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Polymer Core-Polymer Shell Particle Formation Enabled by Ultralow Interfacial Tension Via Internal Phase Separation: Morphology Prediction Using the Van Oss Formalism

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ABSTRACT

The internal phase separation technique is a versatile method for liquid core-polymer shell formation, yet limited to very hydrophobic core materials and actives. The use of polymeric cores instead circumvents this restriction due to the absent mixing entropy for binary polymer mixtures which allows the polymeric core (and the active) to approach the polarity of the shell. Polystyrene *core*-shell and janus particles were formulated using polymethylmethacrylate, poly(lactic acid), poly(lactic acid-co-glycolic acid), poly(ε-caprolactone) or cellulose triacetate as shell-forming polymers. The morphology and the partitioning was experimentally determined by selectively staining the core and the shell with β-carotene and methylene blue respectively. In addition, the van Oss formalism was introduced to theoretically predict the thermodynamic equilibrium morphology. As elucidated using the theoretical predictions as well as experimental optical tensiometry, it was found that the driving force for core-shell morphology is, in contrast to liquid core-polymer shell particles, a low core-shell interfacial tension.

Microencapsulation is an important technology for the protection and/or controlled release of active substances [1–4]. Among the available encapsulation methods, the internal phase separation route [5] has increased in popularity during the last decade [1]. This popularity can be ascribed to its versatility in terms of possible shell (usually polymeric) and core material (usually a liquid), encapsulation efficiencies often approaching 100%, absence of residual reactive species (e.g. monomers or initiators used for interfacial polymerization encapsulation), good control over core and shell dimensions and to its feasibility for industrial scale-up [1]. The theoretical basis and experimental details of the method are discussed on the next page. Most often, the microcapsules comprise liquid cores which may give a faster release than intended due to the high diffusivity of the actives in liquids. This can be circumvented by using alkanes which are solid at room temperatures and by performing the encapsulation at slightly elevated temperatures above their melting temperatures [6]. Another issue with liquid cores is the restriction in terms of their polarity imposed by the spreading requirements of the internal phase separation method [1,5]. This restriction is discussed in detail below. In short, for encapsulation in aqueous media, the core engulfment by the polymeric shell necessitates that the core liquid is sufficiently hydrophobic (e.g. alkanes) [5,7]. This has consequences for moderately hydrophobic actives which, more than occasionally, prefer the shell rather than the core [8].

The use of polymeric cores instead of liquid ones will obviously influence the release rate since the diffusion coefficient of actives in the core will be reduced by orders of magnitude [1]. Yet, more importantly, polymeric cores are allowed to be much more polar than their liquid counterparts, approaching the polarity of the polymeric shell. This is a consequence of the absent mixing entropy for binary polymer mixtures which enables polymers of similar polarity to remain immiscible. Subsequently, a wider range of more polar actives may be encapsulated by using polymeric cores.

In this report, formation of core-shell particles comprising a polystyrene core and various polymeric shells is presented. Dyes of different polarities have been used to selectively envisage the core and shell respectively. In addition, the van Oss formalism is presented as a tool to predict the microcapsule morphology and to determine whether encapsulation is theoretically conceivable or not for a given core-shell

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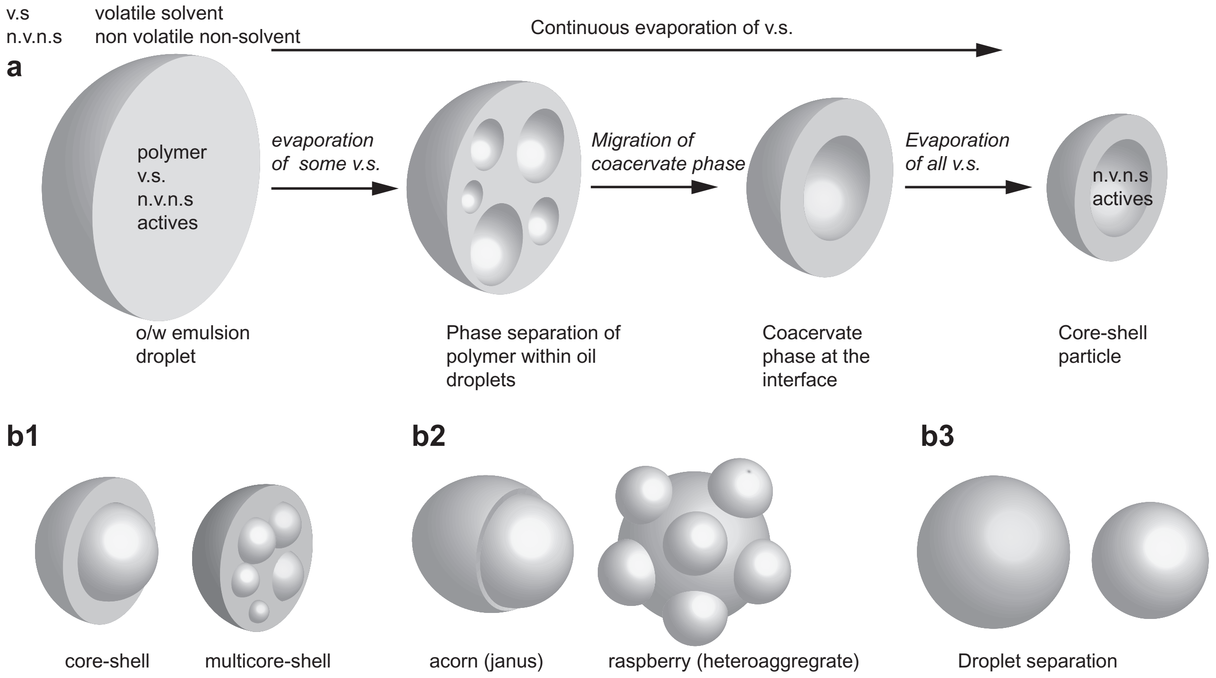

