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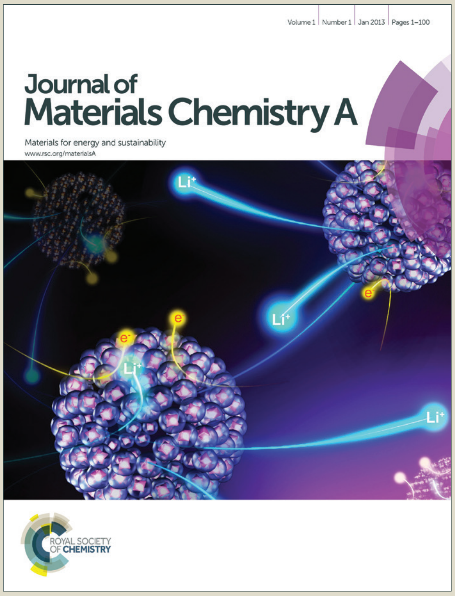

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Journal of

Materials Chemistry A

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ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Facile Preparation of Porous Polymeric Composite Monoliths with Superior Performances in Oil/Water Separation–A Low-molecular Mass Gelators-based Gel Emulsion Approach

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A series of water in oil (W/O) gel emulsions was prepared by using a low-molecular mass gelator (LMMG), a ferrocene derivative of cholesterol, as a stabilizer and tertiary butylmethacrylate (*t*-BMA) as the continuous phase. Via polymerization of the emulsions as created, a series of porous polymeric monoliths with different internal structures was prepared. SEM observation reveals that the internal structures of the monoliths could be largely adjusted via simple variation of the compositions of the gel emulsions. Importantly, introduction of hydrolysable silanes into the continuous phase of the gel emulsion before polymerization significantly alters the mechanical strengths of the porous materials, and remarkably promotes the sorption of the porous materials to some water immiscible and miscible liquids, such as benzene, kerosene, already used transformer oil, ethanol, tetrahydrofuran, etc., of which kerosene is a representative of oils of lower viscosities and the transformer oil a representative of oils of higher viscosities. Furthermore, the oil absorbed by the monoliths could be recovered by centrifugation or squeezing, and the monoliths could be reused by washing them with alcohol or some other suitable volatile organic liquids. The sorption and desorption process could be repeated for at least 13 times. More importantly, the LMMGs-based gel emulsion approach established in the present study for preparing porous polymeric or composite monoliths is facile, versatile and environmentally benign, showing bright future for real-life uses.

Introduction

Creation of porous and low-density polymeric and/or inorganic-organic composite monoliths with good mechanical strength has attracted great attention during the last few decades due to their potential and important real-life applications, including but not limited to catalyst supporting, purification or separation of contaminated liquids or gases, energy storage, structural and even shielding materials, etc.[1-14] Among them, fast and efficient treatment of oil spills, which frequently happens during oil extraction, storage, transportation, and uses, etc., is particularly important because oil spills not only cause waste of valuable resource, but also have long-term damaging impacts on the ecological system upon which our society relies.[15-23] The recent Gulf of Mexico oil-spill[17] and Qingdao oil pipeline blast[24] remind us again of the importance of oil spill cleanup and environmental remediation. It is well known that conventional methods dealing with oil spills are manpower collection, mechanical extraction, absorbent sorption, in situ burning, and bioremediation, etc., of which, however, sorption by absorbents is the most efficient one, in particular for the cleanup of the last residual spills.[19,23] Clearly, the efficiency of the method is highly dependent upon the structures of the absorbents selected, which are normally hydrophobic and porous materials.

In terms of practical uses, the mechanical strengths of the oil absorbents should be good enough, and the possibility for repeated uses is highly concerned. However, preparation of the materials with ideal structures and performances through routine methods is not an easy job even though some extraordinary efforts have been made and some great achievements have been obtained. As examples, Jiang and co-workers developed a very smart oleophilic array of conical needle structures very recently, which mimics the structure of conical spines of cactus.[15,16,25] It was reported that the materials as created function as collectors of oil by sorption of micro-sized oil droplets from water in a continuous manner. Nakanishi and coworkers prepared a new kind of super-hydrophobic materials, and used them as sponges to absorb oil from water.[26] The materials could be recovered by simply squeezing out the oil. Yu and colleagues reported a facile method for the preparation of a new type of monolithic aerogels consisting of carbon nanofibers (CNFs) through a template directed hydrothermal carbonization process.[27] By exploiting the high surface reactivity of the CNFs, the extra-high porosity

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and the robust mechanical properties of the aerogels, they demonstrated the great potential of the materials for simple removal of dye pollutants and oil-spills from water. However, all these methods suffered from drawbacks such as complicated preparation processes, and high costs for reagents and devices, which may prevent their real-life uses. Therefore, it still remains a challenge for developing novel strategies or approaches for creating porous polymeric monoliths with superior sorption properties to oil from oil-water mixtures.

Gel emulsion, which is also named as high internal phase emulsion (HIPE),[28,29] has long been used for the preparation of interconnected porous polymeric monoliths, the so called "polyHIPE".[30] As reported in the literatures, the monoliths prepared by the gel emulsion-based method possess ultra-high permeability though their mechanical strengths are generally weak.[31,32] Furthermore, the internal structures that is the pore structures and sizes of them could be easily adjusted by varying the compositions of the emulsions.[33] Successful preparation of a "polyHIPE" is dependent upon selection of a suitable stabilizer, which is used to stabilize the gel emulsion, and optimized formulation of the gel emulsion under polymerization. The stabilizers as afore-mentioned could be surfactants, micro-/nano-particles, and possibly low-molecular mass gelators (LMMGs), in particular cholesteryl derivatives as reported by our group recently.[34-36] As an important class of LMMGs, cholesteryl derivatives have been extensively studied for more than two decades, and even today they still remain as an actively investigated class of compounds.[37-41] As stabilizers, surfactants are used more frequently than others but they are not very efficient because 5~50% (w/v) of the volume of the continuous phase is required in most of the formulations reported, which may explain why the mechanical strengths of the porous monoliths are generally weak. As for micro-/nano-particles, gel emulsions stabilized by them may suffer from phase-inversion problems, in particular when the volume fraction of the dispersed phase reaches 0.65 to 0.70.[42-45] In contrast, the gel-emulsions created by using LMMGs as stabilizers may be formed and stabilized in a way different from routine stabilizers that is the continuous phase presents in a gel form and the dispersed phase is deposited or physically trapped within the continuous phase. This may explain why much lower amount of stabilizer is required for the formation of the gel emulsions when LMMGs are used as stabilizers. It is well known that for LMMGs-based molecular gels, the gelator concentration, generally speaking, in them is 2% or less than that (w/v). Compared to other kinds of LMMGs, cholesteryl derivatives are much more efficient due to their superior self-assembling properties,[46-49] which lay foundation for their template applications in the preparation of porous polymeric monoliths with superior properties.

