Novel Dendrimer-Like Star Copolymer Architectures Investigated with Scattering Techniques^{*}

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INTRODUCTION

Hyperbranched dendrimer molecules emanating from a central core were successfully synthesized just over a decade ago¹ and have been gaining the interest of polymer scientists due to their unique properties² and promising applications.^{3,4} Several groups have sought structural and dynamic information on dendrimeric molecules with some degree of success.⁵⁻⁷ Most of the studies thus far have focused on dendrimeric structures having relatively short links between branching points and having a uniform distribution of branches throughout the molecule. We are interested in dendrimer-star molecules where polymer chains connect the branch points and the length and placement of these chains can be varied systematically. We have taken one approach to such systems by investigating a series of constitutional isomers (Figure 1) having the same molecular weight and number of branch points and surface functionalities, but varied branch placement to alter the architecture.⁸ In this way, we can study the influence of the architecture on the structure, interactions, and dynamics of these molecules.



Figure 1. The series of six isomeric $poly(\varepsilon$ -caprolactone) dendrimerlike star polymers are schematically drawn to show how the variation of branch placement and chain length alters the polymer architecture. Samples are named beginning with the lower left corner and moving counter clockwise as: A, B, C, E, D, and F.

Our previous work indicated that the architectural differences in this series of isomeric polymers does impact the intramolecular structure as evidenced by the variation in the R_g and R_h values for these polymers.⁹ This motivates us to further investigate the effects of

architecture by focusing on intermolecular interactions. We have begun studying intermolecular interactions through small angle x-ray and neutron scattering experiments at moderate polymer concentrations where the liquid-like structure factor provides an indication of the interactions.

EXPERIMENTAL

Polymer Samples. The series of isomeric polymers was prepared at IBM Almaden. These polymers are constructed from poly(ε -caprolactone) (PCL) using ring-opening polymerization with branching junctures derived from 2,2'-bis(hydroxylmethyl) propionic acid.^{8,9} The samples have low polydispersities (<1.19) and well-defined architectures as confirmed by ¹H and ¹³C NMR. A copolymer series was created from the series of six PCL

A copolymer series was created from the series of six PCL isomeric homopolymers. This was achieved by removal of the surface dendron and attachment of linear poly(methylmethacrylate) (PMMA) to the outer most generation of the PCL dendrimer-like star polymer using an atom transfer radical polymerization (ATRP) synthetic strategy (Figure 2).¹⁰ These PMMA chains can be partially deuterated to provide neutron scattering contrast. The PCL dendrimer-like stars then comprise the cores of the molecules while the PMMA chains emanate from the periphery.

The samples used in the scattering experiments were prepared in either THF or toluene, which are both good solvents for PCL and PMMA, to mass fractions of 0.2 wt% to 30 wt%.



Figure 2. The dendrimer-like star isomeric polymers serve as the cores for the copolymer series. Here, the attachment of PMMA chains to the periphery of the PCL polymer core is schematically shown where isomer B becomes the core of copolymer B.

Experimental Techniques. Small angle x-ray scattering (SAXS) was performed on beamline 1-4 at the Stanford Synchrotron Radiation Laboratory (SSRL). The data was collected using a wavelength of 0.149 nm with a q-range of 0.095 to 1.226 nm⁻¹.

Small angle neutron scattering (SANS) was performed at the National Institute of Standards and Technology Center for Neutron Research (NIST-CNR). The data was collected using a wavelength of 0.6 nm with a q range of 0.038 to 2.099 nm⁻¹. The scattering density of the solvent system was adjusted to match the contrast of the d₅-PMMA chains.

In both scattering experiments, the data was corrected for background scattering and scattering from the sample cell. Onedimensional data was obtained through radial integration routines.

RESULTS AND DISCUSSION

The SAXS studies of the isomeric polymer series at concentrations ranging from dilute to near the overlap concentration illustrated that the position of the branching junctures and the branch lengths impacts the intermolecular interactions of these polymers. Liquid-like ordering was observed at mass fractions of 1 wt% - 5 wt% and increased with concentration to a point, beyond which the ordering

became less pronounced. The loss of structuring at higher mass fractions could be due to the interpenetration of the arms of neighboring molecules or the distortion of the molecules from their original conformation. Both of these effects would result in a less ordered system.

Of the polymers studied, the structure was most significant in the isomer denoted C in Figure 1, in which the branching was concentrated at the center of the molecule in a star-like fashion. The structure factor was determined for this system at varying concentrations. The characteristic intermolecular spacing was estimated from the position of the peak in the structure factor for this star-like isomer. A power law relationship between mass fraction and the characteristic spacing was determined (Figure 3). We noted that the structure diminished above a concentration where the



intermolecular spacing exceeded twice the hydrodynamic radius.

Figure 3. The data for the characteristic spacing (d (nm)) is plotted as a function of the PCL mass fraction (%). The closed triangles represent SAXS data, the open triangle represent SANS data, and the solid line is the power law relationship fit to the data given by the equation shown. The upper dashed line indicates $2R_h$ while the lower dashed line indicates $2R_g$.

Partial deuteration of the PMMA blocks allowed the PCL cores of copolymer C to be highlighted in a core contrast SANS study at varying concentrations yielding information about intermolecular interactions of the block copolymers. The cores of copolymer derived from isomer C showed liquid-like ordering and again the structure factor was determined (Figure 4). In the same manner as for the bare isomer C, a relationship between the average spacing and the mass fraction was derived from the data for the copolymer C.

The characteristic spacing data obtained for the PCL cores in SAXS and for the PCL-PMMA copolymer cores in SANS can be fitted to the same curve as shown in Figure 3. It is evident by the graph that both R_h and R_g of the isomer core are key parameters when considering the important length scales for the structuring phenomena of these molecules. In addition, the fact that the data lie on a single curve suggests that the PMMA chains do not greatly effect the ordering of the PCL cores.



Figure 4. The structure factor for copolymer C was experimentally determined and is shown for mass fractions of 0.5 wt%, 5 wt%, and 15 wt%. The graphs are offset for clarity.

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