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# Journal Name

## COMMUNICATION

### Polymeric Janus nanoparticles from triblock terpolymer micellar dimers†

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**Well-defined polymeric Janus nanoparticles have been synthesized by a novel method of combining self-assembly of simple ABC linear triblock terpolymers into nanostructured dimers and crosslinking of the conjunction between the opposite hemispheres. Surface activity of the prepared Janus nanoparticles and that of their precursors have been compared.**

Janus particles, named after the ancient Roman god "Janus" who possesses two faces, are asymmetric particles comprised of two or more distinct surface regions with different chemistries or polarities. The asymmetry gives rise to unique properties such as surface activity and anisotropy, which make Janus particles potentially useful in a wide range of applications, including but not limited to chemical and biological sensor, switchable devices, phase transfer catalyst, drug carriers, Pickering emulsifiers, etc[1-6] Recently, many synthetic methods of producing Janus-structured particles have been reported, e.g. surface-initiated free-radical polymerization, grafting approaches, interface methods, the Pickering emulsion method, and template approaches.[7-12] However, Janus particles prepared from these above-mentioned methods are either in micrometre size or of anomalous structures. Only few reports were devoted to the synthesis of soft organic Janus structures on nanoscale.[13-15] Polymeric Janus nanoparticles prepared by solution-based methods were seldom reported until researchers investigated the versatile nanostructures self-assembled from several kinds of commercially available polymers in different solvents. By making full use of the incompatibility between the individual blocks of the polymers, as well as the cross-linkable nature of the building blocks, various self-assemblies are reachable.[16-20]

In this communication, we report on a method to produce homogenously spherical polymeric Janus particles using the micellar dimers made from one type of the synthesizable triblock terpolymers as precursors, and compare the surface activity of the triblock terpolymers, the micellar dimers and the prepared Janus nanoparticles. The proposed strategy to generate the Janus nanoparticles is highlighted in Scheme 1. In the first step well defined micellar dimers were formed by step-wise self-assembly of the poly(methyl methacrylate)-*block*-poly(2-(cinnamoyloxy)ethyl methacrylate)-*block*-poly(2-dimethylaminoethyl methacrylate) (PMMA-*b*-PCEMA-*b*-PDMAEMA) triblock terpolymers as the building blocks, in selective solvents. The phase-separated micellar dimers consist of a PMMA domain which connects two PCEMA cores emanating the PDMAEMA corona. Afterwards, the PCEMA cores are fixated by UV-crosslinking, yielding steady Janus nanoparticles by dis-assembly of the micellar dimers in a common solvent. In addition to Müller's work,[16-18] we have not only investigated the surface activity of the Janus nanoparticles by comparing with that of their precursors, but also enlarged the diverse library of the polymers as building blocks forming the nanostructured self-assemblies.

**Scheme 1** Fabrication process of Janus particles by the triblock terpolymer micellar dimers.

A PMMA$_{266}$-*b*-PCEMA$_{121}$-*b*-PDMAEMA$_{269}$ triblock terpolymer (the chemical structure is as shown in Scheme 2) has been used to obtain the initial micellar dimers, synthesized via successive atom transfer radical polymerization (ATRP) followed by selective modification of the middle block as described in our previous report.[21] The molecular weight polydispersity index (PDI, Mw/Mn) was 1.2 and the subscripts denote the degrees of polymerization of the respective blocks.

**Scheme 2** Chemical structure of PMMA-*b*-PCEMA-*b*-PDMAEMA.

PMMA$_{266}$-*b*-PCEMA$_{121}$-*b*-PDMAEMA$_{269}$ triblock terpolymers were first dispersed in a nonsolvent for the PCEMA middle block, isopropanol/acetonitrile (3:1 v/v), to generate core-corona micelles with a PCEMA core and a patchy PMMA/PDMAEMA corona. Subsequent dialysis of these core-corona micelles into a nonsolvent for both PMMA and PCEMA (water) initiates self-assembling into

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micellar dimers. During this step, the corona patches (PMMA/PDMAEMA) rearranged to minimize the energetically unfavorable PMMA/water interface, inducing coalescence along the exposed PMMA patches. Within these micellar dimers, the phase-separated state is permanently fixated by selective UV-crosslinking of the PCEMA cores. Subsequent redispersion in a good solvent for all blocks (acetone) broke up the micellar dimers and liberated single, core-crosslinked polymeric Janus nanoparticles (see Scheme 1).

