

Star-like supramolecular polymers fabricated by a Keplerate cluster with cationic terminated polymers and their self-assembly into vesicles

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Materials and Instruments.

Both 11'-Bromoundecanyl-2-bromoisobutyrate and 11'-(*N,N,N*-trimethylammonium bromide) undecanyl-2-bromoisobutyrate were prepared according to ref. S1. The linear polymers of the ammonium-end poly(styrene) ($S_n^+Br^-$) were synthesized in situ ATRP according to ref. S2. Molecular weight data for ($S_n^+Br^-$) employed in this study were presented in Table S1. $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}] \cdot (H_2O)_{300} \cdot (CH_3COONH_4)_{10}$ (**1**) was prepared according to ref. S3.

IR spectra (KBr) were measured with a Nicolet NEXUS 670 spectrometer. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. Bright-field TEM and HAADF-STEM images, and EDX measurements were performed with a FEI Tecnai F30 operating at 300 kV. Elemental analyses were performed with an Elementar VarioELcube. UV-vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector. It used a series of columns at an oven temperature of 35 °C. The eluent was THF at a flow rate of 1.0 ml/min. PS standards were employed for the GPC calibration. Atomic force microscopy (AFM) measurements were performed on an Agilent SPM 5500 operated in tapping mode. Scanning electron microscopy (SEM) measurements were performed on a field emission scanning electron microscope (Hitachi S-4800). All measurements were tested at 20 °C except for GPC under the temperature of 35 °C.

Table S1 Molecular weights and their distributions of $S_n^+Br^-$.

Sample	M_n	M_w/M_n	n
1	13389	1.06	124
2	18061	1.08	169
3	23178	1.09	218
4	30683	1.16	290

Preparation and Characterization of PSP-1–PSP-4.

PSP-1 was prepared as follows: The Keplerate cluster of

(NH₄)₄₂[Mo₁₃₂O₃₇₂(CH₃COO)₃₀(H₂O)₇₂](H₂O)₃₀₀·(CH₃COONH₄)₁₀ (**1**) (8.31 mg, 2.9×10⁻⁷ mol) was dissolved in water, and then the red brown aqueous solution was vigorously stirred with solid powders of 11'-(*N,N,N*-trimethylammonium) undecanylisobutyrate terminated poly(styrene) (S₁₂₄⁺Br⁻) (102.7 mg, 7.7×10⁻⁶ mol) for 3 days. This process resulted in a completely ionic exchange reaction of **1** with S₁₂₄⁺Br⁻, which was easily judged by the fading aqueous solution and the red brownish product of PSP-1.

PSP-2, PSP-3, and PSP-4 were also prepared by using this method, but with S₁₆₉⁺Br⁻, S₂₁₈⁺Br⁻, and S₂₉₀⁺Br⁻, respectively.

The UV-vis and infrared spectra (IR) of PSP-1–PSP-4 showed the characteristic features of **1**. The IR spectra further indicated the presence of S_n⁺ blocks in the PSPs (Table S2 and Fig. S4).

Table S2. The assignment of infrared spectra of PSP-1, PSP-2, PSP-3 and PSP-4 in their solid state.

PSP-1	PSP-2	PSP-3	PSP-4	Assignment
3081, 3059, 3025	3079, 3059, 3025	3079, 3059, 3025	3081, 3059, 3025	ν _{C-H} (Ar)
2919, 2850	2918, 2848	2920, 2849	2920, 2848	ν _{C-H} (-CH ₂ -)
1944, 1870, 1800, 1750	1942, 1870, 1803, 1752	1940, 1871, 1802, 1748	1942, 1869, 1799, 1750	δ _{C-H} (Ar)
1600, 1492, 1450	1600, 1491, 1449	1600, 1491, 1449	1601, 1492, 1449	ν _{C=C} (Ar)
1541	1543	1544	1543	ν _{as} (COO)
1368, 1309	1369, 1311	1369, 1310	1371, 1311	δ _{C-H}
1153, 1065	1154, 1070	1154, 1068	1153, 1070	ν (C-O)
1027	1026	1027	1027	ν (C-N)
981, 938	978, 941	977, 940	980, 939	ν (Mo=O)
906, 863, 805	907, 863, 807	905, 863, 808	903, 863, 808	ρ (Mo-O-MO)
753, 697	754, 697	753, 696	753, 697	δ _{C-H} (Ar)
622, 572, 540	625, 571, 540	624, 572, 540	623, 567, 538	Mo ₁₃₂ skeletal vibrations

