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The parachute morphology as equilibrium morphology of vesicle-polymer hybrids?

Martin Jung, Dominique H.W. Hubert, Alex M. van Herk, Anton L. German*

Laboratory of Polymer Chemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

SUMMARY: Polymerisation in vesicles leads to novel polymer colloid morphologies. Two morphologies are currently reported: the triple-shell and the parachute morphology. The thermodynamic analysis of these two morphologies, presented here, stresses the importance of considering interfacial energies between surfactant and polymer. Within this framework, the parachute appeared to be the favoured morphology. The theoretical results are supported by experimental studies of vesicle-polymer hybrids.

Introduction

The self-assembly structures of amphiphiles in water are ideal reaction sites for polymerisations in heterogeneous media1). The morphology of the obtained polymeric particles largely depends on the initial amphiphile aggregate structure. In most cases, globular micelles are employed, *e.g.* for the whole family of emulsion polymerisation reactions, leading to solid spherical latices. In order to open the way to new morphologies, *vesicles* have recently attracted considerable interest as a reaction medium for the free radical polymerisation of standard monomers2-8). The idea is to use the closed hollow bilayer surfactant structure of a vesicle as *template* for polymerisation reactions. The procedure consists of three steps: (1) vesicle preparation, (2) solubilisation of an oil-soluble monomer in the vesicle-bilayer, and (3) polymerisation of the solubilised monomer within the vesicle bilayer. The beauty of the concept would be for the polymerisation step to freeze the geometry of the solubilised monomer within the surfactant matrix, and thus deliver a hollow polymer structure as a polymeric one-to-one copy of the vesicle. The resulting morphology of this process could be described as a "triple-shell" structure (see Fig. 1a), where the inner monolayer shell (grey) is surrounded by the polymeric shell (dark) that is covered by the outer monolayer shell (grey). Such a morphology was already proposed by Murtagh and Thomas in their pioneering study2) on this topic in 1986. Lately, other groups, using diverse surfactant and monomer/polymer combinations, interpreted their experiments on

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polymerisation in vesicles as support of the triple-shell morphology[3-7]. However, our investigations on the polymerisation of styrene in dioctadecyl dimethyl ammonium bromide (DODAB) vesicles showed that the polymerisation in these vesicles leads to phase separation between amphiphile and polymer, resulting in the so-called parachute morphology[8] (see Fig. 3a). These two contradicting interpretations of the triple-shell morphology on one hand, and the parachute morphology on the other hand, triggered us to investigate the viability of these two morphologies based on thermodynamic grounds. The applied model takes into account solely interfacial energies. This is analogous to the successful approaches commonly used for the thermodynamic description of complex latex morphologies[9, 10]. Experimental results are discussed in the light of this model.

Model calculations

We compare the triple-shell situation to the parachute geometry with respect to the change in free energy (see Fig. 1). In this approach, interfacial energies of the final products (no intermediates are involved) are calculated with no consideration of entropic factors.

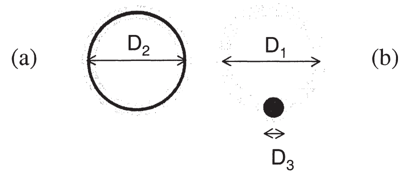

Fig. 1a and 1b: Schematic representation of the two compared morphologies. (a) The triple-shell morphology. (b) The parachute morphology. Parameters and details are explained in the text.

The starting point is to consider a vesicle with diameter D_1 (distance from bilayer mid-plane to mid-plane, see Fig. 1b). The triple-shell model assumes that after addition of monomer and subsequent polymerisation, a polymer shell with outer diameter D_2 and inner diameter D_1 has evolved. The parachute model on the other hand assumes the synthesis of a small latex bead with diameter D_3 , which is linked to the vesicle with diameter D_1. It holds:

$$D_2^3 - D_1^3 = D_3^3 \tag{1}$$

The parameters involved.