To gain clear insight into the self-assembly steps of PMMA$_{266}$-b-PCEMA$_{121}$-b-PDMAEMA$_{269}$ triblock terpolymers towards Janus nanoparticles, TEM was used to probe the samples. Figure 1a shows the formation of the polymeric core-corona micelles with a diameter of around 25 nm. I$_2$ only stains amine in the PDAEMA block, so that a slightly micro-phase separation in the coronas of the core-corona micelles can be seen. As shown in Figure 1b, the average hydrodynamic radius (Rh) of the core-corona micelles is 15.6 nm, which indicates that the average hydrodynamic diameter is 31.2 nm, slightly larger than the corresponding average size estimated from TEM. This may be due to the shrinkage of the well-solubilized corona during TEM sample preparation.[22, 23] Figure 1c shows that the micellar dimers, self-assembled from core-corona micelles, are individually dispersed with a length of 65 nm which is approximately 2-fold the size of the core-corona micelles. The two units of a micellar dimer are connected by PMMA, the light grey domains between the black PDMAEMA regions.

To gain further insight of the micellar dimers, the TEM samples were treated with RuO4 which selectively stains the aromatic groups of PCEMA, as the schematic cartoon depicts in Figure 1f. The PCEMA cores are located as black dots in the center of each unit of the micellar dimers as shown in Figure 1e. After selective UV-crosslinking of the PCEMA cores for 40 min, with a degree of crosslinking around 75% (see Figure S3 in Supporting Information), single Janus nanoparticles were obtained in acetone with a cross-linked PCEMA core and hemispheres of PMMA and PDMAEMA due to dis-assembly of the former micellar dimers. The TEM image in Figure 1g presents the well-defined Janus nanoparticles with two hemispheres of PDMAEMA as the black one and PMMA as the light grey one due to I$_2$ staining. The Janus nanoparticles are well dispersed as individuals with a size of about 20 nm according to the TEM image and the fine homogeneity in morphology is evidenced by the formation of ordered 2D lattices exhibiting third-order reflections in the corresponding Fourier-transformed image, as shown in the inset in Figure 1g. Moreover, DLS CONTIN plot in Figure 1h shows that the average hydrodynamic radius of the Janus nanoparticles is 13.2 nm with a polydispersity index (PDI) of 0.05, which further confirms that the homogeneity of Janus nanoparticles.

**Figure 1** TEM images of a) core-corona micelles (I$_2$ staining: PDMAEMA black), c) micellar dimers (I$_2$ staining: PDMAEMA black), e) micellar dimers (RuO$_4$ staining: PCEMA black), and g) Janus nanoparticles (I$_2$ staining: PDMAEMA black). Hydrodynamic radius distributions of b) core-corona micelles in isopropanol/acetonitrile (3:1 v/v), d) micellar dimers in water and h) Janus particles in acetone. PDI denotes polydispersity index obtained by the CONTIN analysis mode. The cartoon scheme in f) highlights importance of selective staining for TEM observation. The left inset in g) depicts the Fast Fourier Transform of the TEM micrograph.

Close examinations of the surface activity were carried out to confirm the amphiphilicity of the synthesized Janus nanoparticles. According to the equilibrium surface tension isotherms shown in Figure 2, the Janus nanoparticles are able to reduce the surface tension of water. It is obvious that the surface tension of the aqueous solutions decreases as Janus nanoparticle concentration increased until it reaches around 58 mN/m. The surface activity of the Janus nanoparticles at the air/water interface is attributed to the presence of the two hemispheres with distinctly different chemistry: the PMMA-hemisphere hydrophobic and the PDMAEMA-hemisphere hydrophilic. Meanwhile, the surface tensions of the polymer aqueous solutions and the micellar dimer aqueous solutions reduce little with the increase in concentration, as they both reach almost 68 mN/m when the concentration is up to 0.1 g/L. The slight reduction in the surface tension of the aqueous solution of the polymers is mainly due to the amphiphilic nature of the small amount of the dispersed polymers adsorbed at the air/water interface. However large aggregates, formed readily from the polymers in water, are evidenced by DLS as shown in Figure 3b, indicated by the columns highlighted by the green box. The large aggregates of the polymers exhibit non-surface-active nature, since the tangled polymer chains are dynamically frozen as the molecular weight of PMMA$_{266}$-b-PCEMA$_{121}$-b-PDMAEMA$_{269}$ triblock terpolymers reaches up to 92,900 g/mol.[21, 24] As for the micellar dimers, they have an average diameter of 65 nm with a relatively narrow size distribution and hence may act as the Pickering particles at the air/water, reducing the surface tension mildly.[25]

**Figure 2** Equilibrium surface tension as a function of a) concentration and b) logarithmic concentration of the polymers, the micellar dimers, and the Janus nanoparticles in water.

