



Diverse effect of PEO–PPO–PEO and PPO–PEO–PPO triblock copolymers on temperature responsive behavior of luminescent hard–soft colloids

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ABSTRACT

The present work introduces the interaction of hard and soft colloids in aqueous solutions at various temperatures and concentrations, as well as at critical conditions of temperature induced phase separation. Hard and soft colloids are represented by luminescent silica nanoparticles and aggregates of PEO–PPO–PEO and PPO–PEO–PPO triblock copolymers correspondingly. The formation of the mixed aggregates between hard and soft colloids in equilibrium conditions has been revealed by dynamic light scattering measurements. The distribution of silica nanoparticles between aqueous and surfactant rich phases after phase separation highlights the effect of pH, architecture and concentration of triblock copolymers on the mixed hard–soft colloids aggregation at cloud point conditions. The peculiar aggregation and phase behavior of PPO–PEO–PPO plurionics should be assumed as the main reason of enhanced mixed aggregation with SNs at increased temperatures and concentrated conditions.

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1. Introduction

The triblock copolymers, made up of poly(ethyleneoxide) (PEO) and poly(propyleneoxide) (PPO) blocks have been the subject of intense research over last two decades due to their unique solution behavior [1,2] and extensive industrial and biomedical applications [3–7]. The structural parameters of triblock copolymers are important variables influencing their colloidal properties [8–13]. Furthermore, the arrangement of the PPO and PEO blocks in the chain is the key factor affecting self-aggregation and phase behavior of these copolymers. Thus the comparative studies of PEO–PPO–PEO (plurionics or P-type triblock copolymers) and PPO–PEO–PPO (commonly known as reverse plurionics or R-type triblock copolymers) are well documented in literature [8–13]. The temperature induced aggregation and phase behavior of triblock copolymers in aqueous solutions have got great attention during recent decades due to their fundamental and practical importance [9–14]. The adsorption and aggregation of triblock copolymers onto hard colloids is a well known approach to improve many properties of the latter, including biocompatibility and colloidal stability [15–19]. Taking into account the diversity of colloidal properties of triblock copolymers with various architecture the modification of nanoparticles by plurionics as background-supporting colloid fluids

provides a simple new concept of stimuli responsive separation, recovery and redistribution of nanoparticles. The stimuli induced phase behavior plays a significant role in gaining colloidal stability or separation of colloids [19–22], which in turn enables to isolate, purify and redisperse luminescent nanoparticles, such as quantum dots, silica, gold or silver nanoparticles. Luminescent silica nanoparticles (SNs) represent well known type of colloids, which have got wide application in bioanalysis and medicine [23–25]. Thus the interaction between soft (triblock copolymers of various architecture) and hard (silica nanoparticles) colloids is of great fundamental and practical importance. This interaction can modify hydrophilic–lipophilic balance of SNs, which in turn greatly affects their phase behavior. Taking into account that triblock copolymers in aqueous solutions exhibit temperature induced aggregation and phase separation, their interaction with SNs should also be temperature dependent. The interaction of SNs with triblock copolymers in fluid colloids is a way to develop mixed colloids with temperature dependent aggregation and phase behavior. Thus the interaction between luminescent SNs and triblock copolymers in aqueous solutions at equilibrium and critical conditions of phase separation is a goal of the present report. The interaction between soft and hard colloids at phase separation conditions will be analyzed through the distribution of SNs between aqueous and surfactant rich phases after their temperature induced separation. The use of luminescent nanoparticles, where the luminescence arises from the Tb-complex doped into silica matrix, gives additional opportunities to reveal the distribution of nanoparticles between

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