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Importance of Crystallinity of Anchoring Block of Semi-solid Amphiphilic Triblock Copolymers in Stabilization of Silicone Nanoemulsions

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Polymer emulsifiers solidified at the interface between oil and water can provide exceptional dispersion stability to emulsions due to the formation of unique semi-solid interphase. Our recent works showed that the structural stability of paraffin-in-water emulsions highly depends on the oil wettability of hydrophobic block of methoxy poly(ethylene glycol)-block-poly(ϵ -caprolactone) (mPEG-*b*-PCL). Here we investigate the effects of the crystallinity of hydrophobic block of triblock copolymer-based emulsifiers, PCLL-*b*-PEG-*b*-PCLL, on the colloidal properties of silicone oil-in-water nanoemulsions. The increased ratio of L-lactide to ϵ -caprolactone decreases the crystallinity of the hydrophobic block, which in turn reduces the droplet size of silicone oil nanoemulsions due to the increased chain mobility at the interface. All of the prepared nanoemulsions are very stable for a month at 37 °C. However, the exposure to repeated freeze-thaw cycles quickly destabilizes the nanoemulsions prepared using the polymer with the reduced crystallinity. This work demonstrates that the anchoring chain crystallization in the semi-solid interphase is critically important for the structural robustness of nanoemulsions under harsh physical stresses.

Key words: triblock copolymers; emulsions; silicone; dispersion stability; crystallinity

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