In the maximum bubble pressure method, the dynamic surface tension as a function of surface age (the time interval between the onset of bubble growth and the moment of maximum pressure) was measured by varying the speed of bubble formation. The measured dynamic surface tension values of the polymers, the micellar dimers and the Janus nanoparticles at concentration from 0.00001 g/L to 0.1 g/L as a function of surface age are graphed in Figure 3a, Figure 3c and Figure 3e, respectively. The dynamic surface tension isotherms of the polymers and the micellar dimers, as shown in Figure 3a and Figure 3c, are similar. They both decrease gradually from the beginning as the surface ages grow, and both reach an equilibrium after having decreased to about 68 mN/m at the concentration of 0.1 g/L, in accordance with the result of the equilibrium surface tension measurement as shown in Figure 2. The large aggregates formed readily from the polymers in water, as indicated by the columns highlighted by the green box in Figure 3b, exert little influence on the surface tension variations, as mentioned in the last paragraph. But the dispersed polymers, diffusing and adsorbing at the air/water interface rapidly, have contributed considerably to the surface tension reduction since the dynamic surface tension variation during a period of time is

dependent on the diffusion rate of the amphiphiles, which means the faster the surfactants move to the air/water interface, the larger extent the surface tension decreases.[26-29] The increase in concentration of the polymers has little effect on the dynamic surface tension variations as shown in Figure 3a, which implies that the proportion of the dispersed polymers is relatively small, and that the possibility of disassembly of the aggregates near the surface is extremely little during the formation of the bubble. As shown in Figure 3d, the micellar dimers, having hydrophilic PDMAEMA coronas, are well dispersed in water so that they can act as the Pickering particles, adsorbing at the air/water interface firmly. And the dynamic surface tension reduces more and more rapidly as the concentration of the micellar dimers increases, as shown in Figure 3c.

**Figure 3** Dynamic surface tension isotherms of a) the polymers, c) the micellar dimers and e) the Janus nanoparticles at varied concentrations. DLS size distributions of b) the polymers, d) the micellar dimers and f) the Janus nanoparticles, measured in water at the concentration of 0.1 g/L.

However, different from the polymers and the micellar dimers, the dynamic surface tension curves of the Janus nanoparticles exhibit a long induction period (>10 s) before a sharp fall, and show continuous decrease during the time period from 10 s until 100 s, as shown in Figure 3e. In the meantime, large clusters of the Janus nanoparticles are evidenced by the broad and bimodal size distribution as shown in Figure 3f. This is because the Janus nanoparticles tend to self-assemble into clusters in water via the hydrophobic PMMA hemispheres, in spite of their amphiphilic nature that should help adsorb easily at the air/water interface.[16] As can be seen from the DLS plots in Figure 1and Figure 3, the clusters in water are 2 to 30 times as large as the Janus nanoparticles in acetone. This means aggregation number of the Janus nanoparticle clusters falls in the range of 2 to 30. Since the rate of disassembly of the clusters into the Janus nanoparticles is much slower than the diffusion rate of the dispersed Janus nanoparticles, there is a long time for the large amount of clusters to release the Janus nanoparticles to adsorb at the air/water interface, which results in long induction time of the dynamic surface tension variations. It is worth noting that during the period between 10 s and 100 s, generally each dynamic surface tension of the Janus nanoparticles aqueous solutions at the same surface age decreases as the concentration increases. This implies that there were more probabilities for the disassembly of the clusters near the surface during the formation of the bubble if the concentration increased. Unlike the aggregates of the polymers which remained stable and unlikely to disaggregate, the clusters of the Janus nanoparticles tend to disassemble when the bubble formed and the released Janus nanoparticles considerably reduce the surface tension.

