# Structural analysis of multicyclic/linear polystyrene blends and multicylic polystyrene by small-angle neutron scattering

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Macromolecules with cyclic topologies have attracted significant attention because of their unique structures and properties. In recent years, increasing attention has been directed toward the synthesis, properties, and functions of multicyclic polymers, which possess multiple cyclic units within a single molecule. One promising application lies in their use as property-enhancing additives. The phenomenon of threading between cyclic and linear polymers has been demonstrated through simulations and rheological measurements, suggesting the potential of cyclic polymers as property-enhancing additives. However, experimental studies to date have primarily focused on entanglements between monocyclic and linear polymers, while, to the best of our knowledge, no studies have been reported on multicyclic polymers themselves, let alone on blends of multicyclic and linear polymers. In this study, we synthesized multicyclic polystyrenes (mc-PS) and their deuterated counterparts (mc-dPS) by cyclopolymerization. [1] We then used Small-angle neutron scattering (SANS) to examine mc-PS both in the neat bulk and in mixtures with linear polystyrene.[2]

In the neat bulk state, we found that mc-PS had smaller radii of gyration than linear and monocyclic analogs with comparable molecular weights. This result indicates that the multicyclic topology promotes greater chain compaction. Comparison with a Gaussian-chain rosette model further suggested that excluded-volume interactions were not completely screened in the bulk state. The results of the Kratky analysis also supported this interpretation. We also examined the structural behavior of mc-PS in blends with linear polymers (**Figure 1**). The mc-PS exhibited ring-size-dependent swelling: expansion occurred only when the molecular weight of each cyclic unit exceeded the entanglement molecular weight. In addition, the extent of swelling increased as the number of cyclic units increased. These results demonstrate that the topological structure of mc-PS strongly affects both its intrinsic chain conformation and its interactions with surrounding linear polymer chains. The present findings provide useful guidelines for designing polymer materials with controllable structures, properties, and functions through molecular architectural control.

[1] Ebii, Y. et al. *Polym. Chem*., **2023**, *14*, 3099.
[2] Ebii, Y. et al. *Macromolecules*, **2026**, *59*, 2475.

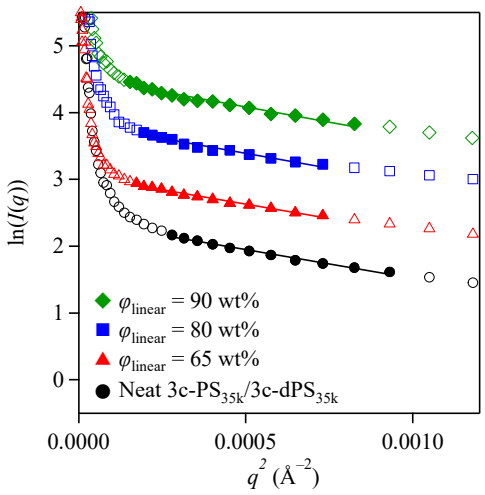


**Figure 1.** Guinier plots for the 3c-$PS_{35k}$/3c-$dPS_{35k}$ bulk blend samples and their blends with *h*/*d*-linear PS. "3c" denotes an average of three cyclic units per molecule, while "35k" represents the molecular weight of each cyclic unit. All measurements were conducted at 25 °C. The curves are offset along the *y*-axis for clarity purposes