Herein, some new gel emulsions with water insoluble monomers and some of the hydrolysable silanes as continuous phase and a ferrocene derivative of cholesterol as a stabilizer were created and used for the preparation of porous polymeric monoliths with superior performances in efficient sorption of kerosene or already used transformer oil from their mixtures with water. This paper reports the details.

Experimental Section

Materials

The details of the preparation and characterization of compound **1** (c.f. Figure 1), the LMMGs, were reported in a previous publication.[50] Tertiary butyl methacrylate (*t*-BMA, 99%, Sigma-Aldrich) and divinylbenzene (DVB, Aldrich) were purified before use by passing through a neutral aluminum oxide column to eliminate the pre-added inhibitor in the reactants. After purification, the monomer and the cross-linker were stored in a freezer if they were not used directly. 2,2′-Azobis(isobutyro-nitrile) (AIBN, 97%) was purchased from Sigma-Aldrich, and used without further purification. The silanes, including 3-aminopropyltriethoxysilane, 3-isocyanato-propyltriethoxysilane, triethoxyoctadecylsilane and tetraethoxy-silane (TEOS), were purchased from Alfa Aesar, and used without further purification. All solvents used in the studies were purified in the way as described in solvents handbooks. Water used throughout was doubly distilled. Other reagents were of, at least, analytical grade, and used directly.

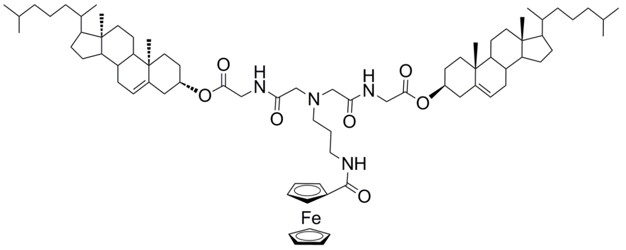

Fig. 1 Molecular structure of compound **1**.

Gel emulsion preparation

The gel emulsions used in the present studies could be prepared in the way as described below. For a typical system, its internal phase or dispersed phase is water, which accounts 80% of the total volume of the gel emulsion to be prepared, and the remaining is the continuous phase, which contains nearly 87% of *t*-BMA, 10% of DVB, 2% of compound **1**, and 1% of AIBN. To make a gel emulsion, a given amount of water was added, in a drop-wise manner, into the organic phase under stirring, and then the system (a homogeneous emulsion) becomes a gel after several hours leaving at room temperature. For the introduction of silanes, two different ways were adopted. One is dissolved into the continuous phase, the oil phase, directly, and the other is physically dispersed into the dispersed phase, water, since they are water insoluble.

Porous polymeric monolith preparation

The gel emulsion as prepared was heated to 40 ºC and maintained at the temperature for 2 h in an oil bath to start pre-polymerization, then the temperature of the bath was raised to 85 ºC and maintained at the temperature for another 20 h to complete the polymerization, and then, the solid as prepared was extracted with methanol in a Soxhlet extractor for more than 3 h to remove the impurities inside. Finally, the polymeric monolith was naturally dried at ambient temperature until its weight became constant.

Characterization of the monoliths

SEM observation

The diameters of the pores and pore throats of the porous polymeric or composite monoliths as prepared were semi-quantitatively calculated by using the images taken on a Quanta 200 Scanning Electron Microscopy spectrometer (Philips-FEI, 15 kV and 10 mA). Prior to observation, approximately 1 cm^3

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of each sample was mounted on a sample holder and sputtered with gold for 80 s to ensure sufficient conductivity. The pore size was also measured through the SEM images using software of Image J. The pore sizes of the porous materials as created were measured in a way adopted by Chen Zhang, that is for each measurement, more than 100 pores were taken into account.[51]

FTIR measurements

The FTIR spectra of the monoliths were recorded in transmission mode using a Bruker VERTEX 70V infrared spectrometer. The monolith sample for FTIR measurement was prepared by mixing a small amount of it with some KBr crystals, then grading, and then pressed into a disc.

TGA measurements

Thermogravimetric analysis (TGA) was conducted on a thermal analyzer (Q1000DSC+LNCS+FACS Q600SDT). All the measurements were run at a heating rate of 10℃/min from 15 to 700℃ in oxygen atomosphere.

Mechanical measurements

Mechanical testing under compression with an CTM 2500 universal testing machine frame, following the testing procedures and specimen length (2.0 cm) to diameter (1.0 cm) ratio specified in ASTM D1621-04a (Standard Test Method for Compressive Properties of Rigid Cellular Plastics).

Hydrophilic and lipophilic tests

The contact angle of the monolith was measured in a routine way on a Dataphysics OCA20 contact-angle system at ambient temperature.

Oil sorption test

To analyze the absorption capacity of a monolith, the monolith with known weight was placed in a small glass beaker filled with 10 mL of a neat organic liquid under test. After a certain time of absorption, the wet monolith was drained for 5 min until no residual droplet left on the surface. The absorption capacity was then calculated via the following equation.

$$q = \frac{m_s - m_0}{m_0}$$

Where q is the absorption capacity (g/g), m_s is the weight of the wet monolith after 5 min of drainage (g), and m_o is the initial weight of the monolith (g). As for absorption capacity represented in a way of g/cm^3, the value can be calculated by times of the q with ρ, the density of the corresponding absorbent.

Reusability test of the monoliths

To test the reusability, a wet monolith was centrifuged as hard as possible to get rid of the oil absorbed. The monolith was then washed completely with alcohol or some other suitable volatile organic solvent, followed by simple air-drying. Finally, the regenerated porous monolith was reused for the selective absorption of oil from water. This absorption and regeneration process was repeated for several times with kerosene-water as an example of oil-water mixture system.

