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## **Structurization & Rheology of Diblock Copolymer/Hydrocarbon Solutions**

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Beamline(s): X27C, X3A2

**Introduction:** Although great progress has been made in the study of phase behavior of block copolymers and their solutions, the rheology of these materials still remains much less understood, especially for the systems forming cubic-packed spherical micro-phases [1, 2, 3]. Here, we studied an abnormal temperature behavior of a diblock copolymer/hydrocarbon system using rheometry and small angle X-ray scattering (SAXS). We discovered that the anomalous rheological behavior was caused by the reformation of colloid crystal structures in the solutions from their original kinematically arrested non-equilibrium random states.

**Methods and Materials:** Squalane solutions (0.5 to 10 wt.%) of a diblock copolymer, hydrogenated polystyrene-block-polyisoprene (SEP, Kraton G1702), were prepared by a cosolvent-casting method at room temperature. Solution rheological properties were studied in dynamic shear mode in the linear viscoelastic regime at different temperatures. The corresponding structure change with temperature in solutions was investigated by SAXS using the synchrotron X-ray beamline X-27C in NSLS, Brookhaven Nation Laboratory.

**Results:** Micellar solutions with blue tinge were formed at low concentrations ( $C < 3$  wt.%). The blue tinge disappeared when the solutions were heated to about 150 °C, signifying the dissolution of micelles in accord with the studies of Watanabe and Hashimoto [4,5], among others. Although no additional phase transformations were observed up to 200 °C, anomalous temperature-rheological behavior in the 5 and 10 wt.% solutions was found. Dynamic temperature/frequency sweeps (Fig. 1) showed that the solutions behaved like solids at very low temperatures ( $T < -30$  °C). Upon increasing the temperature, the solutions melted into viscous liquids with terminal flow behavior at low frequency. Then, at about 40 °C and 70 °C for the 5 % and 10 wt.% solutions, respectively, the storage modulus began to increase abruptly and rose almost one decade within a temperature range of 20 °C and exceeded the loss modulus. At yet higher temperatures, dynamic frequency sweeps demonstrated that the solutions had gelled or solidified. The gel structure didn't melt in both solutions even at temperatures as high as 200 °C. A large hysteresis was observed; the solutions didn't recover to their liquid-like rheological behavior in the cooling process, but did recover their original properties at low temperatures. The kinetics of gelation (Fig. 2) from 30 °C to 150 °C in the 10 wt.% solution appeared to follow the Arrhenius relationship with an activation energy of  $37 \pm 2.7$  kJ/mole. SAXS revealed that this abnormal solidification with increasing temperature was actually caused by the formation of body-centered cubic structures in the solutions (Fig. 3 and Fig.4). SAXS measurements at constant temperature also manifested the kinetics of the formation of this cubic phase from a disordered phase (Fig. 5 and Fig. 6).

### **References:**

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5. Takeji Hashimoto, Mitsuhiro Shibayama and Hiromichi Kawai, *Macromolecules*, 1983, **16**(1), 16-28.

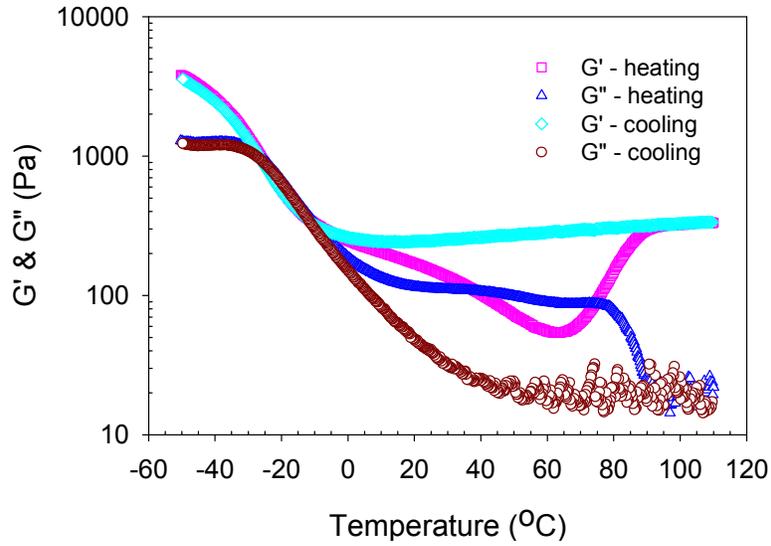


Fig. 1 Dynamic temperature ramp on 10 wt.% SEP/squalane between  $-50\text{ }^{\circ}\text{C}$  and  $110\text{ }^{\circ}\text{C}$ , heating up and then cooling down at  $1\text{ }^{\circ}\text{C}/\text{min}$ ,  $\omega = 1\text{ rad/s}$ ,  $\gamma = 0.01$ .

