Styrene-Hydroxystyrene Gradient and Block Copolymers: Comparisons of Behavior as Compatibilizers of Immiscible, Crystallizable Polymer Blends and in the Neat and Solution States. JUNGKI KIM, JOHN M. TORKELSON, Northwestern University, Evanston, IL 60208 — Styrene-hydroxystyrene (S-SOH) gradient and block copolymers are made by semi-batch nitroxide-mediated controlled radical polymerization of styrene and acetoxystyrene followed by hydrolysis of the acetoxystyrene repeat units to SOH. These copolymers are investigated as compatibilizers for polystyrene (PS)/polycaprolactone (PCL) blends made by melt mixing; the hydroxyl groups on the SOH units undergo attractive hydrogen-bonding interactions with the ester groups on PCL. Gradient copolymers of a wide composition range are effective compatibilizers of PS/PCL blends, with the dispersed phase (PCL) domain size being a function of gradient copolymer composition. Block copolymers are also effective compatibilizers, resulting in very small dispersed-phase domain sizes (~200 nm average diameter). In addition, block copolymer addition has major effects on the crystallizability of the PCL domains; in contrast, only small effects on PCL crystallizability are observed upon addition of gradient copolymer to the blend. The different effects of block and graft copolymers are likely due to greater hydrogen bonding of the PCL with the block copolymer, which impedes crystallization. The properties of the block and gradient copolymers in the neat state and their micellization in solvent and in homopolymer will also be discussed.