



The effects of branching and deuterium labeling on blend miscibility



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ABSTRACT

The individual and combined effects of 4-arm star branching and deuterium labeling on polystyrene (PS) influence its compatibility in upper critical solution temperature (UCST) and lower critical solution temperature (LCST) mixtures. In this article, we use our Locally Correlated Lattice (LCL) model to characterize a set of PS samples in their pure states in order to predict miscibility trends for blends of PS with poly(vinyl methyl ether) (PVME) (LCST-type mixtures) and isotopic variants of PS (UCST-type mixtures). We find that 4-arm star branching and/or deuterium labeling can shift the pure component properties of PS, such as its percent free volume or cohesive energy density, which affects how the properties of PS ‘match’ those of the other mixture component. In another section of this article, we turn to modeling the blends, themselves, and provide fundamental thermodynamic insight about the PS/PVME mixtures by calculating the relative enthalpic and entropic contributions to the free energies of mixing. We observe trends in the values of the entropies and enthalpies of mixing for the PS/PVME blends that qualitatively match our pure component properties analysis of the pure PS samples.

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1. Introduction

Making a structural [1–24] or chemical [25–36] change to one component of a polymer mixture may cause a notable shift in its compatibility with the other component. In this work, we probe how a structural change (backbone branching) and a chemical change (deuterium labeling) influence the physical properties of polystyrene (PS) in its pure state and its compatibility in mixtures. We analyze experimental data for a set of PS samples for which branching and deuterium labeling were systematically varied. To our knowledge, this report contains the first theoretical study of the combined effects of deuterium labeling and 4-arm star branching on the pure component properties of PS, where these properties were calculated directly from experimental data for the pure state. We find that changes in the physical properties of PS caused by branching and/or deuterium labeling can lead to varying degrees of compatibility upon mixing with another component. The mixtures that we analyze in this work include both upper critical solution temperature (UCST)-type and lower critical solution temperature (LCST)-type blends involving PS, namely, isotopic mixtures of PS

and PS/poly(vinyl methyl ether) (PVME) blends, respectively. We find that the relative compatibility of the LCST-type and UCST-type mixtures track with different characteristic pure component properties of the PS samples. We believe that our theoretical study is the first of its kind to consider the combined effects of deuterium labeling and branching in LCST-type blends.

Our approach utilizes information about the pure states to make predictions about their relative compatibilities in a mixture. Using our Locally Correlated Lattice (LCL) theory equation of state (EOS), we have modeled the pressure-volume-temperature (PVT) behavior of linear and 4-arm star unlabeled PS (hPS), deuterium labeled linear and 4-arm star PS (dPS), and PVME. The result of this modeling is a set of characteristic parameters that describe each of the pure components, and from which a number of important physical properties can be calculated, e.g. thermal expansion coefficients, % free volumes, and cohesive energy densities (CEDs). Comparing the relative values of these properties leads us to draw conclusions about the relative compatibilities of linear hPS, star hPS, linear dPS, and star dPS, blended with PVME. Following the same approach, we also predict the compatibilities of isotopic PS pairs, e.g. linear hPS paired with linear dPS. Then we model the PS/PVME blends themselves, using the characteristic molecular parameters we obtained from modeling the pure component experimental data and a single data point for the mixture, the LCST. We explain the shifts in the PS/PVME LCST as a result of branching and

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or deuterium labeling on the basis of thermodynamic quantities, in particular, the enthalpic and entropic contributions to the free energies of mixing. We also test the application of a simple averaging approach to predict the LCST of the 4-arm star dPS/PVME blend, which utilizes only information about the other PS/PVME blends.

First, consider only the possible implications of branching on mixed behavior. In cases where the non-bonded mixed interactions between two components are energetically favorable, then increasing the degree to which one component is branched may screen these favorable interactions and thus *reduce* mixture compatibility [5,24,27]. Conversely, if the mixed interactions between components are energetically unfavorable, then increasing the degree to which one component is branched may reduce the number of unfavorable contacts, thus *enhancing* mixture compatibility [3,7,14,22,23]. In addition to the energetic implications of branching on mixing, the effect of branching on the entropy of mixing also plays a role in influencing mixture compatibility. Due to its structure, a branched molecule is more sterically constrained than a chemically identical linear molecule; i.e., a branched molecule has fewer available molecular configurations from which it can sample. For this reason, mixing branched molecules with a linear component may lead to an enrichment of the concentration of branched molecules in the region near the free surface, which reduces their entropic penalty of mixing [37–41]. This physical picture is consistent with experimental surface tension measurements which have indicated that a mixture of branched and linear molecules has a lower surface tension than that of the pure linear melt [38,39,42]. These results highlight the important role of the entropic contribution to the free energy of mixing for branched and linear molecule mixtures. It has been suggested that the effects of branching on the mixture compatibility may be traceable to changes in the properties of the pure state, such as molecular packing efficiency and/or relative free volumes [14,19,43]. Using our Locally Correlated Lattice (LCL) theory equation of state (EOS), we are in a position to test this hypothesis by characterizing and then comparing the pure component physical properties of linear and branched molecules.

