticipated by the accumulated time required to nucleate the growth of order based on the isothermal ordering kinetics (Fig. 2 and ref. 1). (*D*) Cooling the specimen (2, cooling curve in the *D*) after heating the glassy soft solid (1, heating curve showing a valley-like response in the *D*) induces ordering, which is not reversed upon cooling (3, heating curve in the *D*). The specimen in *D* was initially prepared by cooling from $T > T_{ODT}$ at a rate of 1 °C/min to 0 °C then heating to 15 °C at the same rate.

1. Lee S, Bluemle MJ, Bates FS (2010) Discovery of a Frank-Kasper σ phase in sphere-forming block copolymer melts. *Science* 330(6002):349–353.

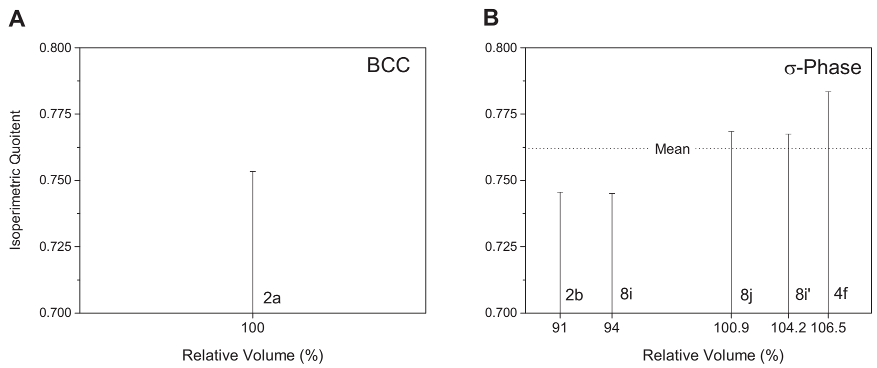

Fig. S5. Isoperimetric quotient ($IQ = 36\pi V^2/S^3$, where V and S are the polyhedral volume and surface area, respectively) (2) of the Wigner–Seitz cells for (*A*) BCC, $(IQ)_{BCC} = 0.7534$, and (*B*) Frank–Kasper σ-phase, $(IQ)_\sigma = 0.7624$. S and V of the Wigner–Seitz polyhedra of the σ-phase were evaluated numerically based on the lattice parameters obtained from the Rietveld analysis of the SAXS pattern reported earlier (1). Each Wigner–Seitz cell was dissected into pyramids of polyhedra facets and the surface areas of each facet and the pyramid volumes were evaluated numerically. $(IQ)_\sigma = 0.7624$ represents the average over the five Wigner–Seitz cells weighted by the indicated occupancy.

1. Lee S, Bluemle MJ, Bates FS (2010) Discovery of a Frank-Kasper σ phase in sphere-forming block copolymer melts. *Science* 330(6002):349–353.
2. G. Pólya, (1954) *Induction and Analogy in Mathematics* (Princeton Univ Press Princeton, NJ).

Table S1. IQ of the Wigner–Seitz cells

	Multiplicity, Wyckoff letter	Isoperimetric quotient
BCC	2a	0.7534
σ-phase	2b	0.7456
	8i	0.7451
	8j	0.7684
	8i′	0.7675
	4f	0.7834
	Mean	0.7624