ADSORPTION AND WETTING BEHAVIOR OF POLYMER DROPLETS THROUGH SIMULATIONS AND EXPERIMENTS

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ABSTRACT

Polymer dewetting at a solid surface involves the formation of sessile droplets; the polymer chains are confined in a spherical cap between the solid substrate and the free polymer surface. We used Monte Carlo computer simulations[1] to investigate the behavior of polymer droplets on solid surfaces as a function of the number of chains making up the droplets (keeping the total number of monomers constant) and varying droplet sizes (changing the total number of monomers). The wetting behavior was analyzed via the ratio of the perpendicular to the parallel component of the effective radii of gyration of the droplets while the droplet shape was quantified by using the principal moments of the radius of gyration tensor. We investigated in depth the conformational behavior of the polymer chains within the droplets. The adsorption statistics revealed that isolated chains exhibit a monotonic adsorption fraction trend with chain length, while chains in multi-chain droplets modify (decrease or increase) their adsorbed fraction with chain length depending on their population. This mode of internal chain adsorption allows the droplet as a whole to arrange the chains at the droplet–substrate interface in the most energetically preferable way. Furthermore, it leads to significant differences in the wetting behavior: Single polymer chain droplets were found to lie flatter and wet the substrate more than chemically identical multi-chain droplets of the same size (same total number of monomers), which attain a more globular shape and wet the substrate less. This marked difference in the wetting behavior is in good agreement with atomic force microscopy (AFM) experiments. In conclusion we have demonstrated that conformational arrangements within droplets affect wetting behavior in an unexpected but predictable way and could be used to control the shape of the polymer droplets on solid surfaces.

REFERENCES

[1] Evangelopoulos AEAS, Rissanou AN, Glynos E, Bitsanis IA, Anastasiadis SH, Koutsos V (2018). *Macromolecules*, 51: 2805–2816.