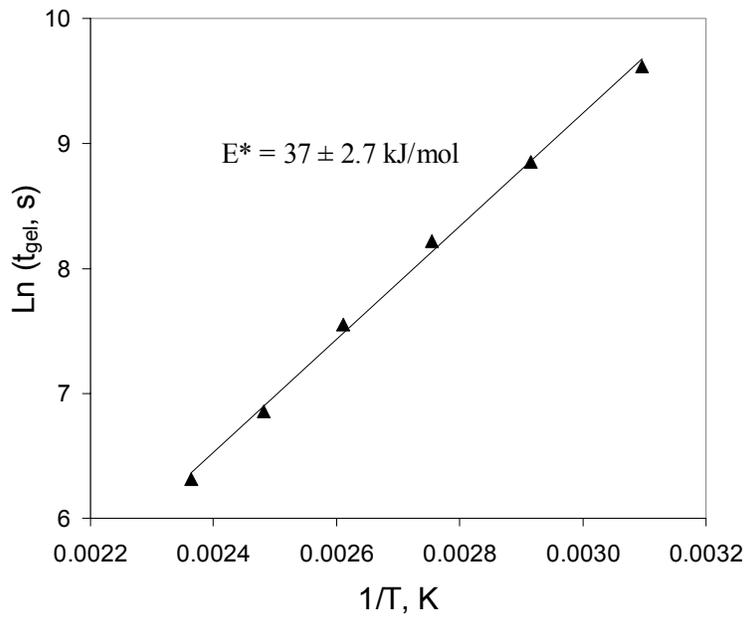
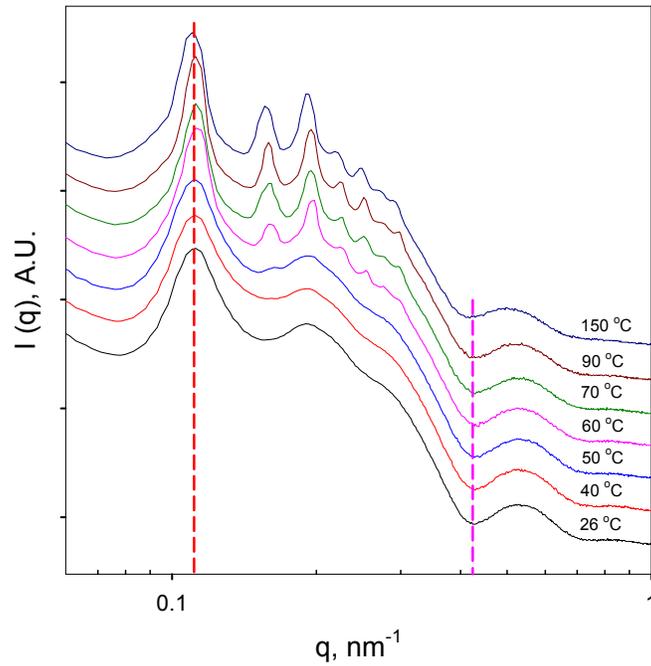
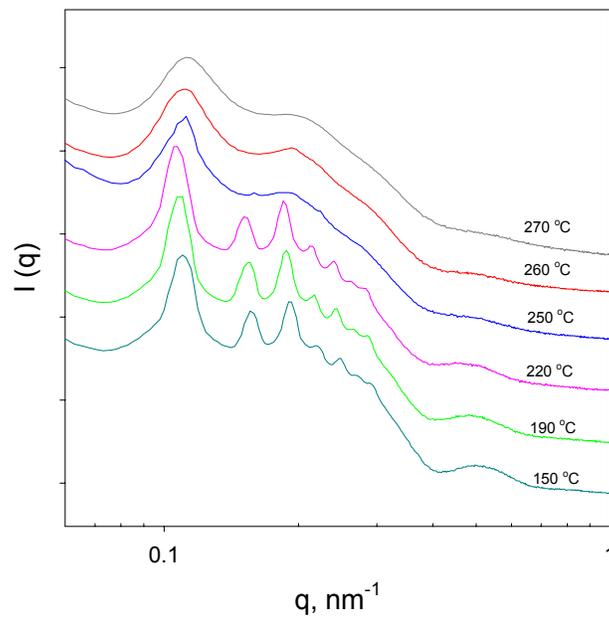


