

Tailoring the Density of Poly(NiPAAm) on Silicate Platelet and Their Aggregating Behavior in Water

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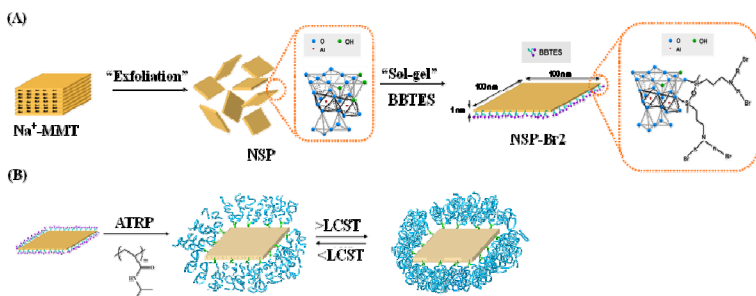
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Abstract A new class of organic-inorganic hybrid was synthesized by the method of tethering the thermoresponsive poly(*N*-isopropylacrylamide) (PNiPAAm) onto nanosilicate platelets (NSP) via covalent bonding. NSP of inherently hydrophilic and the hydrophobic isopropyl group of PNiPAAm imparted the surfactant-like properties. We measured surface tension of critical micelle concentration (CMC) of the NSP-PNiPAAm hybrids with different grafting density and polymer length and demonstrated the factor of grafting densities is the most important factor for the water interaction and surface activity. This is the first time to investigate the specific properties including CMC of the organic-inorganic hybrid.

Keywords: NSP-P(NiPAAm), surface tension, CMC.

In the present study, we used a living polymerization technique to graft moieties to the NSP edge surface through covalent bonding to produce polymer (Scheme 1). This tethering of thermoresponsive polymer strain to NSP via covalent bonding has not yet been reported in the literature. A linker with a dual active site was synthesized and first covalently attached to NSP (Table 1). Subsequent ATRP was carried out to grow the PNiPAAm strain. NSP-PNiPAAm of well-defined chain length and different graft densities lead different water surface properties (Table 2). This unique behavior was investigated using surface tension (Table 3).



Scheme 1. (A) Tethering onto NSP edges by sol-gel reaction; (B) Conceptual diagram of NSP-PNiPAAm formation by the ATRP “Grafting From” method and morphological transformation at LCST.

Table 1. NSP with different density linker.

	Weight ratio (NSP/Initiator)	Grafting mequiv	Reactive site	Density (nm ² /site)
NSP-Br2-1	3/1	0.18	3200	0.25
NSP-Br2-2	15/1	0.04	700	1.10

Table 2. NSP-PNiPAAm Synthesize from different NSP-linker.

	NSP-Br	Molar ratio NiPAAm/ NSP-Br	Organic fraction (wt%)
NSP-P(NiPAAm)-1	NSP-Br2-1	20/1	33
NSP-P(NiPAAm)-2	NSP-Br2-1	50/1	48
NSP-P(NiPAAm)-3	NSP-Br2-1	150/1	70
NSP-P(NiPAAm)-4	NSP-Br2-2	500/1	40

The CMC of PNiPAAm is much smaller than others. It can be explained that the chains of PNiPAAm extended entirely in water and the hydrophobic isopropyl groups will preferentially be oriented toward the air. Moreover, the CMC of NSP-Br2 is larger just because the amount of hydrophobic group on silica plates is less. When PNiPAAm tethered to silica plates, the polymer chains was restricted by NSP. So PNiPAAm can not be extended completely and reduce the amount of hydrophobic groups. This situation make the values of CMC were between NSP-Br2 and PNiPAAm (Figure 1a). The CMC is decreasing with decreasing the grafting density of PNiPAAm on NSP (Figure 1b and Table 3). Furthermore, there is no obvious change of CMC with increasing the organic ratio of NSP-PNiPAAm.

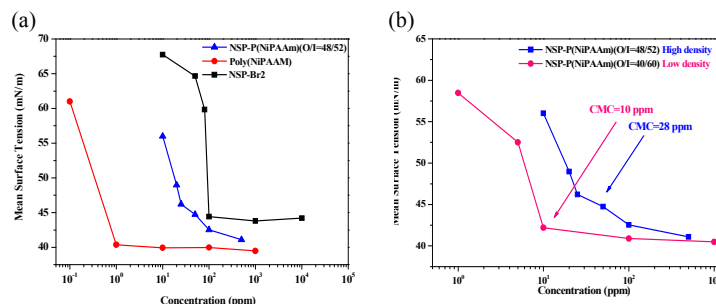


Figure 1. (a) Surface tension of NSP, NSP-Br2 and NSP-PNiPAAm (b) Surface tension of NSP-PNiPAAm with different density.

Table 3 CMC and surface tension of NSP-PNiPAAm.

	CMC (ppm)	Surface Tension of 100ppm (mN/m)
Poly(NiPAAm)	1	39.97
NSP-Br2	100	42.53
NSP-P(NiPAAm)-1	24	41.41
NSP-P(NiPAAm)-2	21	42.53
NSP-P(NiPAAm)-3	28	42.89
NSP-P(NiPAAm)-4	10	40.88

According to the CMC results, there is a conceptual diagram as shown in Figure 2. Polymer chains can extend more freely without restrained because decreasing the density of PNiPAAm on NSP and aggregated chain of PNiPAAm is decreased.

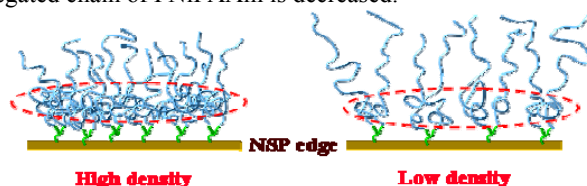


Figure 2. Conceptual diagram of NSP-PNiPAAm with different density.

Conclusions PNiPAAm tethered to NSP hybrids was successfully synthesized by sol-gel method and ATRP. Because of the hydrophilic properties of NSP and the hydrophobic isopropyl group of PNiPAAm imparted the surfactant-like properties, it might change the water/air interface properties. From the investigation, we demonstrated the grafting densities is the most important factor for the water interaction and surface activity. Comparing with the CMC (28 ppm) of high density, lower density caused the lower CMC (10 ppm) just because of that NSP restricted the polymer chains expansion and PNiPAAm can not be extended completely. Therefore, the specific properties including CMC can be tailored by varying the PNiPAAm grafting density on NSP.

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