For PSP-1, UV-vis (CHCl₃): 474 nm, ε = 1.85×10⁵ M⁻¹ cm⁻¹, Elemental analysis calcd. for [Br(CH₃)₂COO(CH₂)₁₁N(CH₃)₃(C₈H₈)₁₂₄]₃₉(NH₄)₃[(H₂O)₅₀ ⊂ Mo₁₃₂O₃₇₂(CH₃COO)₃₀(H₂O)₇₂] 541049.27 : C 87.57, H 7.54, N 0.10. Found: C 87.69, H 7.42, N 0.

For PSP-2, UV-vis (CHCl₃): 474 nm, ε = 1.55×10⁵ M⁻¹ cm⁻¹, Elemental analysis calcd. for

$[\text{Br}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3(\text{C}_8\text{H}_8)_{124}]_{35}(\text{NH}_4)_7[(\text{H}_2\text{O})_{50} \subset \text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$
 651908.58 : C 88.45, H 7.57, N 0.08. Found: C 88.42, H 7.13, N 0.

For PSP-3, UV-vis (CHCl_3): 474 nm, $\epsilon = 2.24 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, Elemental analysis calcd. for $[\text{Br}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3(\text{C}_8\text{H}_8)_{124}]_{30}(\text{NH}_4)_{12}[(\text{H}_2\text{O})_{50} \subset \text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$
 715104.80 : C 88.88, H 7.58, N 0.06. Found: C 89.04, H 7.08, N 0.

For PSP-4, UV-vis (CHCl_3): 474 nm, $\epsilon = 1.84 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, Elemental analysis calcd. for $[\text{Br}(\text{CH}_3)_2\text{COO}(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3(\text{C}_8\text{H}_8)_{124}]_{25}(\text{NH}_4)_{17}[(\text{H}_2\text{O})_{50} \subset \text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$
 787153.70 : C 89.28, H 7.59, N 0.04. Found: C 89.69, H 7.10, N 0.

The elemental analyses indicated that PSP-1, PSP-2, PSP-3 and PSP-4 respectively have 39 ± 3 , 35 ± 5 , 30 ± 3 , and 25 ± 2 S_n^+ chains attached on the surface of **1**.

Preparation of vesicular aggregates: PSPs cannot be dissolved directly in the mixture of chloroform and methanol containing 50% methanol. To prepare the vesicular aggregates, all PSPs were dissolved first in chloroform and then methanol was added. The finally concentrations of PSPs in the solvent mixtures were controlled at 0.33 mg/mL.

Table S3. The collective data of PSP-1, PSP-2, PSP-3 and PSP-4.

	PSP-1	PSP-2	PSP-3	PSP-4
^a Cationic head area / nm ²	0.86	0.95	1.11	1.34
^b D_h in toluene / nm	2.4	2.4	2.6	2.6
^c Core diameter / nm	2.8±0.2	2.8±0.2	2.8±0.2	2.8±0.2
^d Total diameter / nm	26±3	28±2	29±2	33±1
^e D_h in chloroform/methanol mixture solvents (v/v = 1) / nm	105±8	110±5	115±6	120±3
^f Diameter of the vesicles / nm	50-170	70-160	65-140	40-110
^g Diameter of the vesicles / nm	60-150	60-350	50-130	50-115

^a The surface area of **1** divided by the number of the tethered chains is the cationic headgroup area.
^{b and e} obtained by DLS measurements at a concentration of 0.33 mg/mL. ^{c and d} obtained by TEM images of the casting films of the toluene solution without and with staining RuO_4 , respectively. ^{f and g} obtained by TEM and SEM images of the casting films of the chloroform/methanol mixtures containing 50% methanol.

