How surface topography, properties, and nanostructure controls single polymer interfacial diffusion

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Abstract

The diffusion of single polymer chains of poly(ethylene glycol) [PEG] in aqueous solution is described on four different kinds of surfaces: gradient surfaces [1], polymer brushes [2], nanostructured surfaces [3], and surfaces close to their glass transition. The diffusion of dye-labelled PEG is measured using fluorescence correlation spectroscopy. It is shown that a gradient in surface energy is sufficient to direct diffusion, and indeed to cause elevated diffusion over that expected on homogeneous surfaces. Diffusion of PEG is not however, observed on polymer brushes, but rather within them. In this case the scaling behaviour of single polymer diffusion as a function of brush grafting density is seen to be rather similar to that of polymer chains in an equivalent semi-dilute solution. If surfaces are patterned with a nanoscale array of brushes, so that PEG is confined to diffuse within the array, it is shown that a new mode of diffusion appears. This 'slow mode' contributes more with increasing confinement such that for the smallest structures (~100 nm), around 40% of surface diffusion is retarded. Such results may be used to interpret protein motion in the cell membrane. Finally, if PEG is allowed to diffusion on surfaces of polymer films close to the glass transition of that film, an anomalous peak is observed in the diffusion at ~10°C below the bulk glass transition. The origin of this elevated diffusion is unclear, and some speculative explanations will be offered.

References

[1] P. Burgos, Z. Zhang, R. Golestanian, G. J. Leggett, and M. Geoghegan "Directed single molecule diffusion triggered by surface energy gradients" *ACS Nano* **3** 3235-43 (2009)

[2] Z. J. Zhang, S. Edmondson, M. Mears, J. Madsen, S. P. Armes, G. J. Leggett, and M. Geoghegan "Blob size controls diffusion of free polymer in a chemically identical brush in semidilute solution" *Macromolecules* **51** 6312-17 (2018)

[3] C. G. Clarkson, A. Johnson, G. J. Leggett, and M. Geoghegan "Slow polymer diffusion on brush-patterned surfaces in aqueous solution" *Nanoscale* **11** 6052-61 (2019)

[4] M. Mears, Z. Zhang, R. C. D. Jackson, J. M. Torkelson, and Mark Geoghegan "Lateral diffusion of single poly(ethylene oxide) chains on the surfaces of glassy and molten polymer films" preprint.