Results and Discussion

Stability of gel emulsions

The stability of a gel emulsion means its resistance to transform from a macroscopically homogeneous water-in-oil gel emulsion to two separate macroscopic phases. Clearly, the preparation of porous polymeric monoliths via polymerization of the continuous phase of a gel emulsion has to face the problem of its stability during the process. Therefore, stable gel emulsions must be created before any porous polymeric monoliths could be produced via the approach.

Table S1 shows the influence of the nature of some monomers and the volume fraction of the dispersed phase (water) to the stability of the relevant gel emulsion, of which a certain amount of compound **1** (2%, w/v, of the organic phase) was introduced as a stabilizer. Reference to the data provided in the Table S1 reveals that both the nature of the monomers under study and the volume fraction of the dispersed phase show great effect upon the stability of the corresponding gel emulsion. For example, for gel emulsions with *t*-BMA as the continuous phase, the stability of them varies from 25 min to more than 48 h depending on the specific volume fraction of the dispersed phase. However, for gel emulsions with other hydrophobic monomers as continuous phase, the stability of them is much weaker, varying from a few minutes to a few hours. It is well known that for routine gel emulsions, the volume fraction of the dispersed phase should exceed 0.74, which could be simply calculated from the principles of geometrics via adopting a dense packing model.[52,53] It is of this reason that the systems containing 80, 85 and 90% of the dispersed phase were studied (c.f. Table S1). However, the gel emulsions of greater volume fractions of the dispersed phase can be also prepared even though their stability may not be as good as those depicted in the Table. The highest volume fraction of the dispersed phase for this system with the concentration of the stabilizer fixed at 2% (w/v) of the organic phase is around 95%. Of course, a greater volume fraction may be achieved by increasing the concentration of the stabilizer in the system. With regard to the stability of the gel emulsions and the convenience of the following preparation process, the gel emulsion with 80% of water was adopted as a template to conduct the following experiment.

Pore structures

Fig. S1 depicts the SEM images of the porous polymeric monoliths prepared from gel emulsions containing 1%, 2%, and 3% of the stabilizer (accounts for the monomer, w/v), respectively. With reference to the images, in particular those of greater magnification numbers (left hand column), it is seen that the concentration of the stabilizer in the gel emulsions shows great effect upon the internal structures of the final polymeric monoliths. For example, compared to the structure of the monolith prepared from the template containing 1% of the stabilizer, the one prepared from the template with 2% of the stabilizer possesses more small pores which locate in the walls of the big or fundamental pores (c.f. pictures a and b of Fig. S1). Furthermore, with increasing the stabilizer concentration from 1% to 2% makes each pore in the polymeric monolith contain several throats. However, with further increase in the stabilizer concentration, the pore cracks, and the uniformity of the pores decreases. These results may be understood by considering the properties of the gel emulsions. Studies of the system of the stabilizer/*t*-BMA demonstrate that its viscosity increases along with increasing the stabilizer concentration below the critical gelation concentration (CGC) of the system, and above the concentration, the system becomes a gel, of which the hardness increases along with increasing the concentration. This may explain why the internal structures of the polymeric monoliths changes along with the changing of the stabilizer concentration in the template under study because both increasing in viscosity and in hardness of the organic phase (continuous phase) improves the stability of the gel emulsion, and resists the coalescence and Ostwald

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ripening,[44,52-54] which is favorable for maintaining the initial structures of the gel emulsions and avoids increasing of the average void diameters of the resulting porous polymeric monoliths. However, further introduction of the stabilizer (e.g. 3% w/v) resulted in significant cracking of the void walls, a result not good for future uses (Fig. S1c).

From the uniform surface structures of the void walls of the final porous polymeric monoliths, one may deduce that before water was removed the molecules of the stabilizer might be mainly dissolved within the organic phase, which is in agreement with the fact that it is an efficient gelator of the organic phase. Gelation of the organic phase makes the micro-sized water-drops being physically trapped within it, inhibiting accumulation of the water-drops.

Interrogation of the effect of the concentration of the cross-linker, DVB, on the internal structure of the porous polymeric materials revealed that the concentration of DVB shows remarkable effect on the structures, and 10% (v/v) of it is more suitable for getting a relatively homogeneous and unbroken structure (c.f. Fig. S2). This result indicates that DVB may show double-faced effect on the stabilization of the gel emulsion and subsequent structures of the final porous materials, that is at one hand addition of DVB enhances the stability of the gel emulsion by increasing the strength of the continuous phase via cross-linked polymer formation, which must be favorable for formation of a final product possessing ideal structures, but at another hand addition of it may also cause de-stabilization of the system or cracking of the continuous phase due to excessive cross-linking of the continuous phase.[30,55,56] After optimization of the parameters, a stable gel emulsion was obtained, of which the recipe is listed in Table 1:

Table 1 A typical recipe of a stable gel emulsion

	Components	Amounts
Organic phase continuous phase	Monomer	18% of the total volume (v/v)
	Stabilizer	2% of the monomer (w/v)
	Cross-linker	10% of the monomer (v/v)
	Initiator	1% of the monomer (v/v)
Aqueous phase dispersed phase	Water	80% of the total volume (v/v)

With this recipe, a low-density, highly porous poly-*t*-BMA monolith was obtained, of which the average pore diameter is about 60 μm, the bulk crush strength 1.2 MPa, and the density 0.21 g/cm^3. The SEM images of the internal structures of this monolith (M-1) are shown in Fig. 2.

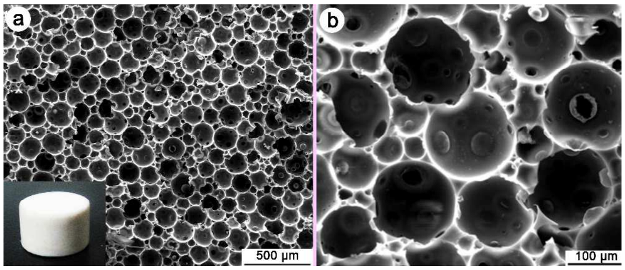

Fig. 2 A photo of the porous monolith (inset of the SEM image on the left), M-1, and the SEM images of its internal structures with different magnification times.

