Micellar Structures in Molten Polyethylene-Graft-Poly(Ethylene Oxide) Copolymers, and Crystalline Structures in the Solid Phase

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Abstract

Structure and crystallization behavior of polyethylene-*graft*-poly(ethylene oxide) graft copolymers were investigated by variable temperature x-ray scattering measurements and thermal analyses. Three copolymers with PEO graft lengths of 25, 50 and 100 ethylene oxide units were studied. Small-angle x-ray scattering data show that the polymer passes through three distinct structures at ~10 nm length scales with increase in temperature (T): PE lamellae constrained by PEO crystallites at $T < T_m^{PEO}$, PE lamellae unconstrained by PEO crystallites at $T_m^{PEO} < T < T_m^{PE}$, and micelles at $T > T_m^{PE}$ when both PE and PEO are molten (T_m refers to the melting temperature). Diffraction peaks in the wide-angle x-ray scans at room temperature could be assigned to crystalline phases of PEO side-chains and PE main-chains, and this indicates that the backbone and grafts crystallize into separate domains, especially in the cases of the longer grafted chains (50 and 100 repeats). The crystal structure of PE and PEO domains are similar to those of the corresponding homopolymers. However, small differences are seen in the melting behavior of each of the domains, and large differences in the crystallization kinetics. In the copolymer with shorter grafted chains (25 repeats), the melting of PEO crystals in the copolymer is broad and not distinct, whereas at longer graft lengths it approaches the behavior of PEO crystals in a homopolymer The degree of supercooling for crystallization to occur is larger for both the PE backbone and PEO grafts in the graft copolymer than found in the corresponding homopolymers. The PEO domains can be dissolved in water or ethanol without altering the mechanical integrity of the film. The significance of these findings is discussed.