

Effect of Macromolecular Architecture on the Thermal Properties of Poly(methyl methacrylate) / Poly(ethylene oxide) Blends

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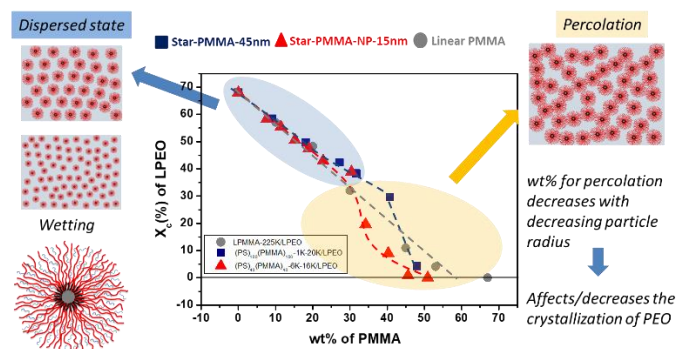
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The properties of polymer materials can be significantly altered by the addition of nanoparticles and depends strongly on the particle dispersion state. The latter, can be controlled and tuned by regulating the interactions between the particles and the polymer host. The crystallization behavior of semi-crystalline polymers continues to attract considerable attention as affects significantly the final properties. Here, we show that one may control the crystallization behavior of poly(ethylene oxide), PEO, by the addition of nanostructured polymer particles that are composed of high functionality miktoarm star copolymers, in which n polystyrene (PS) arms complement n poly(methyl methacrylate) (PMMA) arms, $(PS)_n(PMMA)_n$. For $(PS)_n(PMMA)_n$ particles with PMMA arms longer than the PS arms, the degree of crystallization of an oligomeric PEO ($M_w = 0.5$ kg/mol), X_c , shows a sigmoidal-like dependence with particle wt%. For low particle loadings, X_c decrease linear with particle wt%, in a very similar manner to the corresponding PEO / linear PMMA blends. With increasing nanoparticle loadings, a sudden drop in X_c occurs at a critical wt% that is associated with the formation of a percolation network by the $(PS)_n(PMMA)_n$ nanoparticles. At this stage, the formation of a chaotic percolating network, composed of hard walls suppress further the crystallization of PEO. By changing the molecular weights of the PS and PMMA arms, we were able to tune the dispersion state of the particles and the critical wt% for particle percolation and tune, in vary systematic manner, the crystallization behavior of PEO. Key to our approach is the fact the final morphology of the all-polymer nanostructured material is the result of two competing interactions that may be precicely controlled via the macromolecular characteristics of the $(PS)_n(PMMA)_n$ paprticles : (i) inter-molecular attractions between the PS, which promote aggregation, as they are immiscible with the oligomeric PEO, and (ii) the favorable enthalpic interactions of the PMMA arm with the oligomeric PEO host that promote particle dispersion.



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