Scheme 1. a) Encapsulation process via the internal phase separation route. b) Possible morphologies and outcomes of the microencapsulation: b1) core-shell, b2) acorn-shaped morphology, and b3) droplet separation. The most common system, used for encapsulation of hydrophobic dyes, is an O/W emulsion. The aqueous phase contains a dispersant (typically a water-soluble polymer such as PVA) and the oil phase contains a volatile solvent (v.s), the shell-forming polymer, the core material (usually an oil which is a non-solvent for the polymer, n.v.n.s) [1,6] (see Chart 1).

pair.

Encapsulation based on internal phase separation relies on the internal segregation and subsequent spreading of coacervate phases inside an emulsion droplet (see Scheme 1a). The means for phase separation is the continuous evaporation of the v.s. which subsequently leads to phase segregation as the ternary composition reaches the binodal curve of the phase diagram and eventually to solidification. An oil which is too polar will either remain miscible with the polymer (see Chart 1) or prevent polymer spreading as discussed below.

For microencapsulation and core-shell formation, it is necessary that the shell polymer (assigned S) wets the core material (usually an oil or as in this report, a polymer, assigned C) and the aqueous phase (assigned W) (see Scheme 1). The spreading coefficient S_S is defined by the free energy for cohesion ΔG_S^c and adsorption ΔG_S^a in Eq. (1) as;

$$S_S = \Delta G_S^c - \Delta G_S^a = \gamma_{C/W} - (\gamma_{S/W} + \gamma_{C/S}) \tag{1}$$

The spreading coefficients were used by Torza and Mazon [9] to determine the morphology of a system comprising three immiscible liquids. The theory was later used to encompass phase segregating polymers [5,7,10]. Assuming that $\gamma_{C/W} > \gamma_{C/S}$, three possible sets of spreading conditions are obtained (Eqs. (2)–(4)) [5,9];

$$S_C < 0; \quad S_W < 0; \quad S_S > 0 \tag{2}$$

$$S_C < 0; \quad S_W < 0; \quad S_S < 0 \tag{3}$$

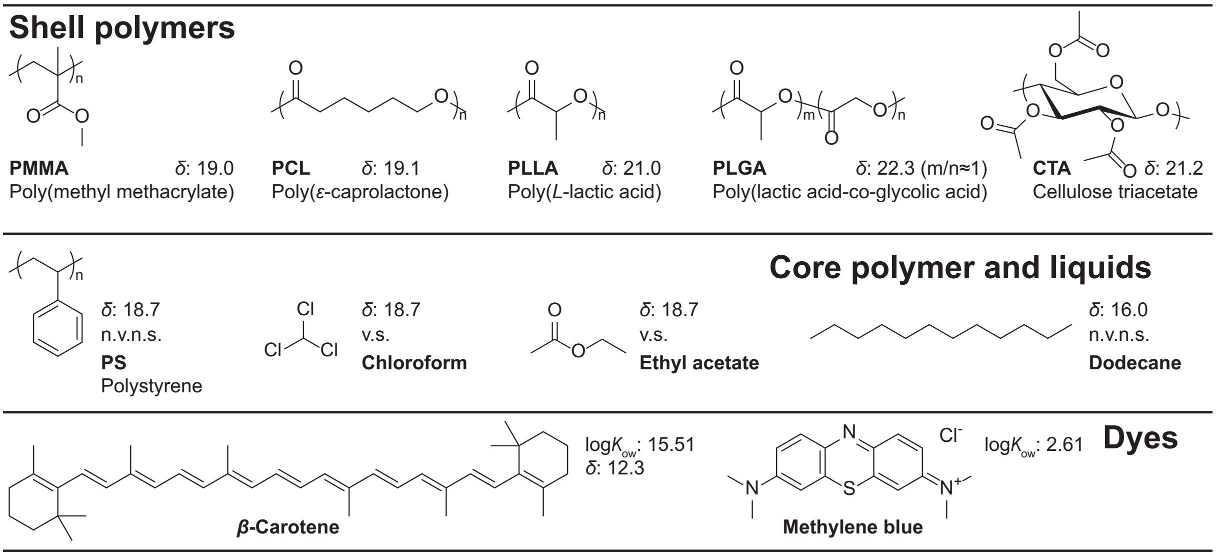

Chart 1. Polymers used for shells, oils/polymers used for cores and dyes used for encapsulation. Solubility parameters (δ[$MPa^{1/2}$]) and the logarithm of the octanol-water partition coefficient (log K_{ow}) are provided, as obtained from chemical databases (see the Supplementary Material, Table S1).