In conclusion, well-dispersed core-corona micelles with a patchy corona have been prepared successfully from the synthesized PMMA$_{266}$-$b$-PCEMA$_{121}$-$b$-PDMAEMA$_{269}$ triblock terpolymers in isopropanol/acetonitrile (3:1 v/v). Upon dialysis against water, the selective solvent for PDMAEMA, these core-corona micelles rearranged and then self-assembled

spontaneously into nanoscale micellar dimers due to strong hydrophobic interactions between PMMA patches. The Janus nanoparticles are yielded from dis-assembly of the UV-crosslinked micellar dimers in acetone. They have a hydrophobic PMMA-hemisphere and a hydrophilic PDMAEMA-hemisphere. They show surface-active nature since the surface tension of their aqueous solutions decreased as the concentration increased. Thanks to their amphiphilic nature from the two different hemispheres, the Janus nanoparticles reduced larger extent of the surface tension than the polymers and the micellar dimers did. Clustering took place easily for the Janus nanoparticles in water, which resulted in slow diffusion rate as indicated by the dynamic surface tension measurement. However, the clusters of the Janus nanoparticles were proven indirectly to disassemble at the surface, by the surface tension reduction variation with the increasing concentration.

The facile strategy we developed to produce polymeric Janus nanoparticles using the nanostructured micellar dimers as template to achieve asymmetrization, could be reproduced with PMMA-$b$-PCEMA-$b$-PDMAEMA triblock terpolymers of different length and/or micellar dimers with different sizes, thus allowing the creation of nanoparticles with different sizes and aspect ratios. Janus nanoparticles of various chemical natures could then be generated by changing the nature of the block forming the corona of the dimers and/or the block coalescing into the nano-domains in the middle of the dimers. In addition, the investigation into the surface activity of the prepared Janus nanoparticles compared to their precursors are believed to have laid a foundation for further research on the application of the Janus nanoparticles about their attractive surface-active nature.

## Acknowledgements

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Figures with Captions:
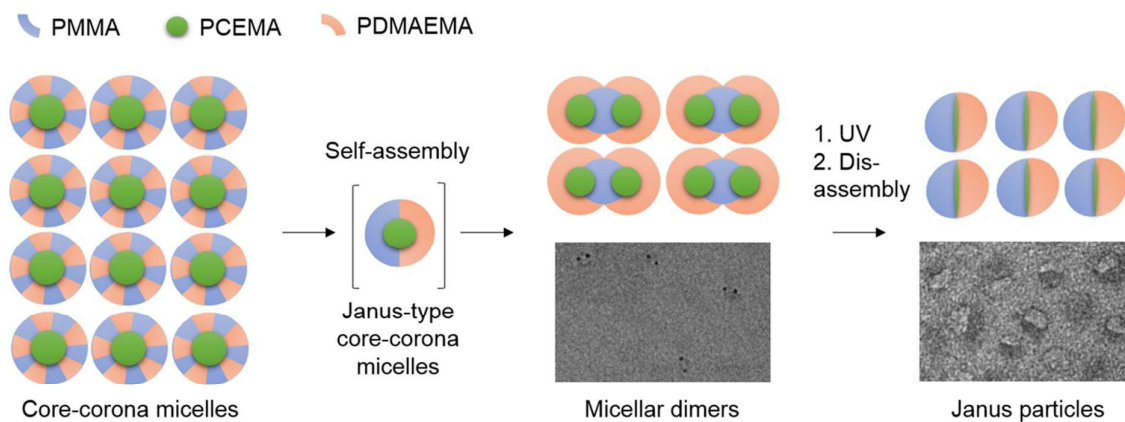


**Scheme 1** Fabrication process of Janus particles by the triblock terpolymer micellar dimers.
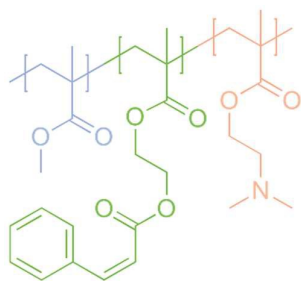


