

Phase Behavior of Mixtures of Polymer Functionalized Nanoparticles And a Polymer Matrix

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Abstract

In this study, the thermodynamic interactions of polystyrene (PS) grafted onto spherical silica particles (15 nm in diameter) with poly(vinyl methyl ether) (PVME) are investigated. The characteristics of the PS hybrid nanoparticles as well as its blending behavior with the PVME matrix are analyzed using light and x-ray scattering techniques.

1. Introduction

Organic-inorganic hybrid materials are known to exhibit polymeric features that are significantly enhanced by the inclusion of small and hard inorganic particles in the melt matrix. The favorable interactions between these two entities contribute to improved thermal, mechanical and electronic properties that are otherwise compromised in the pure materials. Previous efforts in dispersing nanoparticles, whether in solution or with another polymer, have shown that such phenomenon is largely driven by entropic and enthalpic contributions to the total free energy. Favorable particle-polymer interactions in which the Flory interaction parameter of the melt matrix with the grafted polymer brush is negative ($\chi < 0$) lead to dispersion; while strong van der Waals attractions between the particles result in aggregation.

2. Objective

The objective of this study is to understand the interplay among the tunable characteristics of the nanoparticles on the phase behavior and concentration fluctuations for strongly interacting polymer blends of PS-silica hybrids and PVME using Dynamic Light Scattering (DLS) and Small Angle X-ray Scattering (SAXS).

3. Analyses

PS-silica hybrid nanoparticles with a tethered brush molecular weight of 16,000 g/mol were synthesized and characterized using thermogravimetric analysis (TGA), gel permeation chromatography (GPC) and DLS. These nanoparticles were solution mixed with PVME having a molecular weight of 18,000 g/mol to yield a polymer blend of the desired PS:PVME weight composition. The inter-particle distance d derived from the scattering vector q for the pure hybrid and PS-PVME blends was obtained using SAXS.

4. Discussion

The design and synthesis of these PS hybrid nanoparticles involve the atom transfer radical polymerization (ATRP) technique which allows control over the grafting density, composition and molecular weight of the tethered polymer. Results from TGA and GPC reveal a polymer grafting density and grafting efficiency of 0.5 chain/nm² and 45%, respectively. In addition, a monodisperse PS brush with a weight average molecular weight of 16,000 g/mol and polydispersity index of 1.16 was obtained.

The size of the hybrid nanoparticles dispersed in toluene was found to be 48.48 (± 0.10) nm, as indicated by DLS results. The change in the inter-particle distance for the PS16k/PVME18k blend with increasing temperature was monitored using SAXS. It was found that at a critical composition of 20/80 (PS16k/PVME18k), q shifts to higher values, indicating a change to smaller inter-particle distance as the lower critical solution temperature (LCST) phase transition is reached. Such behavior signifies swelling of tethered PS brush by PVME which facilitates the dispersion of the PS-silica hybrid within the PVME matrix.

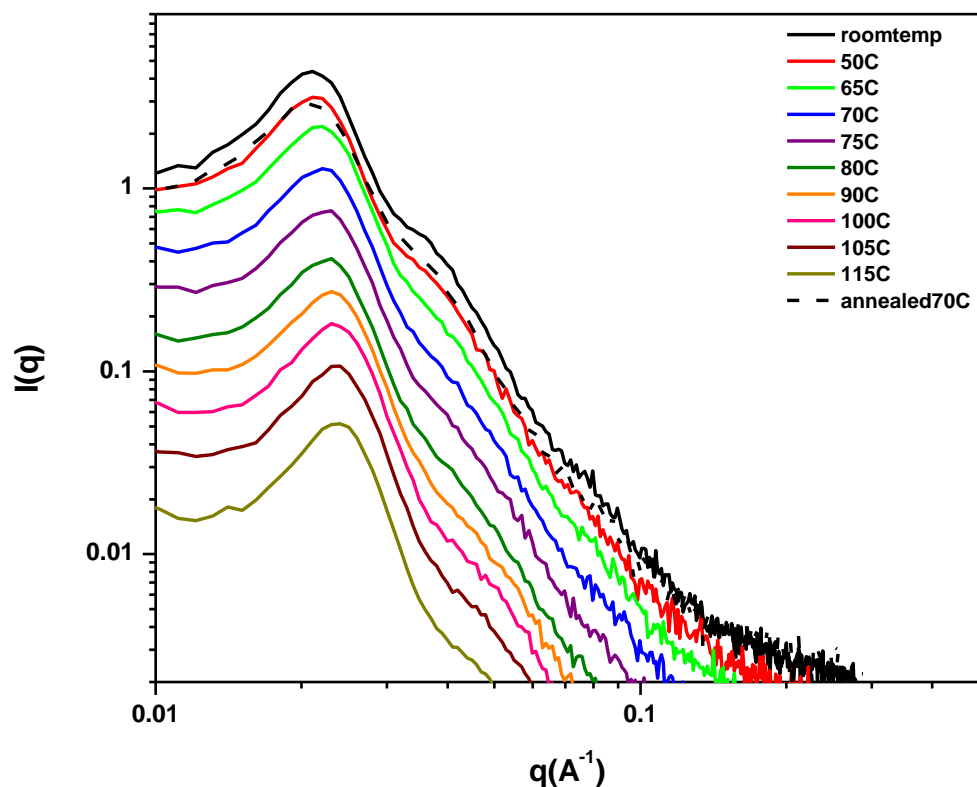


Figure 1. SAXS data for a 20/80 PS16k-PVME18k blend at different temperatures.

5. Conclusions

PS-hybrid nanoparticles can be prepared by ATRP to produce materials with controlled molecular weight, composition and grafting density. The LCST phase transition for a 20/80 PS16k/PVME18k blend composition is observed at higher temperatures.

6. Acknowledgement

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7. References

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