pH and Solubility Effects as Control Mechanisms for Vesicle Interfaces

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It was shown some time ago that in diblock copolymer vesicles the corona chains are segregated by length with short block inside and long blocks outside. More recently, it was shown that a triblock copolymer consisting of a long polystyrene segment with short segments of poly(acrylic acid) and poly(-4-vinyl pyridine) at each end could be converted into vesicles which, depending on the pH during preparation, could have either PAA or P4VP on the outside. For example a low pH, at which the 4VP is protonated, leads to P4VP on the outside because those chains become longer than the nonionic PAA. Furthermore, inversion of the vesicles from PAA outside to P4VP outside is possible by dropping the pH of the solution. It is now shown that under extreme pH conditions in dimethylformamide, the inside and outside interfaces are behaving exactly opposite to what it is expected. For example, at very low pH (3), at which the P4VP should be ionic and therefore longer than PAA, it is found that the PAA is on the outer interface of the vesicle, while the P4VP is inside. The reason for such behavior can be found in the solubilities and coil dimensions of the quaternized P4VP, which is poorly soluble in DMF at low pH and also the poor solubility of the poly(sodium acrylate) in DMF at high pH. The poor solubilities overwhelm the coil expansion accompanying ionization at moderate pH. This solubility effect thus provides us with an added mechanism for controlling the interior and exterior interfaces of vesicles, in addition to the block length and the simple pH effect. This work is based on the MSc Thesis of Renata Vyhnilkova, McGill University, 2005.