

# Influence of monomer sequence on microstructure of nonadditive hard chain copolymers: Simulation and equation of state

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Influence of copolymer structure on self-assembly of the copolymer was investigated by introducing nonadditive size interactions among different type segments in copolymers composed of touching hard spheres. The copolymer structures investigated are diblock, alternating, multiblock, and random. The copolymers were simulated using discontinuous molecular dynamics simulation. Equations of state of the different model copolymers were developed using the TPT1 theory. Diblock copolymers were found to self assemble readily at high values of the nonadditivity parameter  $\Delta$  and at high densities. Multiblock and random copolymers self assembled to a smaller extent and the alternating copolymer self-assembled only at very high  $\Delta$  and densities. The TPT1 equation of state provided good prediction of the compressibilities of the different copolymer systems at negative and small positive values of  $\Delta$ . Deviations between the model and simulation results were observed at high  $\Delta$  and high densities. Deviations were associated with self-assembly of the copolymers. © 2003 American Institute of Physics. [DOI: 10.1063/1.1615513]

## INTRODUCTION

Copolymers are chain molecules formed by copolymerization of different types of monomers. Copolymerization provides an opportunity to tailor new materials with desirable properties for specific applications. Properties of copolymers depend not only on structure of the monomers but also on the way these monomers are arranged in a chain. The microphase behavior of polymers is expected to have substantial impact on future technologies, for example, molecular semiconductors, high density magnetic storage devices, optical materials, and catalysis.<sup>1</sup>

Self-assembly in copolymers is microscopic in nature because of the chemical bonding among different components of the copolymer. Microscopic self-assembly can result in production of materials which order on a scale much smaller than found in polymer blends or composites. The size and shape of micro-domains depend on the nature of the copolymer components (size, shape, etc.), the way they are arranged in the copolymer, and interactions among the different copolymer constituents.

The behavior of copolymers at the order to disorder transition (ODT) has received considerable theoretical attention.<sup>1</sup> The developed theories predict the ODT as well as spacing between structural units and shape of microstructures as a function of copolymer structure, volume fraction and strength of interaction among components of the copolymer.<sup>2-10</sup> Mean field theories were developed to predict the periodic spacing in copolymers in the weak as well as strong segregation regimes (SSR).<sup>2-4,9</sup> Banaszak and White-

more developed a self-consistent field theory (SCFT) to predict the properties of copolymers in the SSR and intermediate segregation regime (ISR).<sup>11</sup> The thermodynamic properties of block copolymers such as internal energy and entropy as well as structural properties were examined using an improved version of the SCFT.<sup>7,12</sup>

The phase behavior of block copolymers has also been investigated using Monte Carlo (MC), molecular dynamics (MD), and dissipative particle dynamics (DPD) computer simulation techniques to reveal microscopic characteristics of the copolymers that are difficult to characterize experimentally.<sup>13-18</sup> Larson used MC to study the influence of copolymer length on the location of order-disorder transition, concentration profiles and periodic spacing of lamellar structures of symmetric copolymers in selective solvents.<sup>13</sup> Besold and co-workers studied the ODT in symmetric copolymers and found lamellar and cylindrical structures.<sup>14</sup> Hoffmann and co-workers observed lamellar, disordered and cylindrical structures in asymmetric chains of length 24.<sup>15,16</sup> Murat and co-workers used MD simulation to study the effect of varying chain length and strength of interaction on periodic spacing, radius of gyration, end-to-end distance, and diffusion constant in symmetric block copolymers.<sup>17</sup> Groot and Madden used DPD to study influence of volume fraction of the block and interaction strength on the phase behavior.<sup>18</sup> They observed disordered, lamellar, perforated lamellar, cylindrical, and bcc spherical phases.

In order to describe the volumetric behavior of copolymers, equation of state theories have been developed. Hall and co-workers extended Flory's probabilistic assumptions about lattice chains in continuous space to develop theories for the hard chain fluid.<sup>19,20</sup> Two equations of state were

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