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Kinetics of Anionic Polymerization of Polybutadienyl Lithium in Benzene: An Osmotic Effect on Propagation Process. HIROSHI WATAN-ABE, ICR, Kyoto University — The anionic polymerization (propagation) kinetics of polybutadienyllithium (PBLi) in benzene was examined with H-NMR. The PBLi chains formed aggregates with an average aggregation number f = 4 through their Li ends. The residual monomer fraction y(t) did not rigorously exhibit the singleexponential decay expected for the conventional propagation mechanism through the dissociated chains, suggesting a competing propagation mechanism through the transiently fused 2f-mer aggregates (detected with Li NMR): This fusion-aided propagation should have been osmotically suppressed on a decrease of y (increase of the PB concentration) to give the deviation from the conventional behavior. The propagation became slower in the presence of chemically inert, neutral PB chains that just tuned the osmotic environment for the aggregates, lending support to molecular picture. Furthermore, the y(t) data in the absence/ presence of the neutral PB chains were semi-quantitatively described by a simple model considering the competition of the propagation through the fused 2f-mer aggregates and dissociated chains.

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