Modification of the porous polymeric monoliths

Influence of tetraethoxysilane (TEOS)

In terms of practical uses, the strengths of the porous polymeric monoliths are not strong enough, and they need to be improved before they are considered for application studies. For this reason, tetraethoxysilane (TEOS) was specially chosen as a modifier. This is because hydrolyzation of it is controllable, and the product of the hydrolyzation is an inert inorganic oxide, silica, which may provide the final porous composite materials extra strength. Experimentally, tetraethoxysilane (TEOS) could be introduced into either the dispersed phase, the aqueous phase, or the continuous phase, the organic phase. Fig. 3 shows the SEM images of the morphologies of the composite materials as obtained through the two different strategies. References to the images shown in the figures, it is clearly seen for the materials obtained through introduction of TEOS into the aqueous phase, the silica particles resulted deposited on the surfaces of the void walls of the polymeric materials. But for the one obtained through introduction of TEOS into the organic phase, no significant deposition of silica particles was observed. It is believed that the inorganic oxide as produced should have deposited within the polymeric materials (c.f. Fig. S5 and discussion presented there). In other words, oil phase dissolution of TEOS favors the integration of the produced silica into the polymeric materials obtained. Integration of the inorganic oxide into the polymeric monoliths was further confirmed by FTIR analysis.

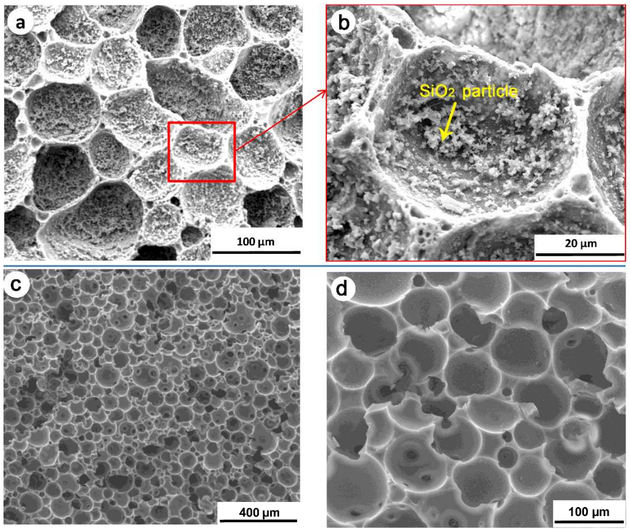

Fig. 3 SEM images of the TEOS (5%, v/v) modified porous polymeric monoliths: (a, b) aqueous phase modification; (c, d) oil phase modification.

It is well known that FTIR spectroscopy is a powerful tool for verifying specific functional groups within a compound or polymer. For this reason, the FTIR spectra of *t*-BMA, poly-*t*-BMA, SiO_2/poly-*t*-BMA produced via dispersed phase hydrolyzation, and the same composite produced via continuous phase hydrolyzation were recorded and the results are shown in Fig. 4. Reference to the spectrum shown in Fig. 4a, it is seen that the stretching vibration bands for C=C and C=O appear at 1640 cm^{-1} and 1719 cm^{-1}, respectively. After polymerization, the characteristic band for C=O shifted to1725 cm^{-1}, and the one for C=C became so weak, indicating successful polymerization of *t*-BMA (c.f. Fig. 4b, 4c and 4d). With introduction of TEOS, a new broad band around 3428 cm^{-1} (c.f. Fig. 4c) or 3422 cm^{-1} (c.f. Fig. 4d) appears, suggesting

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existence of a SiO-H group, in support of the integration of the inorganic silica into the polymeric materials. Considering the signals may also come from water, to make sure what is the origin of the signals, TGA analyses of the composite materials were conducted, and the results are shown in Figure S3. Reference to the traces reveals that there has been almost no mass loss before and around 100 ℃, indicating that the samples are almost water free. Therefore, the signals do come from the silicon hydroxyl groups. To understand the effect of silane type on the structures and properties of the porous composite materials produced, similar experiments also need to be conducted by employing other silanes as precursors.

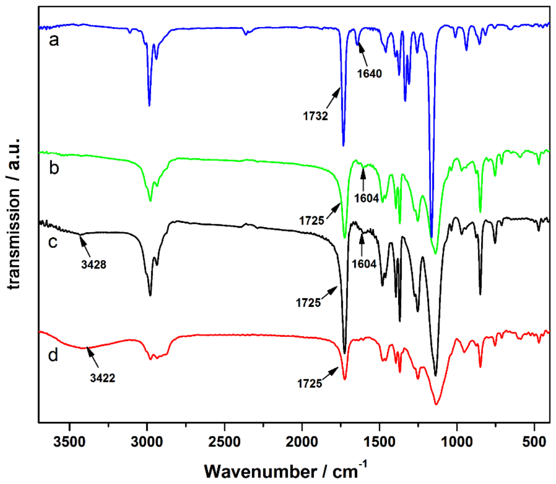

Fig. 4 FTIR spectra of *t*-BMA (a), pure polymeric monolith (b), silica modified polymeric monolith obtained via dispersed phase modification (c), and the one via continuous phase modification (d).

Silane type effect

The silanes used for the present studies are 3-aminopropyltriethoxysilane, (3-isocya-natopropyl)triethoxysilane, triethoxyoctadecyl-silane and tetraethoxysilane, respectively. Polymeri-zation of the gel emulsions containing one of the above mentioned silanes resulted in M-2, M-3, M-4 and M-5, respectively (Table 2). Incorporation of the silanes into the porous materials was supported by the results from thermogravimetric analysis (TGA) analysis. The results are presented in Figure S3. Reference to the figure and in particular the inset of it reveals that the five materials adopt similar decomposition mechanism in an oxygen atmosphere, and for all the systems some residues are remained after the calcinations. Considering the composition of the systems, it should be no difficult to understand that the residues should be mixtures of Fe_3O_4 and SiO_2 due to presence of the stabilizer, which is a compound containing ferrocene, and one of the silanes. Accordingly, for M-1 the residue should be only Fe_3O_4 because there is no silianes during preparation of M-1, but for others SiO_2 remained are differences of the total residues and those of Fe_3O_4. Furthermore, for the five samples, the amount of Fe_3O_4 in the residues should be the same due to same amount of the stabilizer was introduced in the preparation processes, and thereby SiO_2 remained for M-1, M-2, M-3, M-4 and M-5 are 0, 3.9, 7.3, 5.7 and 3.8%, respectively.

