Dynamics of Capillary Imbibition of Poly(ethylene oxide) Melts in Nanoporous Alumina

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Understanding the behavior of polymer fluids through nanochannels is not only of fundamental interest but also important for applications in nanotechnology. Nearly hundred years ago, Lucas and Washburn derived Lucas-Washburn Equation (LWE) for Newtonian liquids penetrating a cylindrical capillary with radius R. The penetrating length is proportional to $t^{1/2}$, t is the wetting time. Herein, we investigate the penetration of a series of entangled poly(ethylene oxide) melts within nanopores of self-ordered alumina. In general, the penetration follows $t^{1/2}$ behavior according to LWE. However, LWE breaks-down because of differences in the prefactor. We observe a reversal in dynamics of capillary rise with polymer molecular weight. Chains with 244 entanglements or more display a faster capillary rise than theoretically predicted. Moreover, it is the first time to our knowledge that a slower capillary rise is observed for chains with 50 or less entanglements. The reversal in imbibition can be interpreted by the competition between a polymer dead zone next to the nanopore surface and the reptation of polymer chains under a pressure gradient. Lastly, we discuss the imbibition of PEO mixtures composed from long and short chains and show that it can result to the fractionation of short/long chains.

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Acknowledgement: We thank F. Henrich and Dr. S. Wooh for help during the surface tension and dynamic contact angle measurements as well as to Dr. G. Auernhammer and Dr. D. Vollmer for fruitful discussions and suggestions. We also thank A. Best and A. Hanewald for help with reflection microscopy and rheology.

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