Additional results and discussion.

(a) At the beginning, we try to prepare the PSPs by extracting an aqueous solution of **1** with S_n^+Br^- into dichloromethane, chloroform, or toluene. However, such phase-transfer reactions failed to obtain PSP-1, PSP-2, PSP-3, and PSP-4, although this method is successful to prepare organosoluble surfactant-encapsulated clusters (Ref. 8). Therefore, we prepared PSPs by using a heterogeneous method in aqueous phase, which was successful for the preparation of POM-block copolymer composites in our previous work (Ref. 9b). Basically, the Keplerate cluster of **1** was dissolved in water, and then the red brown aqueous solution was vigorously stirred with solid powders of S_n^+Br^- . The Keplerate cluster of **1** was somewhat excessive with the molar ratios between S_n^+Br^- and **1** controlled at 27:1, 26:1, 21:1, and 20:1, respectively, in contrast to their charge ratio of 1:42. During the stirring process, the ionic exchange between **1** and S_n^+Br^- occurred and was basically completed within one day judged by the fading aqueous solution and red brownish solids of PSPs. To obtain a full ionic exchange, the stirring time was prolonged to 3

days. Elemental analyses indicated that the final molar ratios between S_n^+ and **1** in PSP-1, PSP-2, PSP-3, and PSP-4 were 39:1, 35:1, 30:1, and 25:1, respectively. Therefore, **1** is always kept to be excessive during the stirring processes.

The UV-vis absorption spectra were used to monitor such an ionic exchange process in the aqueous solution. For example, the Keplerate cluster of **1** (6.0 mg, 2.1×10^{-7} mol) was dissolved in 15 ml water, and then the red aqueous solution was vigorously stirred with solid powders of 11'-(*N,N,N*-trimethylammonium) undecanoylisobutyrate terminated poly(styrene) ($S_{218}^+Br^-$) (100.0 mg, 4.3×10^{-6} mol). After one day, the absorbance of the band at 580 nm decreased from 1.203 to 0.386, indicating that 67.91% **1** was intercalated into the polymer. After three days, the absorbance was basically unchanged. The elemental analysis revealed that PSP-3 have $30 \pm 3 S_n^+$ chains attached on the surface of **1** with TMU groups by electrostatic interactions. This showed 68.55% ionic exchange degree of **1** with $S_{218}^+Br^-$, which rather consistent with the result monitored by UV-vis absorption spectra.

On the other hand, the $S_n^+Br^-$ molecules with a hydrophilic cationic head were not totally hydrophobic. During the stirring processes, the hydrophilic cationic head should stretch into water, similar to the behavior of the amphiphilic compounds at the air/water interface. In this sense, a local homogeneous microenvironment was established and therefore it was not strange that ionic exchange occurred during the stirring processes.

Combining these observations together with the previous studies on polyoxometalate/(macro)surfactant electrostatic self-assemblies (Ref. 8 and 9), we believe that such ionic exchanges were almost quantitative and all the S_n^+ chains is adsorbed on the cluster surface by electrostatic interactions. However, we cannot exclude the possible presence of a trace amount of free $S_n^+Br^-$ existing in PSPs.