Table 2 Crush strengths, apparent densities, theoretical porosities, and absorption capacities to kerosene of the porous composite monoliths produced via a gel emulsion template approach and their parent porous polymeric monolith.

Porous Monoliths	Crush strength (MPa)	Apparent density (g/cm^3)	Porosities (Φ)	Absorption capacity (g/g)	Absorption capacity (g/cm^3)
M-1	1.2	0.21	0.79	5.33	1.119
M-2	5.5	0.29	0.71	5.40	1.566
M-3	0.7	0.12	0.88	8.17	0.9804
M-4	3.2	0.17	0.83	5.89	1.001
M-5	4.6	0.23	0.77	3.56	0.8188

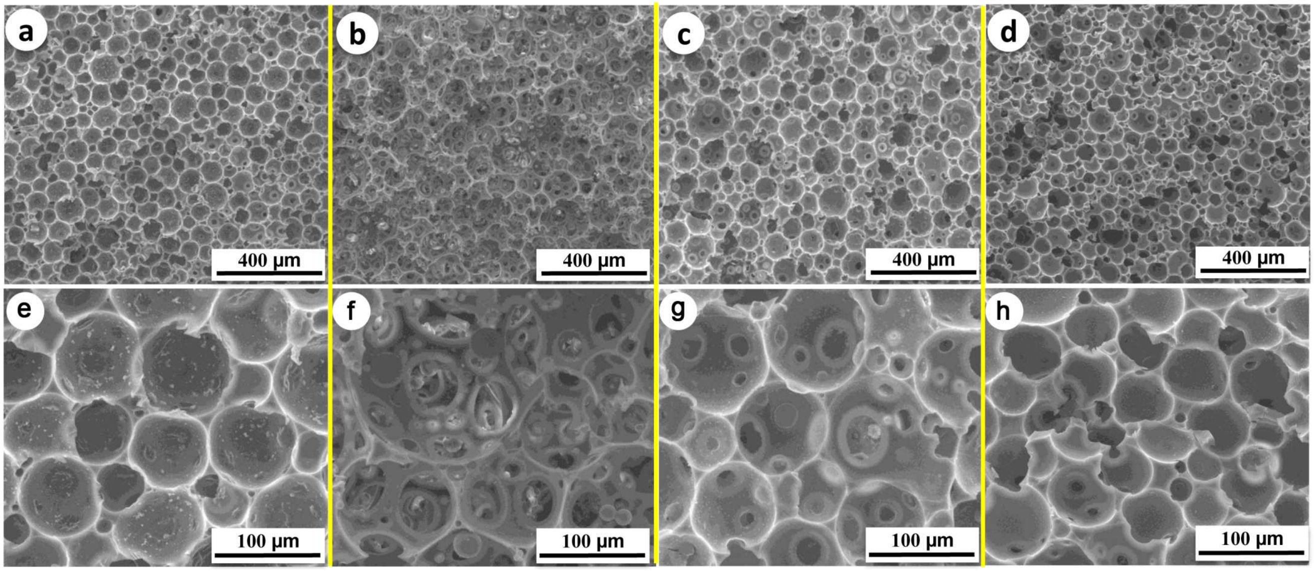

Fig. 5 SEM images of the porous composite monoliths produced by using the gel emulsion template method with the presence of 5% (v/v) of (a, e) 3-aminopropyl-triethoxysilane ($C_9H_{23}NO_3Si$), (b, f) (3-isocyanatopropyl)triethoxysilane ($C_{10}H_{21}NO_4Si$), (c, g) triethoxyoctadecylsilane ($C_{24}H_{52}O_3Si$) and (d, g) tetraethoxysilane ($(C_2H_5O)_4Si$), respectively, in the monomer phase. The corresponding monoliths are named as M-2, M-3, M-4 and M-5, respectively.

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SEM studies of the micro-structures of the porous composite monoliths show that the pore structures of these composite materials are very different to that of the original porous polymeric monolith (c.f. Fig. 2). Taking M-3, modified with (3-isocyanatopropyl)triethoxysilane, as an example, it is seen that this composite porous materials possesses much larger pore sizes and pore throats (c.f. Fig. 5b and 5f), which are, in average, 80 μm and 17 μm, respectively. Furthermore, the sizes of some of the pores in the composite could be double those of the pure polymeric material, M-1. Hence, the addition of silanes to the gel emulsion templates shows remarkable effect on the structures of the template and the porous composite materials from it. Furthermore, introduction of the silanes also shows great effect to the crush strengths, and even the theoretical porosities (c.f. Table S2 and the discussions thereof) of the porous materials as shown in Table 2 even though the changes in apparent densities are not very much.

The mechanism for the pore throat formation in porous polymeric monoliths is still under debate in the literature, but it has been accepted that the films separating the droplets in the emulsion templates must be sufficiently thin in order to break and form pore throats. The actual role of the added silanes in the pore throat formation presented here is unclear and needs further investigation. Nevertheless, our results give some vital clues about the interplay between the silanes and the stabilizer in the synthesis of porous composite monoliths. It is important to note that the silanes alone did not allow formation of a stable gel emulsion under the investigated conditions. Hence, it is the LMMG that acts as the primary stabilizer of the gel emulsions.

Hydrophobic and lipophilic property

To test the hydrophobic and hydrophilic properties of the porous composite materials, their contact angles to water were systematically measured, and the results are shown in Fig. 6. Reference to the pictures and data shown in Fig. 6, it reveals that the advancing contact angles of the materials are 123.4°, 109.0°, 105.6°, 134.9°, and 126.0°, respectively, indicating that the materials are all hydrophobic, a result in consistent with the expectation from the chemical compositions of the materials.

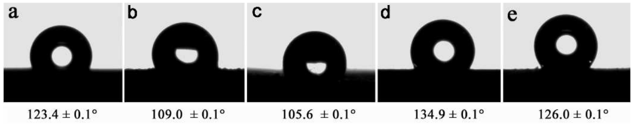

Fig. 6 Images of contact angles of five porous materials, where a, b, c, d and e are the images of the materials of M-1, M-2, M-3, M-4 and M-5, respectively.