1. The thickness of the polymer shell (triple-shell geometry) or respectively the size of the latex bead (parachute geometry) is determined by the *surface* of the template vesicle and a "loading" parameter C, which summarises all the system inherent parameters such as amount of monomer per surfactant, partitioning of monomer, density of polymer. This

parameter depends on the type of surfactant and monomer.

Obviously, the ratio of *shell volume* (shell model) or the *latex volume* (parachute), to the template *surface* is constant:

$$\frac{D_2^3 - D_1^3}{D_1^2} = \frac{D_3^3}{D_1^2} = C \qquad (2)$$

In order to reduce variables and simplify calculations, we normalise the loading parameter by the vesicle diameter to obtain a dimensionless variable

$$S = \frac{C}{D_1} = \frac{D_2^3 - D_1^3}{D_1^3} = \frac{D_3^3}{D_1^3} \qquad \text{leading to} \qquad (3)$$

$$D_2 = D_1 * \sqrt[3]{S+1} \quad (4) \qquad \text{and} \qquad D_3 = D_1 * \sqrt[3]{S} \quad (5)$$

2. The interfacial tension between surfactant chains and polymer, γ_1 , and the interfacial tension between surfactant and water, γ_2 , can be defined by the ratio $\gamma = \gamma_1/\gamma_2$.

Now, we can calculate the change in free energy for the synthesis of either a shell morphology ΔG_s , or the parachute ΔG_p.

$$\Delta G_s = \pi\gamma_1(D_1^2 + D_2^2) + \pi\gamma_2(D_2^2 - D_1^2) = \pi D_1^2\left[\gamma_1((S+1)^{2/3} + 1) + \gamma_2((S+1)^{2/3} - 1)\right] \qquad (6)$$

$$\Delta G_p = \pi\gamma_1 D_3^2 + \pi\gamma_2(D_3^2 - D_3^2/4) = \pi D_1^2 S^{2/3}(\gamma_1 + \frac{3}{4}\gamma_2) \qquad (7)$$

The reduced Gibbs free energy is given by:

$$\Delta\Gamma = \frac{\Delta G}{\pi\gamma_2 D_1^2} \qquad (8)$$

Finally, the difference in reduced free energy between shell and parachute reads:

$$\Delta\Delta\Gamma = \Delta\Delta\Gamma(\gamma, S) = \Delta\Gamma_s - \Delta\Gamma_p = \gamma((S+1)^{2/3} - S^{2/3} + 1) + ((S+1)^{2/3} - \frac{3}{4}S^{2/3} - 1) \qquad (9)$$

The order of magnitude of the involved parameters.

1. The loading parameter C is estimated to vary between 0.001 and 20 nm. For DODAB vesicles at 25°C and full swelling it is 7.6 nm (58nm latex, 160nm vesicles)[8]. If our model calculations are restricted to vesicle diameters of 30 to 500 nm, this leads to typical values of S varying between $2*10^{-6}$ and 0.6. For our standard situation[8] of vesicle diameter 160 nm and C = 7.6nm, one calculates S = 0.048.
2. Interfacial tensions between surfactant chains and polymers, γ_1, are hardly reported in literature. Instead, values for the interfacial tension between linear polyethylene (PE) and selected polymers are taken as approximations. Here, values between 5 to 15 mN/m are found[11] (see Tabel 1). The interfacial tension between vesicle surface and water, γ_2, is often derived from monolayer experiments[12,13] and is given with ~30 mN/m, although

values between 10 and 80 mN/m can be found as well. Consequently, the γ ratio can be estimated to range between 0.05 and 1.5.

