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Graphic abstract

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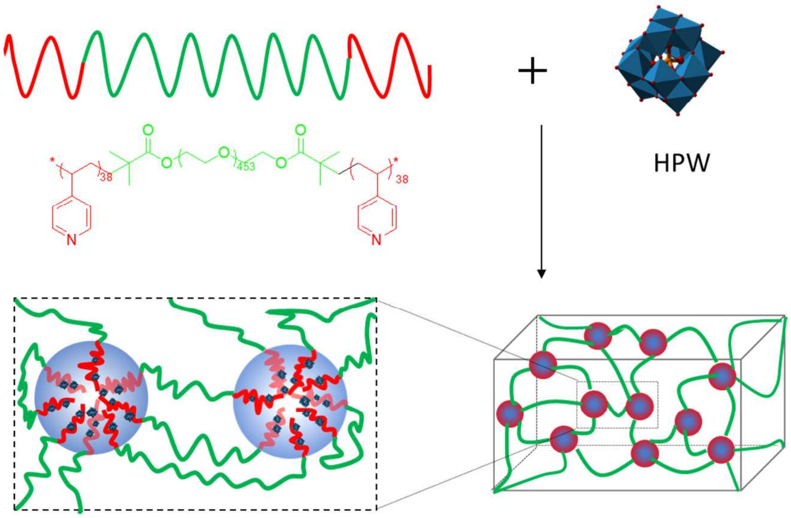

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Polyoxometalate-based hybrid organogels prepared from a triblock copolymer via charge-driven assembly

Tao Zhang and Qipeng Guo*

We report a novel approach for preparation of polyoxometalate-based hybrid organogels from a triblock copolymer via charge-induced assembly. The triblock copolymer used is poly(4-vinyl pyridine)-*block*-poly(ethylene glycol)-*block*-poly(4-vinyl pyridine) ($4VP_m$-EG_n-$4VP_m$), and polyoxometalate (POM) is phosphotungstic acid (HPW). The ionic interaction between the pyridine groups of the $4VP_m$-EG_n-$4VP_m$ and HPW drives the assembly of the triblock copolymer to form solvophobic cores. The PEG middle blocks connect and stabilize the different cores to form hybrid organogels. The structures of POM remain unchanged in these hybrid organogels, and the properties of POMs can be preserved, which has been confirmed by the existence of photo-reduction properties of POM in the hybrid organogels.

Introduction

Polyoxometalates (POMs) are discrete inorganic transition-metal oxide clusters with distinct size, charge and shape,[1] and they have obtained widespread applications[2] because of their properties from photochromism,[3] electrochromism,[4] magnetism,[5] catalysis [6] to chirality.[7] Most studies have been focused on the design and preparation of new POMs, and the growth of single crystals of POMs.[1, 8] However, the processing of POMs directly is still challenging because of their inherently large anions.[9] Considerable efforts have been made to build interfaces by modifying POMs for practical application.[10-12] The most applicable route to build bridges between POM and organic molecules are to modify POMs by covalent [10, 13] or non-covalent modifications.[5, 11] Compared to covalent modification, non-covalent modification has advantages such as easier purification and higher yield. In the last few years, some nanostructures such as nanofibers,[14] nanotubes,[15] nanocones [15] and nanosphers.[16] have been developed from surfactants encapsulating POMs. Non-covalent modification is through dynamic interactions, which provide a fast and controllable approach for POMs processing. However, most of the assembled materials failed to become available.

Recently, POM-based hybrid gels have attracted considerable attention.[16, 17] Wan and co-workers reported hybrid hydrogels from POMs and triblock copolymers, and the luminescence of the POMs was successfully preserved in the hybrid hydrogels.[16] Wang and co-workers reported hybrid organogels from POMs and surfactants, and the supramolecular organogels are an excellent platform for POMs processing.[17] However, organogels from surfactants and POMs are only suitable for certain POMs with specific structures, which limits the wide applicability. In order to process POMs effectively, novel approaches with general applicability for processing and applications of POMs are still required.

We have recently demonstrated that co-assembly of a triblock ionomer and a diblock copolymer or polypropylenimine dendrimers can be an effective approach to fabricate three-dimensional networks in organic solvents, and the assembly is dynamic, which has been verified by the responsiveness of the organogels to external environment.[18] Herein, we present a novel strategy for the preparation of block copolymer/POM hybrid organogels by charge-induced assembly. More specifically, hybrid organogels are prepared from a triblock copolymer, namely poly(4-vinyl pyridine)-*block*-poly(ethylene glycol)-*block*-poly(4-vinyl pyridine) ($4VP_m$-EG_n-$4VP_m$), and Keggin type POM, phosphotungstic acid ($H_3PW_{12}O_{40}$, denoted as HPW). Ionic interaction between POMs and polymers is quite common, and thus we believe this novel approach can be generally applied in the processing and applications of POMs materials.