Oil absorption

The absorption capacities of the five porous materials to kerosene and the absorption amount as a function of time for each of the materials was shown in Fig. 7. Reference to the plots shown in Fig. 7, it is seen that the absorption is fast, and 60 s is enough for them to reach equilibrium. Among them, M-3 is superior to others because it possesses not only a faster absorption rate but also a much larger absorption capacity, about two times more than those of M-2 and M-5, 40% and 30% more than those of M-1 and M-4, respectively. Specifically, the average maximum absorption capacities of the materials to kerosene are 5.33, 3.40, 8.17, 5.89 and 3.56 g/g, respectively, a result similar to those reported by others.[35,57-60] The reason behind this observation may be attributed to the differences in the interconnections of the pores in the materials. Reference to the SEM images shown in Fig. 5 reveals that M-3 is the one possessing most and larger throats if compared to those of other composite materials. In other words, the samples with better interconnected pores show faster adsorption rate and larger absorption capacities.

To determine the maximum absorption capacities of the monoliths, taking M-3 as an example, to organic liquids, absorption test to some water immiscible and miscible liquids, such as *n*-hexane, benzene, dichloromethane, THF, ethanol, methanol, acetone, kerosene and already used transformer oil, were conducted, and the results are shown in Fig. 8a. Reference to the Figure, it is seen that the absorption capacities of the materials to the nine liquids are 3.86, 15.37, 17.33, 13.42, 5.61, 4.52, 3.43, 8.17 and 4.98 g/g, respectively.

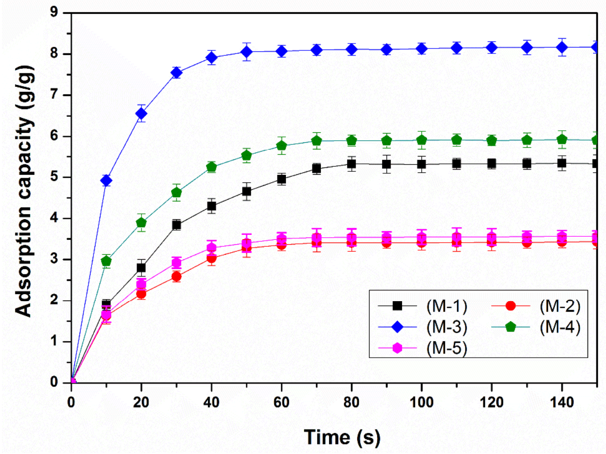

Fig. 7 Plots of the absorption capacities of the porous materials to kerosene against absorption time, where Y axis stands for the mass of the oil absorbed by a unit mass of the materials.

As it is well known that the re-usability of an absorbent is crucial for its practical uses, and thereby, the re-usability of the porous materials was tested, and the results are depicted in Figure 7b. It is seen that the absorption processes are fully reversible, and could be repeated for at least 13 times. Considering the absorption capacity, the absorption rate and the re-usability, it is safe to say that the materials, particularly M-3, developed in the present study possess a very bright future for real-life uses. As for why M-3 is superior to others, it might be rationalized by considering its internal structure as shown in Fig. 5b. Clearly, unlike others, it possesses larger pores and more throats which would be favourable for absorption of kerosene. Furthermore, the density of this material is significantly lower than others, which make it possess apparent larger absorption capacity when considered by mass to unit mass. However, for real-life uses, the situation might be different, and the materials named M-2 might be more suitable for using due to its larger absorption capacity when considered from the view point of mass to unit volume (c.f. the data shown in the most right column of Table 2). The observation that M-2 possesses larger absorption capacity might be originated from the fact that it occupies more organic structures within a given volume of it if compared to other relevant materials.

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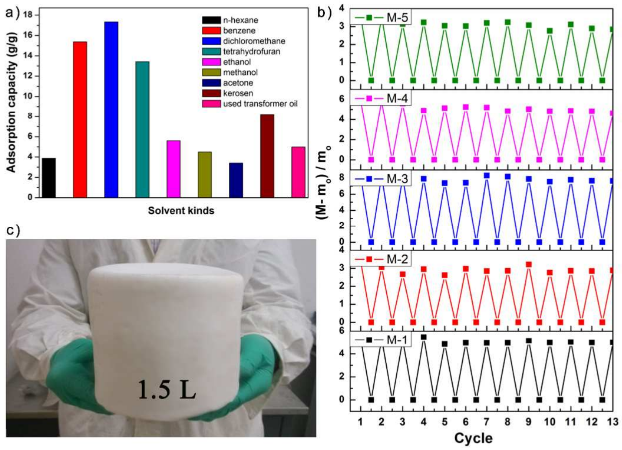

Fig. 8 Maximum oil absorption capacities of the monolith of M-3 to nine different liquids (a), the reversibility of the absorption processes (kerosene as an example oil) (b), and a photo of a typical monolith of M-3 (c).

Unlike other oil-removing materials reported in the literatures, the materials reported here can be facilely prepared, purified, dried and used repeatedly. Moreover, the densities of the materials are low, which provide them additional convenience because they can float on water surface when they are used for collection of oil on water surface.

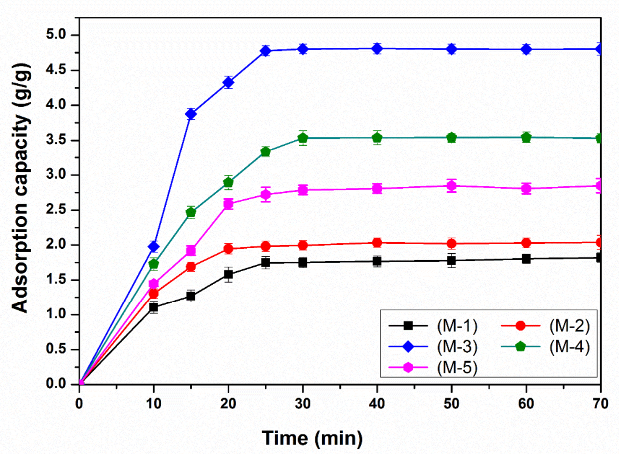

Fig. 9 Absorption capacity of already used transformer oil as a function of absorption time. The sorbents under test are the porous materials as prepared in the present work. (Y-axis stands for absorption capacity of unit mass)