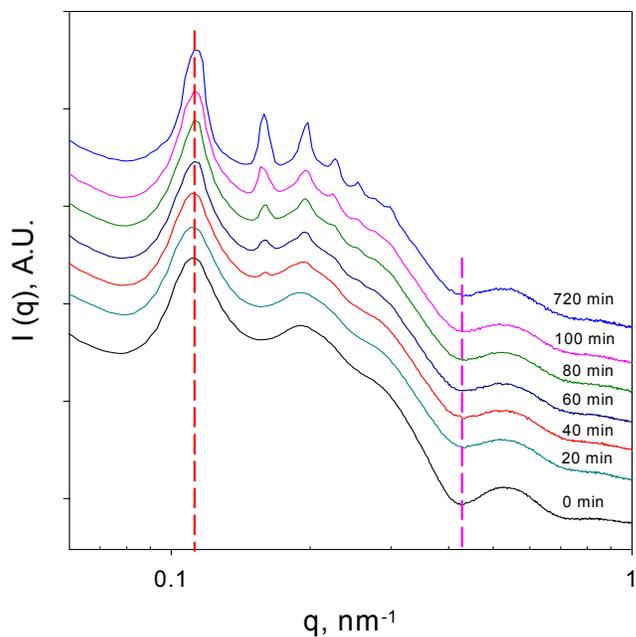
Fig. 2 Arrhenius plot of gelation time ( $t_{\text{gel}}$ ) in the 10 wt.% SEP/SQ solution. The gelation time was taken as the time required for both  $G'$  and  $G''$  to reach equilibrium, and was measured by a dynamic time sweep at constant temperatures with  $\omega = 1\text{ rad/s}$ ,  $\gamma = 0.01$ .



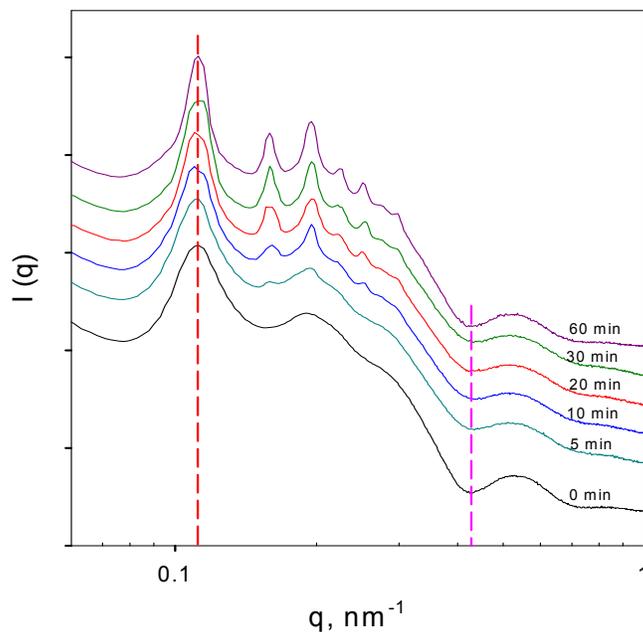
**Fig. 3** Azimuthally averaged scattering intensities of 10% SEP/squalane at different temperatures, indicating the change from disordered arrangement of spherical micelles in the as-cast solution to highly ordered body-centered-cubic packing of spherical micelles in the solution at elevated temperatures, where the SAXS peaks appear at:  $(q_1:q_2:q_3:q_4:q_5:q_6:q_7)^2 = 1:2:3:4:5:6:7$ .



**Fig. 4** Azimuthally averaged scattering intensities of 10% SEP/squalane at high temperatures, signifying the melting of highly ordered body-centered-cubic packing of spherical micelles to disordered arrangement of spherical micelles in the solution, which occurs around 260 °C.



**Fig. 5** Azimuthally averaged scattering intensities of 10% SEP/squalane at 50 °C, indicating the slow change (more than 100 min) from disordered arrangement of spherical micelles in the as-cast solution to highly ordered body-centered-cubic packing of spherical micelles in the solution, where the SAXS peaks appear at:  $(q_1:q_2:q_3:q_4:q_5:q_6:q_7)^2 = 1:2:3:4:5:6:7$ .



**Fig. 6** Azimuthally averaged scattering intensities of 10% SEP/squalane at 80 °C, showing a faster transformation (about 30 min) from disordered arrangement of spherical micelles in the as-cast solution to highly ordered body-centered-cubic packing of spherical micelles in the solution, where the SAXS peaks appear at:  $(q_1:q_2:q_3:q_4:q_5:q_6:q_7)^2 = 1:2:3:4:5:6:7$ .