Experimental

Preparation of hybrid organogels. Hybrid organogels were obtained by neutralization of the triblock copolymer, $4VP_m$-EG_n-$4VP_m$ (see ESI, 1), with HPW. $4VP_m$-EG_n-$4VP_m$ and POM were dissolved into *N,N*-dimethylformamide (DMF) to obtain 10 % (w/v) of triblock copolymer solution and 50 % (w/v) of POM solutions, respectively. Hybrid organogels with different ratios of $[H^+]/[4VP]$ were obtained by addition of different amount of POM solution to 1 ml of triblock copolymer solution. In the experiments, HPW solutions were used immediately after dissolving HPW into DMF. After addition of the triblock copolymer solution into HPW solution, the mixture was stirred acutely on a Vortex mixer.

Fourier-transform infrared (FTIR) spectroscopy. FTIR spectra of all samples were recorded on a Bruker Vertex 70 FTIR spectrometer. $4VP_{36}$-EG_{454}-$4VP_{36}$ solution (the subscripts denote the degrees of polymerization calculated from ^{1}H-NMR results; see ESI, 1), $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels, and HPW solution were dropped onto KBr disks, and the solvent was evaporated under vacuum at room temperature for 10 hours before measurement. The spectra were recorded by the average of 32 scans in the wavenumber range of 600 - 4000 cm^{-1} at a resolution of 4 cm^{-1}.

Rheological experiments. Rheological measurements were conducted on a TA DHR 3 rheometer with cone–plate geometry at 25 °C. A cone with a diameter of 40 mm and a tilt angle of 2° was used, and gap width was set to be 51 *u*m. A solvent trap was used to minimize the effect of evaporation. Frequency sweeps with an angular frequency from 0.1 to 600 rad s^{-1} were performed at a strain amplitude of 2.83 %. For accuracy, the results from 0.1 to 300 rad s^{-1} were used.

Photochromic behaviour. The photochromic behaviour was observed in an ELC-500 UV curing chamber with four 450 nm or 365 nm lamps.

Small-angle X-ray scattering (SAXS). SAXS experiments were carried out at the Australian Synchrotron on the small/wide-angle X-ray scattering (SAXS/WAXS) beamline. All the samples were put into a flat plate sample holder, and the background correction was carried out by measuring the scattering of air and correcting for sample absorption. The X-ray wavelength used is 1.0332 Angstrom, and the sample-to-detector distance is 3255 mm.

Results and discussion

Hybrid organogels formed in 10 to 30 seconds upon mixing $4VP_{36}$-EG_{454}-$4VP_{36}$ solution and HPW solution, and the formation of hybrid organogels was confirmed by tube-inversion method[19] (ESI, Movie: hybrid organogel formation). $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels prepared are transparent without visible heterogeneity, indicating that HPW is well-dispersed in the organogels. To our best knowledge, this is the first example of transparent hybrid organogels prepared from POMs and polymers. The $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels are slightly yellowish.

DMF was selected as solvent for POMs since HPW has high solubility in it,[20] and meanwhile, $4VP_{36}$-EG_{454}-$4VP_{36}$ is completely soluble in DMF. The strong interaction between P4VP blocks and POM was verified by the facts that insoluble P4VP/POM complexes formed when P4VP homopolymer and POMs solutions were mixed in DMF. Contrary to the instant precipitation of P4VP/POMs complex, no precipitate was formed when POMs solution was added to $4VP_{36}$-EG_{454}-$4VP_{36}$ solutions. This is because the PEG block is also highly soluble in DMF and when PEG block is long enough, it has the capability of avoiding precipitation of the P4VP/POMs complex.

The gelation behaviour of $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW is time-sensitive, and the organogel formation depends on the storage of POMs solutions. $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels were prepared by mixing the triblock copolymer solution with fresh HPW solutions, while no hybrid organogels formed when stored for 2 days' HPW solution was used. This interesting behaviour may result from the decomposition of DMF with strong acid.[21] After decomposition, the formic acid and dimethylamine from DMF react competitively with triblock copolymer and HPW, respectively, and prevent the complex formation between the triblock copolymer and HPW. The triblock copolymers with different compositions, i.e. $4VP_{87}$-EG_{227}-$4VP_{87}$ and $4VP_{11}$-EG_{136}-$4VP_{11,}$ were also employed to prepare hybrid organogels with HPW, but only white precipitates were obtained, displaying that macrophase separation happened.