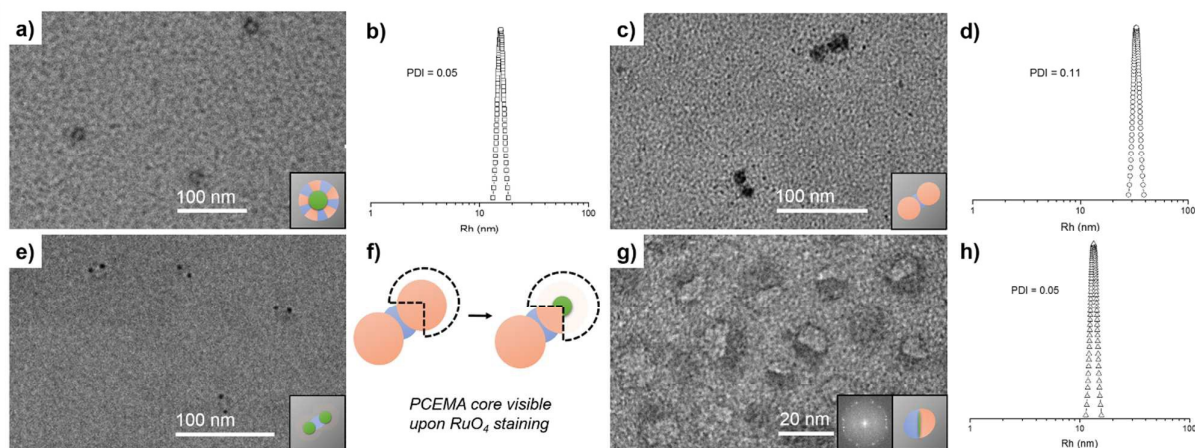**Scheme 2** Chemical structure of PMMA-b-PCEMA-b-PDMAEMA.