(b) According to previous studies on POM-based organic/inorganic hybrids,^{1,2} 11'-(*N,N,N*-trimethylammonium) undecanoylisobutyrate (TMU), the cationic headgroup of S_n^+ chains should point to the negatively charged cluster surface as shown in Fig. 1 and Fig. S5. The PSP structure model is consistent with their solubility in common organic solvents, such as chloroform, dichloromethane or toluene. Therefore, actually, the molecular areas of S_n^+ should be the area of cationic headgroups attached onto the cluster surface by electrostatic interactions. The cationic headgroup areas of alkyltrimethylammonium were ca. 0.6 nm^2 (Ref. S4), which was somewhat smaller than the calculated values from 0.86, 0.95, 1.11, to 1.34 nm^2 in PSP-1, PSP-2, PSP-3, and PSP-4, respectively. In the star polymers, the S_n^+ segments were radiated from the cluster core **1** by electrostatic connections and the occupied areas of the S_n^+ segments increased with the increasing distance away from the core (Fig. S5). The molecular length of TMU was estimated to ca. 1.8 nm by assuming an all-trans conformation. And the TMU-encapsulated cluster (TEC) should have a total diameter of 6.4 nm, and thus the surface area of TEC was calculated to be ca. 128.70 nm^2 . Therefore, the interfacial areas between TMU and polystyrene were calculated to ca. 3.30, 3.68, 4.29, and 5.15 nm^2 , which were somewhat larger than the interfacial areas per chain of block ionmers in their suprastrong segregation micelles (Ref. S5). The order of the S_n^+ areas was consistent with the increase in their molecular weight and thus the easier formation of a relatively coiled S_n^+ chains on the cluster surface. On the basis of above considerations, there is enough space to accommodate the S_n^+ chains on the surface of **1** and the chains cannot adopt a random-coil conformation but are in a relatively coiled conformation or a somewhat stretched state.

(c) We also used hexane as a poor solvent for the replacing methanol, in which the precipitation occurred within 12 hours. This situation makes us to focus on chloroform/methanol mixture systems. The vesicles were extremely stable in the mixture

solvents of chloroform and methanol containing 50% methanol even after the solutions were prepared for ca. 6 months. Therefore, methanol not only acts as a poor solvent, but also keeps stable dispersions of PSP-1, PSP-2, PSP-3, and PSP-4.

References

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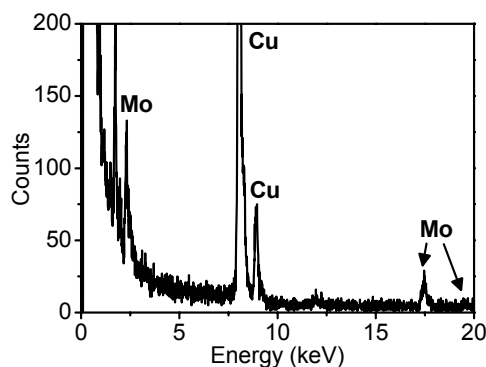


Fig. S1 EDX spectra of the casting film of PSP-2 toluene solution.

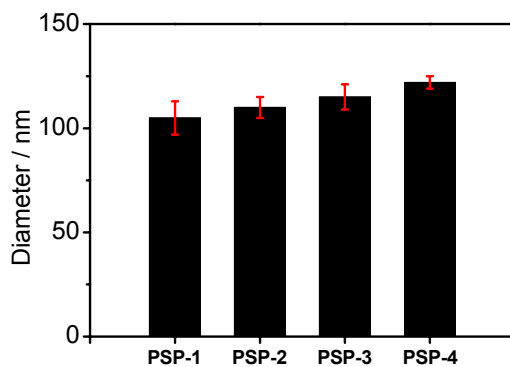


Fig. S2 The hydrodynamic diameters of PSP-1–PSP-4 measured from DLS in chloroform/methanol mixture solvents ($v/v = 1$, 0.33 mg/mL).