Table 1: interfacial tensions, γ_1, between linear PE and selected polymers[11)] at 20°C :

polymer	PS	PVAc	PMMA	PnBMA	PnBA
interfacial tension γ_1 [mN/m]	8.3	14.6	11.8	7.1	5.0

Results

Model calculations. According to eq. (9), the main criterion to assess the favoured morphology is the sign of $\Delta\Delta\Gamma$. A positive sign of $\Delta\Delta\Gamma$ is indicative of the preference of the parachute. Figure 2a and 2b show the results of the model calculations of $\Delta\Delta\Gamma$ in dependence of γ and S. Two important observations are made: (1) The calculations suggest that the parachute morphology is always thermodynamically favoured since $\Delta\Delta\Gamma>0$. (2) $\Delta\Delta\Gamma$ increases linearly with γ for a given value of S (see Fig 2a), as it is derived in equation (9). In general, the ratio of interfacial tensions, γ, plays *the* predominant role for the level of $\Delta\Delta\Gamma$(see Fig. 2b), whereas the dependence on the normalised loading parameter S is comparatively small– except for very high degrees of loading (high values of S). As a consequence, it is to expect that only for very small values of γ, the triple-shell morphology and the parachute morphology start to become thermodynamically equivalent. In order to reach this limit, the required values of γ should be not much higher than 0.10 (see Fig. 2b). Taking into account the above given values (Table1) for γ_1 (taking γ_2 as 30 mN/m), one would propose that PnBA –if any– with γ=0.17 would be the most promising candidate to fulfil the requirements for a triple-shell morphology. An even less polar polymer would be preferred.

Experimental evidence[14]. In fact, we wondered if the application of less polar polymers could lead to the triple-shell morphology. In order to test this hypothesis experimentally, we polymerised *isoprene* within the DODAB vesicles. The interfacial tension between the apolar polyisoprene and the alkyl chains of the amphiphile, albeit not found in literature, should be lower than that for PnBA. In addition, the rubber character of polyisoprene should be advantageous for the solubilisation of the polymer within the bilayer. However, cryo-TEM micrographs (Fig. 3b) unambiguously illustrate that the phase-separation between polymer and vesicle matrix cannot be prevented by the choice of an expectedly more compatible polymer. The vesicle-polymer particles clearly exhibit the typical parachute architecture where one polyisoprene bead is linked to one DODAB vesicle. In most cases, only one polymer bead per vesicle is formed and occasionally a small second bead is observed. All this was described earlier for the polymerisation of styrene in DODAB vesicles[8)].

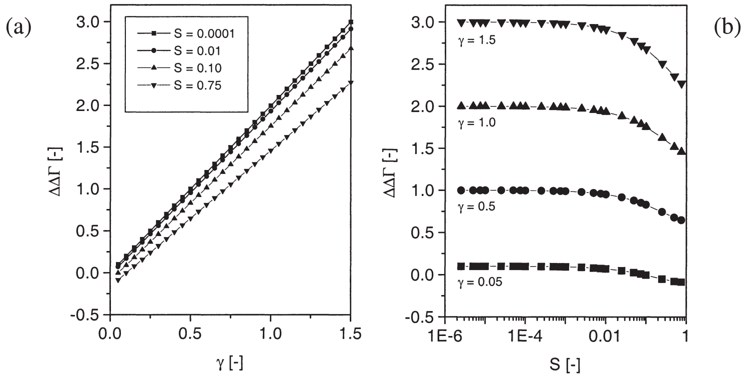

Fig. 2a and 2b: Model calculations of $\Delta\Delta\Gamma$ according to eq. (9).

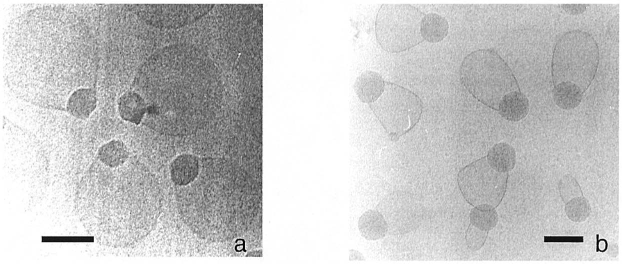

Fig 3a and 3b: Cryo-TEM micrographs after polymerisation of styrene (Fig. 3a) or isoprene (Fig. 3b) in extruded DODAB vesicles. Phase separation occurs in both cases and gives rise to parachute-like structures. Scale bars correspond to 100 nm.

