## A Soluble Star-Shaped Silsesquioxane-Cored Polymer—Towards Novel Stabilization of pH-Dependent High Internal Phase Emulsion

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Figure S1. 3D molecular model and structural formula of  $CMSQ-T_{10}$ .



Figure S2. FTIR spectrum of CMSQ-T<sub>10</sub>.



Figure S3. <sup>29</sup>Si NMR spectrum of CMSQ-T<sub>10</sub>.



**Figure S4.** <sup>1</sup>H NMR spectrum of CMSQ-T<sub>10</sub>.



Figure S5. MALDI-TOF MS spectrum of CMSQ-T<sub>10</sub>.



Figure S6. Structural formula of cyanoisopropyl dithiobenzoate (CPDB).



Figure S7. <sup>1</sup>H NMR spectrum of cyanoisopropyl dithiobenzoate (CPDB).



Figure S8. <sup>29</sup>Si NMR spectrum of CMSQ/PDMA.



Figure S9. DSC curves of CMSQ-T<sub>10</sub> and CMSQ/PDMA.



Figure S10. FTIR spectra of PDMAEMA and CMSQ-T $_{10}$ /PDMAEMA star polymer.



Figure S11. TGA curves of PDMAEMA and CMSQ-T<sub>10</sub>/PDMAEMA star polymer.



**Figure S12.** Fluorescence emission spectra of 5-aminofluorescein and the product obtained from aza-Michael addition reaction of  $CMSQ-T_{10}/PDMAEMA$  star polymer and 5-aminofluorescein.

The number of polymer arms in the CMSQ-T<sub>10</sub>/PDMAEMA star polymer could be also proved by detecting the unreacted double bonds. We used 5-aminofluorescein as the marker to react with CMSQ-T<sub>10</sub>/PDMAEMA star polymer under a certain proportion. From the results of fluorescence emission spectra, we could calculate the number of the double bonds in the star polymer molecule. Generally, fluorescein possesses photoluminescence property due to its typical conjugated structure. The emission wavelength will change if the electron cloud density around the conjugated structure is interfered. 5-Aminofluorescein contains amino group, and its maximum emission wavelength lies at approximately 538.0 nm.<sup>[]</sup> We mixed the as-prepared PDMAEMA-star polymer with 5-aminofluorescein in proper quantity via aza-Michael addition reaction with cerium ammonium nitrate (CAN) as catalyst. Subsequently, the reaction product was purified and characterized by fluorescence spectrum detection.

As shown in Figure S10, the emission wavelength of the product was lied at approximately 523.0 nm, less than that of 5-aminofluorescein. This was likely to be attributed to the change of the electron cloud density around the conjugated structure between amino group and benzene ring of 5-aminofluorescein molecule after the reaction of amino and double bonds in PDMAEMA-star polymer molecules. We could conclude the existance of methacryloyl functions in the star polymer. The content of double bonds was analyzed quantificationally by the fluorescence intensity. The pure 5-aminofluorescein and the product obtained from aza-Michael addition reaction were measured with same qualities, and the star polymer reacted adequately by adding sufficient 5-aminofluorescein. The fluorescence intensity of pure 5aminofluorescein is approximately 74.0 a.u.; the product is about 3.03 a.u.. The molecular weights of CMSQ-T<sub>10</sub>/PDMAEMA star polymer and 5-aminofluorescein are 45700 and 347 g/mol, respectively. Therefore, we could calculate that the average number of double bonds engaged in aza-Michael addition reaction per star polymer molecule is 5.7. The result further verified the number of the PDMAEMA polymer arms in the star polymer molecules.



**Figure S13.** The AFM images of CMSQ/PDMA star-shaped polymer in different pH values.