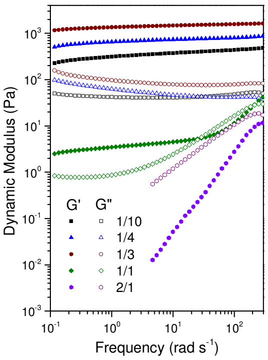

Fig. 1 Dynamic moduli G' (filled) and G" (hollow) of the $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels with $[H^+]/[4VP]$ = 1/10, 1/4, 1/3, 1/1 and 2/1 as a function of oscillatory shear frequency.

The formation of hybrid organogels was further confirmed by rheological measurements. Dynamic frequency sweep measurements of the hybrid organogels were carried out after mixing the $4VP_{36}$-EG_{454}-$4VP_{36}$ and HPW solutions in 30 seconds, and the results are plotted in Fig. 1. Fig. 1 shows that for the $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels with $[H^+]/[4VP]$ ratios of 1/10, 1/4 and 1/3, there is no crossover between the elastic modulus (G') and viscous modulus (G") in the frequency range from 0.1 to 300 rad s^{-1}, implying that the physical junctions in these hybrid organogels have a longer life-time than probed during the experiment. The G' is always higher than the corresponding G", showing rubber-like behaviour over the frequency range. The results also show that both G' and G" increase with the increase of $[H^+]/[4VP]$, indicating the hybrid organogels become stronger and stronger. However, when the $[H^+]/[4VP]$ ratio reaches to 1/1, G' and G" decrease with a crossover at about 30 rad s^{-1}, showing that the strength of the hybrid organogel is sensitive to rapid movement and the physical junctions in the hybrid organogel start to break at this critical frequency. Upon further increase of the $[H^+]/[4VP]$ ratio to 2/1, the rubber behaviour is replaced by liquid-like behaviour.

The interaction between $4VP_{36}$-EG_{454}-$4VP_{36}$ and HPW was revealed by Fourier transform infrared (FTIR) spectroscopy, and the results are given in Fig. 2. As shown in Fig. 2(a), the intensity of carbon–nitrogen stretching vibration of unprotonated pyridine rings at 1598 cm^{-1} decreases with the addition of HPW. Meanwhile, a new absorption band appears at 1633 cm^{-1}, which is the characteristic absorption of protonated pyridine rings on P4VP. The decrease in intensity of pyridine absorption and the appearance of new peaks can be attributed to the formation of pyridnium replacing pyridine.[22] The result verifies that it is ionic interaction between $4VP_{36}$-EG_{454}-$4VP_{36}$ and HPW.

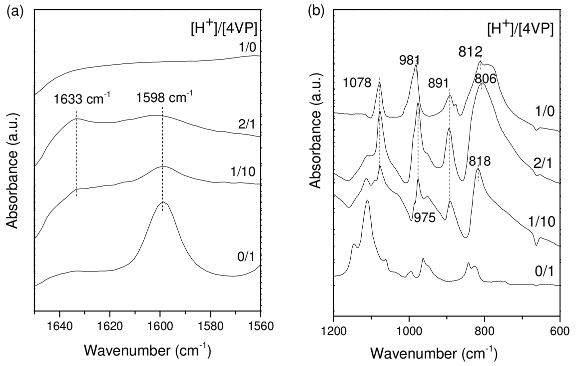

Fig. 2 FTIR spectra of $4VP_{36}$-EG_{454}-$4VP_{36}$ ($[H^+]/[4VP]$ = 0/1), HPW ($[H^+]/[4VP]$ = 1/0) and $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels with $[H^+]/[4VP]$ = 1/10 and 2/1 in the ranges of (a) 1650-1560 cm^{-1} and (b) 1200-600 cm^{-1}.

The structures of HPW in the hybrid organogels were also studied by FTIR and the results are shown in Fig. 2(b). HPW has four characteristic bands, which are the fingerprint of the Keggin structure.[23] There are four kinds of oxygen atoms in HPW (O_a, oxygen in the PO_4 tetrahedron; O_b, corner sharing oxygen; O_c, edge sharing oxygen; O_d, terminal oxygen atom to W) giving rise to characteristic bands at ν_{as} (P-O_a) 1078 cm^{-1}, ν_{as} (W-O_b-W) 891 cm^{-1}, ν_{as} (W-O_c-W) 812 cm^{-1} and ν_{as} (W-O_d) 981 cm^{-1}. The FTIR spectra of $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels are in agreement with a superposition of the spectra of parent HPW and $4VP_{36}$-EG_{454}-$4VP_{36}$ triblock copolymer, suggesting that the Keggin structure stayed intact upon organogel formation.