Here we examine one type of branched architecture, 4-arm star molecules, and how changing from a linear to a star shaped molecule affects physical properties and mixture compatibility. Star molecules are of particular interest because they can yield unique and sometimes more useful macroscopic properties than a material comprised of chemically identical linear molecules. Some examples include: the addition of star molecules into a polymer blend [1,14] or nanocomposite [21], which can improve mixture compatibility and/or desirable mechanical properties. Also, star shaped molecules have been found to be particularly useful in biomedical applications, as highlighted in a recent review by Wu et al. [44].

There are two fundamental characteristics of star molecules that influence their physical properties: the *number* of star arms and the *molecular weight* (MW) of each arm. Here we provide a brief overview of how changes in the number of star arms and/or the MW of each arm may affect a number of macroscopic properties. First, consider star molecules which are comprised of low MW arms. In this case, there are a number of reports in the literature [45–55] that the behavior of a star molecule may notably differ from that of a chemically identical linear molecule whose MW roughly matches that of each star arm. For example, surface tension measurements reported by Qian and coworkers [39] showed that (MW = 7000 g/mol) 4-arm and 11-arm star polystyrene (PS) melts have lower surface tensions than that of a linear PS melt. For the 11-arm star PS melt, the surface tension was lower than that of linear PS by 15% [39]. In other recent work, McKenna and coworkers [42] reported that the surfaces of glassy 3-arm and 8-arm star PS

samples were more compliant than that of their linear analog.

Other differences between the properties of low MW star molecules and linear molecules that have been observed include: molecular packing [45,46] and the glass transition temperature (T_g) [45,46,49,56]. Molecular dynamics (MD) simulations performed by Chremos and coworkers [45] indicated that the number bead density increases by ~10% from a linear chain to a 12-arm star molecule, when the number of beads comprising an arm matched that of the linear chain, and was equal to 5. Turning to the glass transition, simulations [45,46] and experimental measurements [49] show that for low molecular weight species, the *bulk* T_g decreases as the number of arms increases; i.e. from a linear molecule to one with many arms. In nanometrically thin *films*, however, Glynos and coworkers [49] have recently reported that low molecular weight star molecule films may exhibit a range of thickness-dependent T_g behavior, which is determined by the number of star arms. For example, as the thickness of a 3-arm star PS (arm MW = 10,000 g/mol) film decreased below 100 nm, its T_g was *suppressed* from that of the bulk value [49]. The thickness-dependent T_g behavior observed for the 3-arm star PS film, is consistent with that reported for linear PS films [49]. In contrast, as the thickness of a 16-arm star PS (arm MW = 10,000 g/mol) film decreased below 100 nm, it exhibited T_g *enhancement* relative to the bulk value [49].

In contrast to the results for low MW star molecules described above, there is some evidence that suggests that the physical properties of star molecules converge with those of their linear analog as the MW of each arm increases. Chremos and coworkers [45] found that the number bead densities and bulk T_g values of 3 through 16 arm star molecules approach that of their linear counterpart as the length of the star arms reach ~40 beads. Experimental bulk T_g measurements reported by Glynos and coworkers [49] also show that increasing the MW of each arm brings the star T_g closer in value to that of the linear species. Further, the thickness-dependent T_g behavior of films also converges between star and linear molecules as the star arm MW increases [49].

In cases such as these, where the physical properties of high MW star and linear molecules are similar in the pure state, one might expect that their behavior in the mixed state would also be comparable. Experimental results for linear and star PS blends with poly(vinyl methyl ether) (PVME) support this conclusion. Pava-wongsak et al. [12] reported that the cloud point temperatures of linear PS (MW = 275,000 g/mol) blended with PVME (MW = 99,000 g/mol) was only 3 °C greater than that of a 3-arm star PS (MW = 255,000 g/mol) sample blended with the PVME. In other work, Sremcich et al. [15] performed cloud point measurements on higher functionality star PS samples, including 14, 18, and 22-arm star PS (MWs ranging from roughly 500,000–1,000,000 g/mol) blended with PVME (MW = 99,000 g/mol), as well as the analogous linear PS/PVME blends for comparison. From their measurements, Sremcich and coworkers [15] concluded that there was no observable difference between the miscibility of a high MW linear PS/PVME blend and a star PS/PVME blend. Taken together, the results of both studies suggest that branching has a negligible effect on the miscibility of PS/PVME blends when the MW of PS is approximately greater than 200,000 g/mol.

In addition to branching, a chemical change (e.g., isotopic labeling) may also influence mixture compatibility. This is particularly relevant for Small Angle Neutron Scattering (SANS) studies. SANS is an experimental technique that is able to characterize the compatibility of a mixture; it requires that one component be deuterium labeled. The zero angle scattering intensity collected as a function of temperature from SANS measurements is directly related to the second derivative of the free energy of mixing as a

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