**Figure 1** TEM images of a) core-corona micelles (I2 staining: PDMAEMA black), c) micellar dimers (I2 staining: PDMAEMA black), e) micellar dimers (RuO4 staining: PCEMA black), and g) Janus nanoparticles (I2 staining: PDMAEMA black). Hydrodynamic radius distributions of b) core-corona micelles in isopropanol/acetonitrile (3:1 v/v), d) micellar dimers in water and h) Janus particles in acetone. PDI denotes polydispersity index obtained by the CONTIN analysis mode. The cartoon scheme in f) highlights importance of selective staining for TEM observation. The left inset in g) depicts the Fast Fourier Transform of the TEM micrograph.
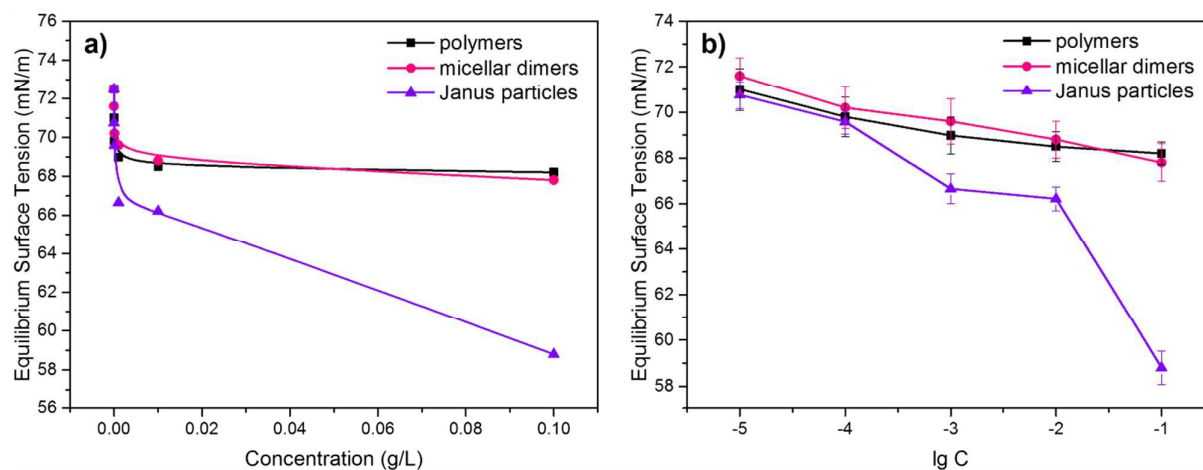
**Figure 2** Equilibrium surface tension as a function of a) concentration and b) logarithmic concentration of the polymers, the micellar dimers, and the Janus nanoparticles in water.
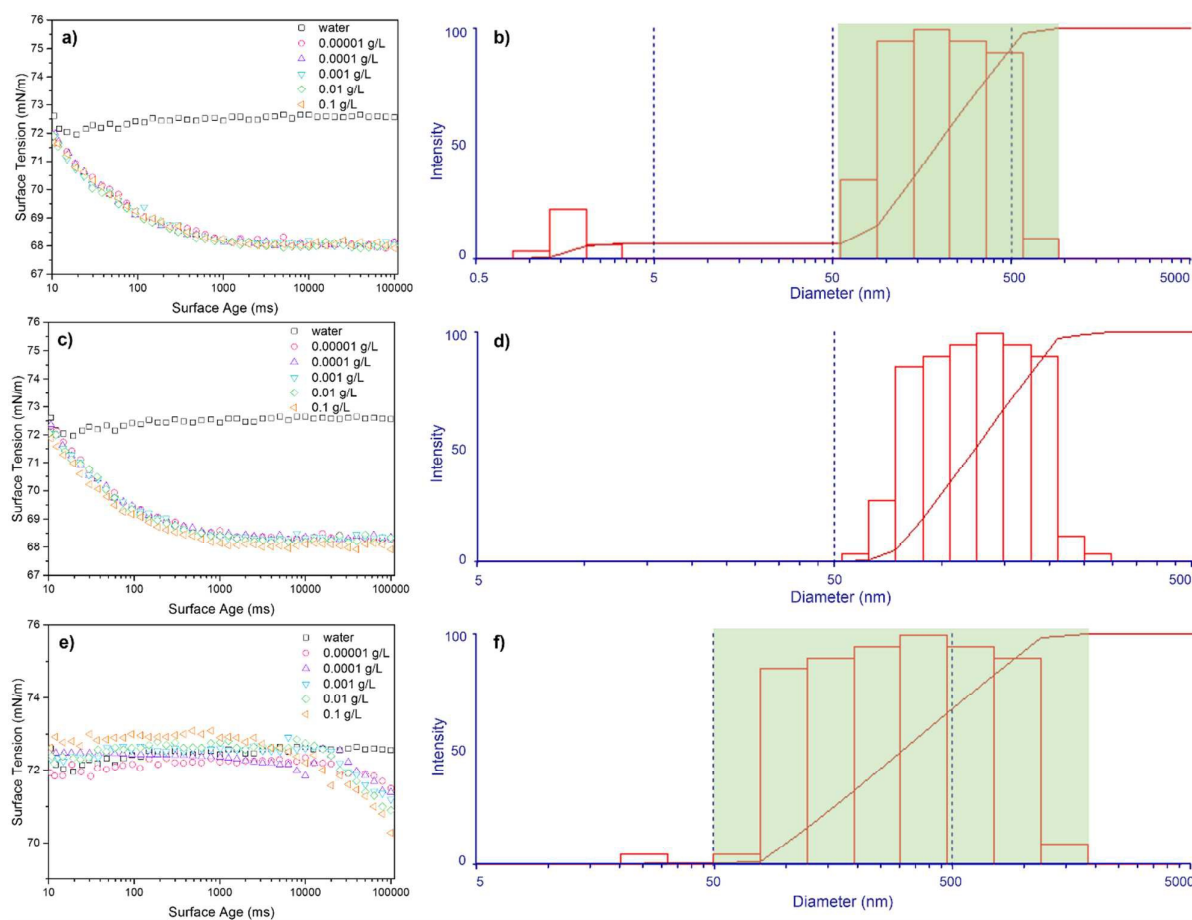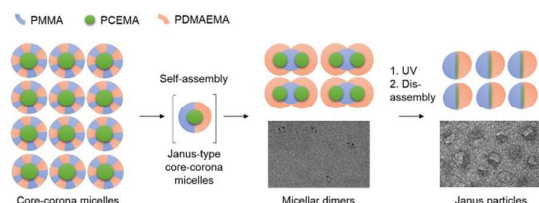


**Figure 3** Dynamic surface tension isotherms of a) the polymers, c) the micellar dimers and e) the Janus nanoparticles at varied concentrations. DLS size distributions of b) the polymers, d) the micellar dimers and f) the Janus nanoparticles, measured in water at the concentration of 0.1 g/L.



**Graphical Abstract**