The slight shift in wavenumbers observed for both W-O-W vibrations (corner and edge shared) is likely due to the anion-anion repulsion between oxygens of the neighbouring PW anions after HPW incorporated in the P4VP block. Thus the shift in the frequencies further verified the existence of ionic interaction between $4VP_{36}$-EG_{454}-$4VP_{36}$ and HPW.[23]

To elicit the morphology of the hybrid organogels, small-angle X-ray scattering (SAXS) measurements for all samples were performed at room temperature, and their profiles are shown in Fig. 3(a). As expected, no peak is observed for $4VP_{36}$-EG_{454}-$4VP_{36}$ solution, indicating no microphase separation in the triblock copolymer solution. Well-defined peaks are observed for $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels, and q values are dependent on the $[H^+]/[4VP]$. From q value, it is calculated that the average distance between neighbouring domains varies from 31 to 51.9 nm for hybrid organogels with different $[H^+]/[4VP]$. The first peaks for hybrid organogels with $[H^+]/[4VP]$ = 1/6 and 1/8 are narrower, implying more order structures in these two hybrid organogels.

Quantitative information on size and distribution of the spherical microdomains was obtained by fitting the SAXS experimental data to a spheres and shell model with a structure factor of hard spheres and a form factor of star polymers. Fig. 3(b) shows the fitting curves with a hard-sphere radius of 15.8 nm for $[H^+]/[4VP]$ = 1/5. The cores originate from the solvophobic ionic complexes between the P4VP blocks of the $4VP_{36}$-EG_{454}-$4VP_{36}$ and HPW. The middle PEG blocks of the triblock copolymer connect and stabilize the different cores to form a three dimensional networks.

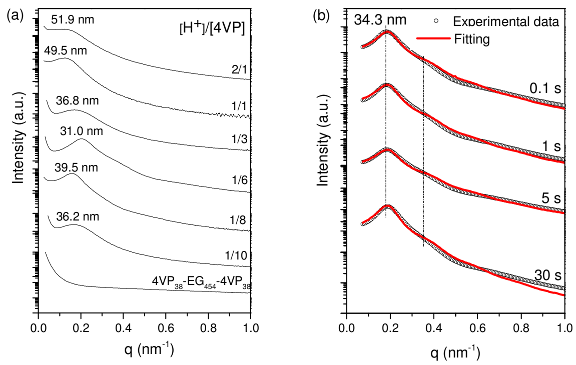

Fig. 3 (a) SAXS profiles for $4VP_{36}$-EG_{454}-$4VP_{36}$ solution and $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels with $[H^+]/[4VP]$ = 1/10, 1/8, 1/6, 1/3, 1/1 and 2/1; (b) SAXS curves for the $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogel with $[H^+]/[4VP]$ = 1/5 at exposure time of 0.1, 1, 5 and 30 seconds. The full lines in (b) show the fitting curves according to a spheres and shell model.

The hybrid organogels turned blue upon exposure to X-ray, and it is believed that the photochromic behaviour of the hybrid organogels results from the photo reduction of tungsten.[3] The results show that the photochromic properties of HPW are preserved in the hybrid organogels. The reduction effects of HPW on the morphology of the $4VP_{36}$-EG_{454}-$4VP_{36}$/HPW hybrid organogels were studied. The SAXS experiments showed that the hybrid organogel turned blue upon the exposure to X-ray as fast as in 0.1 seconds, and the SAXS data collected with exposure times from 0.1 to 30 seconds are shown in Fig. 3(b). It is noted that the shapes and positions of the peaks do not vary with the exposure time, indicating the structures of hybrid organogels remained unchanged at the nanometre scale during the photo-reduction process.

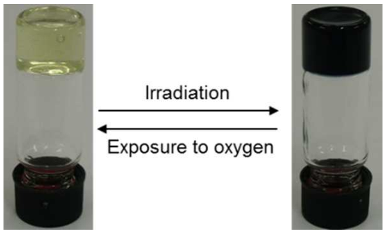

Fig. 4 Reversible photochromic behaviour of the hybrid organogels when irradiated with UV light.