Besides kerosene afore mentioned, viscous oils, such as already used transformer oil can be also efficiently and selectively collected from water surface as shown in Fig. 9. It is clear that at this case, the sorption rate is significantly slower than the sorption rate of kerosene. Generally speaking, approximately 25 min is needed to reach equilibrium. Similar to that of kerosene absorption, M-3 is superior to others in considering of absorption capacity in a mass to mass standard. The maximum absorption capacities of the five materials to this viscous oil under test are 1.88, 2.03, 4.91, 3.56, and 2.80 (g/g), or 0.3948, 0.5887, 0.5892, 0.6052, and 0.6440 (g/cm^3), respectively. Clearly, for collection of already used transformer oil, the absorption capacities of the four porous composite materials are similar if considered in a mass to unit volume way, but they are significantly better than that of the parent porous polymeric monolith (M-1), indicating the merit of introduction of silanes.

Conclusions

A ferrocene derivative of bi-cholesterol, a typical LMMG, has been successfully used as a stabilizer to create a gel emulsion of water/*t*-BMA. Based upon this gel-emulsion, a porous polymeric monolith, and a number of relevant porous composite monoliths have been prepared via polymerization of the system or the system with suitable silanes in the continuous phase. It has been demonstrated that the internal structure and the macroscopic properties of the porous materials could be easily adjusted by simple variation of the composition of the gel emulsion. Furthermore, the porous composite monoliths are ideal sorbents for kerosene, a representative of less viscous oils, and already used transformer oil, a representative of viscous oils. The sorbents after sorption could be recovered by simple centrifugation or squeezing, washing and natural drying. Considering the fast sorption rate, the relatively large absorption capacity, the adaptability to less viscous oil and to viscous oil, as well as re-usability, it is safe to say that the present study has paved a way for the porous composite materials to find real-life uses. Moreover, the approach developed in the present work is simple, low-cost, versatile and environmentally benign, and thus showing a bright future for synthesizing advanced, in particular, ultra-low density materials with superior performances.

Acknowledgements

We thank the Natural Science Foundation of China (91027017 and 21273141) and the Ministry of Education of China for its “Program for Changjiang Scholars and Innovative Research Team in University” of China (IRT1070).

Notes and references

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† Electronic Supplementary Information (ESI) available: [Influence of the nature of water insoluble monomers and the volume fraction of the dispersed phase (water) to the stability of a given gel emulsion (stabilizer, 2%, w/v, of the organic phase); SEM images of the porous polymeric monoliths prepared from gel emulsions containing different amount of the stabilizer (w/v): (a) 1%; (b) 2%; (c) 3%; SEM images of the porous polymeric monoliths prepared with different concentrations of the cross-linker, DVB: (a) 5%, (b) 10%, (c) 15%; Video of Selective absorption of kerosene from water by using M-3 as absorbent; Video of Selective absorption of THF from water by using M-3 as absorbent]. See DOI: 10.1039/b000000x/

(1) Leventis, N., Sotiriou-Leventis, C., Mohite, D. P., Larimore, Z. J., Mang, J. T., Churu, G., Lu, H., *Chem. Mater.* 2011, **23**, 2250.

(2) Sadekar, A. G., Mahadik, S. S., Bang, A. N., Larimore, Z. J., Wisner, C. A., Bertino, M. F., Kalkan, A. K., Mang, J. T., Sotiriou-Leventis, C., Leventis, N., *Chem. Mater.* 2011, **24**, 26.

(3) Tanaka, N., Kobayashi, H., Nakanishi, K., Minakuchi, H., Ishizuka, N., *Anal. Chem.* 2001, **73**, 420 A.

Journal of Materials Chemistry A Accepted Manuscript

(4) Chung, C. M., Chou, T. P., Cao, G., Kim, J. G., *Mater. Chem. Phys.* 2006, **95**, 260.

(5) Chen, X., Wang, X., Fu, X., *Energy Environ. Sci.* 2009, **2**, 872.

(6) Yang, X.-Y., Leonard, A., Lemaire, A., Tian, G., Su, B.-L., *Chem. Commun.* 2011, **47**, 2763.

(7) Twigg, M. V., Richardson, J. T., *Ind. Eng. Chem. Res.* 2007, **46**, 4166.

(8) Brun, N., Babeau-Garcia, A., Achard, M.-F., Sanchez, C., Durand, F., Laurent, G., Birot, M., Deleuze, H., Backov, R., *Energy Environ. Sci.* 2011, **4**, 2840.

(9) Flexer, V., Brun, N., Courjean, O., Backov, R., Mano, N., *Energy Environ. Sci.* 2011, **4**, 2097.

(10) Flexer, V., Brun, N., Backov, R., Mano, N., *Energy Environ. Sci.* 2010, **3**, 1302.

(11) Mamak, M., Coombs, N., Ozin, G., *Adv. Mater.* 2000, **12**, 198.

(12) Brun, N., Janot, R., Sanchez, C., Deleuze, H., Gervais, C., Morcrette, M., Backov, R., *Energy Environ. Sci.* 2010, **3**, 824.

(13) Wu, D., Xu, F., Sun, B., Fu, R., He, H., Matyjaszewski, K., *Chem. Rev.* 2012, **112**, 3959.

(14) Silverstein, M. S., *Prog. Polym. Sci.* 2014, **39**, 199.

(15) Alagha, L., Wang, S., Xu, Z., Masliyah, J., *The J. Phy. Chem. C* 2011, **115**, 15390.

(16) Long, J., Li, H., Xu, Z., Masliyah, J. H., *Energy & Fuels* 2011, **25**, 701.

(17) Schnoor, J. L., *Environ. Sci. Technol.* 2010, **44**, 4833.

(18) Ceylan, D., Dogu, S., Karacik, B., Yakan, S. D., Okay, O. S., Okay, O., *Environ. Sci. Technol.* 2009, **43**, 3846.

(19) Lim, T.-T., Huang, X., *Chemosphere* 2007, **66**, 955.

(20) Lin, C., Huang, C.-L., Shern, C.-C., *Resources, Conserv. Recycl.* 2008, **52**, 1162.