Conclusions

On the basis of the presented thermodynamic model calculations it appears that the parachute morphology is the least energetic morphology for almost all combinations of amphiphile and polymer. As long as the reaction remains under *thermodynamic control*, the phase separation between polymer and vesicle template seems an inevitable fact. Experimental evidence of the parachute morphology is found for more polar polymers like PS and equally for more apolar polymers like polyisoprene and many other polymers. Therefore, we find it difficult to understand why the application of slightly different polymers such as PnBMA[6,7)] or polyisodecylacrylate[4)] would not lead to the parachute formation. Nevertheless, it is realised that our model suffers from several oversimplifications. Particularly, entropic factors are not included although entropy will contribute significantly to the thermodynamics of solubilisation of a macromolecule within vesicle bilayer. The constrained, two-dimensional vesicle bilayer (thickness ~4nm!) as host for a polymer layer would force the polymer chains into a flat chain conformation. The loss of entropy for such a flat, extended polymer molecule is not favoured and will cause a polymer collapse to regain a random coil conformation. Entropy is consequently considered to be a major driving force for the phase separation, and the accompanied parachute formation becomes even more probable. Other draw-backs of our model calculations are uncertainties in the applied parameters and the assumption of well defined geometric interfaces between polymer and amphiphile. In reality, the interfaces will always posses a certain roughness which increases the interfacial area, thus favouring again phase separation. Finally, it needs to be stressed that our model considers solely the final state of a polymerisation reaction in vesicles, assuming that the reaction pathway readily allows the formation of such a morphology. All *intermediate* morphologies, the involved thermodynamics and the required diffusion processes of polymer, monomer and amphiphile were not addressed. These issues are currently under investigation.

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References

1. C.M. Paleos, *Polymerization in Organized Media*, Gordon and Breach Science Publishers, Philadelphia 1992
2. J. Murtagh, J.K. Thomas, *Faraday Discuss. Chem. Soc.* **81**, 127 (1986)
3. J. Kurja, R.J.M. Nolte, I.A. Maxwell, A.L. German, *Polymer* **34**, 2045 (1993)
4. N. Poulain, E. Nakache, A. Pina, G.J. Levesque, *Polym. Sci. Polym. Chem.* 34, 729 (1996)
5. J.D. Morgan, C.A. Johnson, E.W. Kaler, *Langmuir* **13**, 6447 (1997)
6. J. Hotz, W. Meier, *Langmuir* **14**, 1031 (1998)
7. J. Hotz, W. Meier, *Adv. Mater.* **10**, 1387 (1998)
8. M. Jung, D.H.W. Hubert, P.H.H. Bomans, P.M. Frederik, J. Meuldijk, A.M. van Herk, H. Fischer, A.L.German, *Langmuir* **26,** 6877 (1997)
9. for review see: D. Sundberg, Y.G. Durant, in: *Polymeric Dispersions: Principles and Applications*, J.M. Asua (Ed.), Kluwer Academic Publishers, Dordrecht 1997, p.177 ff
10. R.M. Fitch, *Polymer Colloids*, Academic Press, San Diego, California 1997, p.41 f
11. S. Wu, *Polymer Interface and Adhesion*, Marcel Dekker, New York 1982, p. 126-128
12. S.M.B. Souza, H. Chaimovich, M.J. Politi, *Langmuir* **11**, 1715 (1995)
13. G. Cevc, D. Marsh, *Phospholipid Bilayers*, John Wiley & Sons, New York 1987, p.357
14. Experimental details are given in Ref. 8. The preparation of polystyrene-vesicle hybrids is described there. For the preparation of the polyisoprene-vesicle hybrids, 100mM isoprene was injected in a vesicle suspension of 10 mM DODAB and polymerised at 20°C. Vesicle preparation, characterisation and other polymerisation conditions are identical to those in Ref. 8.