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Retention behavior of star-shaped polymers near the chromatographic critical condition JESSE ZIEBARTH, YONGMEI WANG, University of Memphis, KYUHYUN IM, HAE-WOONG PARK, YOUNGTAK KIM, SUN-YOUNG AHN, TAIHYUN CHANG, Pohang University of Science and Technology — The retention behavior of star-shaped polymers near the liquid chromatographic critical condition (LCCC) was investigated with 2-D liquid chromatography of polystyrene (PS) and lattice Monte Carlo simulations. At the LCCC for linear PS, stars with short arms elute after linear PS, while stars with long arms show a cross-over from late to early elution as branch number increases. Monte Carlo simulations show that two factors, excluded volume interactions and attractive end-effects resulting from initiator butyl groups, are required to explain the elution of star polymers. When polymers are modeled by random walk chains without excluded volume interactions, all stars are slightly more attracted to pores than corresponding linear chains. When polymers are modeled as self-avoiding walks (SAW) that include excluded volume interactions, stars with short arms elute later and stars with long arms elute earlier compared to linear chains. Incorporating more attractive-ends in SAWs results in the cross-over elution shown by long-armed stars in experiments. More attractive ends in PS star samples were confirmed through chromatographic retention of model monomers.

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