It is interesting to find that both X-ray and UV light (at 450 or 365 nm) can induce the photochromic behaviour of the hybrid organogels. However, a longer exposure time (several seconds) is needed for UV light to turn the hybrid organogels blue. The photochromic time is quite shorter in comparison with organogels from surfactants and POMs reported by others.[17] The colour faded when the hybrid organogels were exposed to air for about half a day, and the colour change is completely reversible (Fig. 4). Furthermore, the dark blue hybrid organogels were put in oxygen and nitrogen atmosphere, respectively, and the decolouration was faster in oxygen than in nitrogen.

Conclusions

In conclusion, we have established a novel approach for preparation of polyoxometalate-based hybrid organogels from a triblock copolymer through charge-induced assembly. As the structures of POMs in the hybrid organogels remain unchanged, it is expected that the properties of POMs can be preserved. Ionic interaction between POMs and polymers is quite common and hybrid organogel is a good platform for POMs processing. We believe this approach is generally applicable in the processing and applications of POMs materials.

Acknowledgements

The SAXS measurements were conducted on the SAXS/WAXS beamline at the Australian Synchrotron, Victoria, Australia, and we would like to thank Dr Adrian Hawley for his technical assistance.

Notes and references

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Electronic Supplementary Information (ESI) available: [Synthesis and Characterization of $4VP_m$-EG_n-$4VP_m$, SAXS Fitting and, Movie]. See DOI: 10.1039/b000000x/

1 Y. F. Song and R. Tsunashima, *Chem. Soc. Rev.* 2012, **41**, 7384.

2 H. Zeng, G. R. Newkome and C. L. Hill, *Angew. Chem.* 2000, **112**, 1841; T. Yamase, *Chem. Rev.* 1998, **98**, 307; D. Fan, X. Jia, P. Tang, J. Hao and T. Liu, *Angew. Chem.* 2007, **119**, 3406.

3 T. He and J. Yao, *Prog. Mater. Sci.* 2006, **51**, 810.

4 T. Zhang, S. Liu, D. G. Kurth and C. F. J. Faul, *Adv. Funct. Mater.* 2009, **19**, 642.

5 J. M. Clemente-Juan, E. Coronado and A. Gaita-Arino, *Chem. Soc. Rev.* 2012, **41**, 7464.

6 J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.* 2011, **133**, 16839.

7 H. Tan, Y. Li, Z. Zhang, C. Qin, X. Wang, E. Wang and Z. Su, *J. Am. Chem. Soc.* 2007, **129**, 10066.

8 D. L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.* 2007, **36**, 105.

9 A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh and G. Izzet, *Chem. Soc. Rev.* 2012, **41**, 7605.

10 D. Ma, L. Liang, W. Chen, H. Liu and Y.-F. Song, *Adv. Funct. Mater.* 2013, **23**, 6100.

11 P. Yin, T. Li, R. S. Forgan, C. Lydon, X. Zuo, Z. N. Zheng, B. Lee, D. Long, L. Cronin and T. Liu, *J. Am. Chem. Soc.* 2013, **135**, 13425.

12 D. L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed.* 2010, **49**, 1736.

13 J. Zhang, Y. F. Song, L. Cronin and T. Liu, *J. Am. Chem. Soc.* 2008, **130**, 14408.

14 X. Lin, Y. Wang and L. Wu, *Langmuir* 2009, **25**, 6081.

15 A. Nisar, J. Zhuang and X. Wang, *Chem. Mat.* 2009, **21**, 3745.

16 H. Wei, S. Du, Y. Liu, H. Zhao, C. Chen, Z. Li, J. Lin, Y. Zhang, J. Zhang and X. Wan, *Chem. Commun.* 2014, **50**, 1447.

17 P. He, B. Xu, H. Liu, S. He, F. Saleem and X. Wang, *Sci. Rep.* 2013, **3**, 1833.

18 T. Zhang and Q. Guo, *Chem. Commun.* 2013, **49**, 5076; T. Zhang and Q. Guo, *Chem. Commun.* 2013, **49**, 11803.

19 A. R. Hirst and D. K. Smith, *Langumir* 2004, **20**, 10851.

20 X. Lin, F. Liu, H. Li, Y. Yan, L. Bi, W. Bu and L. Wu, *Chem. Commun.* 2011, **47**, 10019.

21 J. Muzart, *Tetrahedron* 2009, **65**, 8313.

22 O. Ikkala, J. Ruokolainen, G. t. Brinke, M. Torkkeli and R. Serimaa, *Macromolecules* 1995, **28**, 7088.

23 W. Xu, C. Liu, X. Xue, Y. Su, Y. Lv, W. Xing and T. Lu, *Solid State Ionics* 2004, **171**, 121.