(21) Lin, Q., Mendelssohn, I. A., Carney, K., Miles, S. M., Bryner, N. P.,Walton, W. D., *Environ. Sci. Technol.* 2005, **39**, 1855.

(22) Whitfield, J., *Nature* 2003, **422**, 464.

(23) Rajakovic, V., Aleksic, G., Radetic, M., Rajakovic, L., *J. Hazard. Mater.* 2007, **143**, 494.

(24) In xinhuanet http://news.xinhuanet.com/english/china/2013-11/22/c_132909668.htm, 2013.

(25) Li, K., Ju, J., Xue, Z., Ma, J., Feng, L., Gao, S., Jiang, L., *Nat Commun* 2013, **4**.

(26) Hayase, G., Kanamori, K., Fukuchi, M., Kaji, H., Nakanishi, K., *Angewandte Chemie International Edition* 2013, **52**, 1986.

(27) Liang, H.-W., Guan, Q.-F., Chen, L.-F., Zhu, Z., Zhang, W.-J., Yu, S.-H., *Angew. Chem. Int. Ed.* 2012, **51**, 5101.

(28) Binks, B. P., Rodrigues, J. A., *Angew. Chem. Int. Ed.* 2005, **44**, 441.

(29) Binks, B. P., Rodrigues, J. A., *Angew. Chem. Int. Ed.* 2007, **46**, 5389.

(30) Cameron, N. R., *Polymer* 2005, **46**, 1439.

(31) Menner, A., Powell, R., Bismarck, A., *Macromolecules* 2006, **39**, 2034.

(32) Menner, A., Haibach, K., Powell, R., Bismarck, A., *Polymer* 2006, **47**, 7628.

(33) Ikem, V. O., Menner, A., Horozov, T. S., Bismarck, A., *Adv. Mater.* 2010, **22**, 3588.

(34) Chen, X., Liu, K., He, P., Zhang, H., Fang, Y., *Langmuir* 2012, **28**, 9275.

(35) Jing, P., Fang, X., Yan, J., Guo, J., Fang, Y., *J. Mater. Chem. A* 2013, **1**, 10135.

(36) Peng, J., Xia, H., Liu, K., Gao, D., Yang, M., Yan, N., Fang, Y., *J. Colloid Interface Sci.* 2009, **336**, 780.

(37) Steed, J. W., *Science* 2002, **298**, 976.

(38) Zhao, L., Jiang, L., Han, Y., Xian, Z., Huang, J., Yan, Y., *Soft Matter* 2013, **9**, 7710.

(39) Yu, C., Zhao, L., Wang, S., Cui, Z., Peng, J., Li, J., Zhai, M., Huang, J., *Soft Matter* 2013, **9**, 5959.

(40) Yang, Y., Yue, L., Li, H., Maher, E., Li, Y., Wang, Y., Wu, L., Yam, V. W.-W., *Small* 2012, **8**, 3105.

(41) Ma, Y., Liang, J., Sun, H., Wu, L., Dang, Y., Wu, Y., *Chem. – Eur.* 2012, **18**, 526.

(42) May, A., Aramaki, K., Gutiérrez, J. M. a., *Langmuir* 2011, **27**, 2286.

(43) Dunstan, T. S., Fletcher, P. D. I., Mashinchi, S., *Langmuir* 2011, **28**, 339.

(44) Chen, Y., Ballard, N., Gayet, F., Bon, S. A. F., *Chem. Commun.* 2012, **48**, 1117.

(45) Savic, S., Lukic, M., Jaksic, I., Reichl, S., Tamburic, S., Müller-Goymann, C., *J. Colloid Interface Sci.* 2011, **358**, 182.

(46) Liu, K., He, P., Fang, Y., *Sci. China Chem.* 2011, **54**, 575.

(47) Sangeetha, N. M., Maitra, U., *Chem. Soc. Rev.* 2005, **34**, 821.

(48) Liu, J., He, P., Yan, J., Fang, X., Peng, J., Liu, K., Fang, Y., *Adv. Mater.* 2008, **20**, 2508.

(49) Xu, Z., Peng, J., Yan, N., Yu, H., Zhang, S., Liu, K., Fang, Y., *Soft Matter* 2013, **9**, 1091.

(50) He, P., Liu, J., Liu, K., Ding, L., Yan, J., Gao, D., Fang, Y., *Colloids Surf. A: Physicochem* 2010, **362**, 127.

(51) Wang, J., Zhang, C., Du, Z., Xiang, A., Li, H., *J. Colloid Interface Sci.* 2008, **325**, 453.

(52) Lissant, K. J., *J. Colloid Interface Sci.* 1966, **22**, 462.

(53) Lissant, K. J., Peace, B. W., Wu, S. H., Mayhan, K. G., *J. Colloid Interface Sci.* 1974, **47**, 416.

(54) Cohen, N., Silverstein, M. S., *Macromolecules* 2012, **45**, 1612.

(55) Barbetta, A., Cameron, N. R.,Cooper, S. J., *Chem. Commun.* 2000, 221.

(56) Menner, A., Bismarck, A., *Macromol. Symposia* 2006, **242**, 19.

(57) He, H.,Li, W., Lamson, M., Zhong, M., Konkolewicz, D., Hui, C. M., Yaccato, K., Rappold, T., Sugar, G., David, N. E., Damodaran, K., Natesakhawat, S., Nulwala, H., Matyjaszewski, K., *Polymer* 2014, **55**, 385.

(58) He, H., Li, W., Zhong, M., Konkolewicz, D., Wu, D., Yaccato, K., Rappold, T., Sugar, G., David, N. E., Matyjaszewski, K., *Energy Environ. Sci.* 2013, **6**, 488.

(59) He, H., Zhong, M., Konkolewicz, D., Yacatto, K., Rappold, T., Sugar, G., David, N. E., Gelb, J., Kotwal, N., Merkle, A., Matyjaszewski, K., *Adv. Funct. Mater.* 2013, **23**, 4720.

(60) He, H., Zhong, M., Konkolewicz, D., Yacatto, K., Rappold, T., Sugar, G., David, N. E., Matyjaszewski, K., *J. Mater. Chem. A* 2013, **1**, 6810.

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