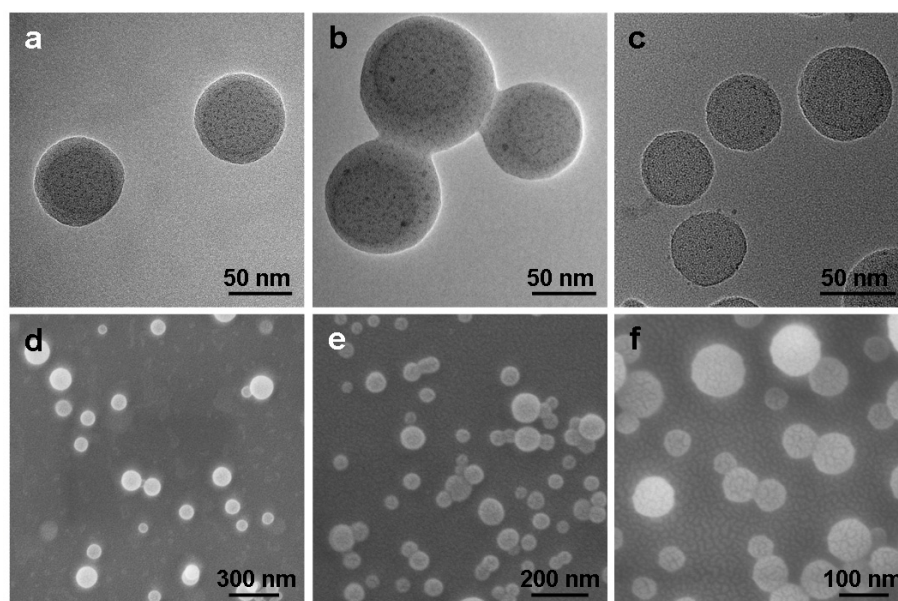


Fig. S3 BF-TEM and SEM images of PSP-1 (a and d), PSP-3 (b and e), and PSP-4 (c and f) as drop-cast from 0.33 mg/mL chloroform/methanol mixture solvent (v/v = 1).

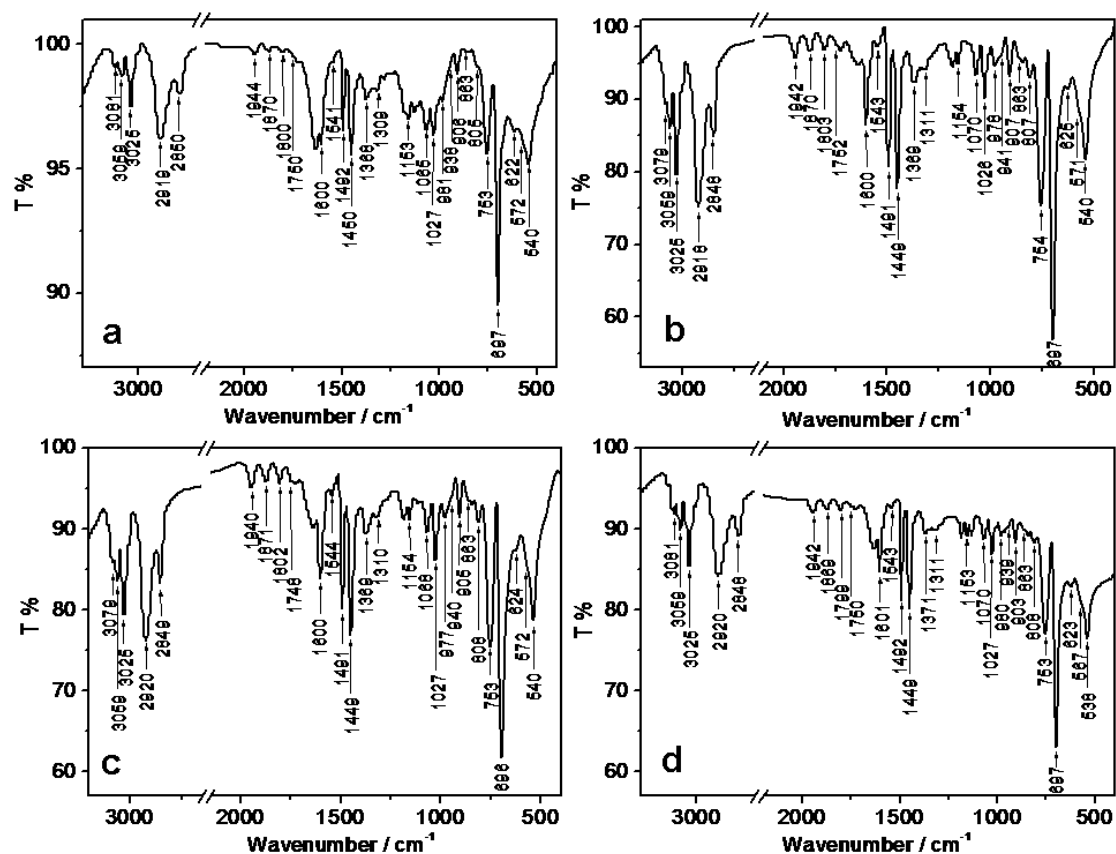


Fig. S4 The infrared spectra of PSP-1 (a), PSP-2 (b), PSP-3 (c), and PSP-4 (d).

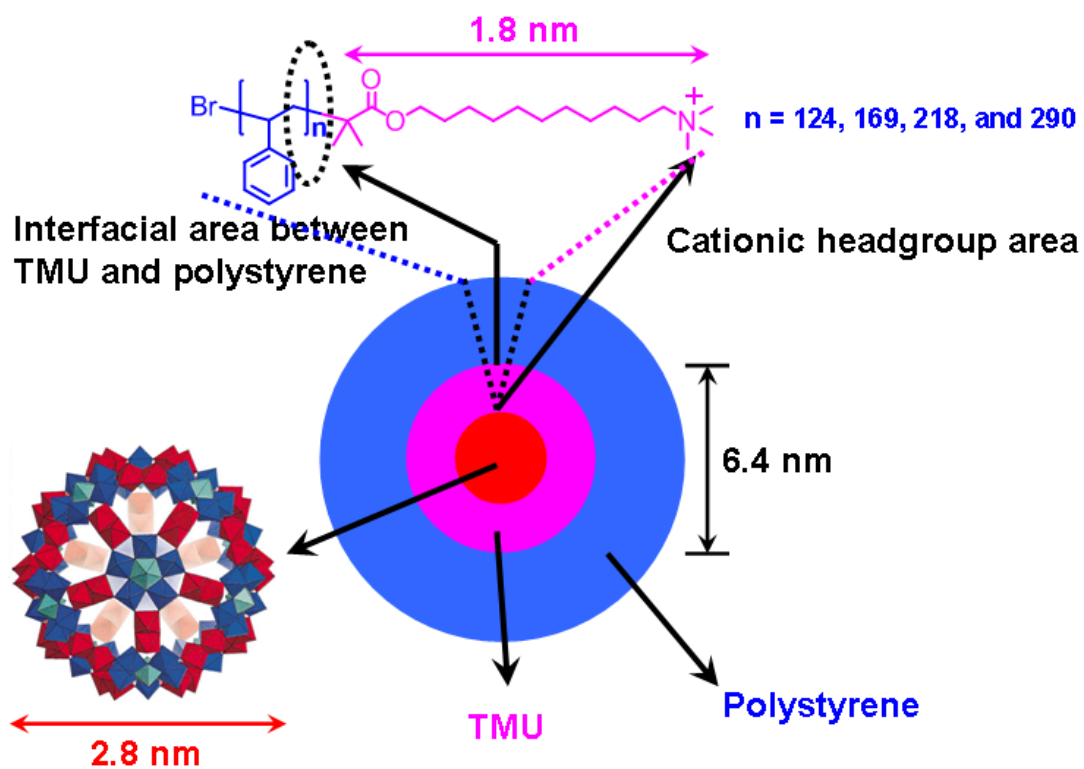


Fig. S5 The schematic illustration of POM-based star polymers with a **1** core and polystyrene shell.