Toluene diisocyanate based phase-selective supramolecular oil gelator for effective removal of oil spills from polluted water

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HIGHLIGHTS

- An alkyl bicarbamate oil gelator was synthesized and applied to selectively gelate oils from oil/water mixtures.
- The gelator could self-assemble into 3D networks in many oils immobilizing oil phases to form thermal reversible organogels.
- The optimal conditions for using the oil gelator were experimentally determined.
- Taking gasoline as the co-congealed solvent, complete gelation of oil phase could be achieved within 15 min.

GRAPHICAL ABSTRACT
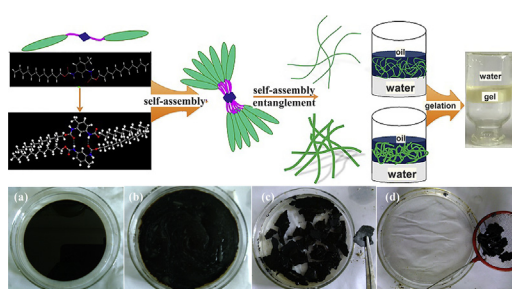
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ABSTRACT

Due to tremendous resource wastes and great harm to ecological environment caused by the accidental oil spills, an alkyl bicarbamate supramolecular oil gelator was synthesized and applied to selectively gelate oils from oil/water mixtures. Interestingly, the oil gelator could be self-assembled in a series of organic solvents, i.e., edible oils and fuel oils to form 3D networks and then turned into thermally reversible organogels, allowing easy separation and removal of oil spills from oil/water mixtures. The possible self-assembly mode for the formation of organogels was proposed. What's more, the optimal conditions for using the oil gelator to recover oils were experimentally determined. Inspiringly, taking gasoline as the co-congealed solvent, a complete gelation of oil phase was achieved within 15 min with high oil removal rate and oil retention rate after convenient salvage and cleanup of oil gels from oil/water mixtures. The oil gelator had some advantages in solidifying oil spills on water surface, exhibiting fast oil gelation, convenient and thorough oil removal and easy recovery. This work illustrates the significant role of oil gelators in the potential cleanup of spilled oils for water purification.

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1. Introduction

The petroleum resource is important in the development of modern civilization. However, the oil spills, especially the marine

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petroleum spills, have been occurring inevitably during the process of exploitation, transportation and usage of petroleum resource. The impacts of oil spills on the ecosystem are severe and cannot be overemphasized because about 5 million tons of petroleum are transported annually across the seas around the world, putting the marine lives and ecosystem in a dire risk (Al-Majed et al., 2012). Many effective materials and techniques have been studied to remove the spilled oils in recent years. Major methods for controlling spilled oil including physical, chemical, biological methods, or their combination are usually used for the overall cleanup of oil spills. Da Silva et al. investigated the conjugation of flotation and photo-Fenton techniques for oil removal and reported an overall removal of up to 99% (Da Silva et al., 2015). Inorganic materials including expanded graphite (Ding et al., 2014), silica aerogel (Yang, 2011), polymer (such as polyethylene, polypropylene) fibers, and some natural materials (sawdust, straw husk based oil adsorbents) (Hai et al., 2012) have been used in the physical methods. Recently, organic gels and their aerogels (Lee and Rogers, 2013), cellulose aerogels (Chin et al., 2014), graphene aerogels (Hu et al., 2014; Li et al., 2014) and other aerogels have also been used as oil adsorbents with excellent and high oil adsorption capacity. Kizil et al. (Kizil et al., 2015). reported poly(alkoxysilane) reusable organogels for the removal of oil/organic solvents from water surface with an adsorption capacity of 50–725%. Wu et al. (Wu et al., 2015). prepared a three-dimensionally bonded spongy graphene material with high oil adsorption ability of 1900 V/V pump oil. Among the chemical methods, oil gelling agent can solidify the liquid oils into solid or viscous semi-solid aggregates for convenient recovery. The traditional oil solidifying agents have been studied widely in recent decades, such as the derivatives of polyvinyl alcohol (Sun and Chen, 1999), soybean protein (Sun et al., 2001), sorbitol (Yao et al., 1993) and chitosan (Zhao et al., 2005). Nowadays, low molecular weight organogelators (LMOGs) have received increased attentions in gelling oils, including the derivatives of sugar (Jadhav et al., 2010; Man et al., 2010; Mukherjee and Mukhopadhyay, 2012; Prathap and Sureshan, 2012), amino acid (Basak et al., 2012; Bhattacharya and Krishnan-Ghosh, 2001; Bhattacharya and Pal, 2008; Pal et al., 2007; Suzuki et al., 2006), cholesterol (Peng et al., 2008; Xue et al., 2009; Zhang et al., 2011a, 2011b), organic salt (Ballabh et al., 2006; Mallia and Weiss, 2014; Trivedi et al., 2003, 2004; Trivedi and Dastidar, 2006), etc. These LMOGs can create entangled 3D supramolecular networks through intermolecular self-assembly usually driven by the specific non-covalent interactions like hydrogen bonding, π-π stacking, electrostatic interaction and van der Waals forces, etc. The entangled networks can entrap oil phase to realize effective gelation or immobilization. Among the LMOGs, the capability of gelating one solvent preferentially over another in a given two-phase mixture is termed as phase selective organogelators (Mukherjee and Mukhopadhyay, 2012). Unlike chemical gels, these physical gels formed by LMOGs and oils can realize reversible sol-gel phase transition under external stimuli, such as heating, mechanical shear, ultrasound (Yu et al., 2014), light, and pH (Liu et al., 2009), and can be used for the recovery of oil gelators and gelled oils.

So far, it is still difficult to predict the gelation property simply based on the molecular structures (Wang et al., 2011). From reported literatures (Moniruzzaman et al., 2003; Moniruzzaman and Sundararajan, 2004; Khanna et al., 2009; Furer, 1999), carbamates are one class of LMOGs and the molecular structures of carbamates including alkyl chains, urethane groups or aromatic rings can generally create effective self-assembly driving forces like hydrogen bonds, π-π stacking, van der Waals interactions, etc. Mohammad M. (Moniruzzaman et al., 2003; Moniruzzaman and Sundararajan, 2004), Khanna S (Khanna et al., 2009) and Furer V.L (Furer, 1999) have prepared some carbamates LMOGs mainly

based on linear isocyanate and studied the influence of double hydrogen bonds and alkyl chains on the gelation of carbamate LMOGs. However, the application of carbamates based LMOG as phase-selective oil gelling agents has not been explored.

In this work, an alkyl bicarbamate supramolecular oil gelator was prepared by toluene diisocyanate (TDI) and lauryl alcohol. The formation mechanism of gelator was proposed and justified. The phase-selective gelling properties for different organic solvents and oils from oil/water mixtures were studied and the optimal conditions for removing oil from oil-water mixture was experimentally determined. Many kinds of organic solvents and oils were tested for gelling by the gelators. The gelling rate, oil removal rate and oil retention rate were used to evaluate the capability of the synthesized gelators.

2. Experimental

2.1. Materials

Toluene diisocyanate (TDI, containing 80% toluene-2,4-diisocyanate and 20% toluene-2,6-diisocyanate) was purchased from Tokyo Kasei Kogyo Co., Ltd.(TCI). Lauryl alcohol (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. The oils for gelling tests include Russian crude oil (Daqing Oil Field Co.), diesel (0#) and gasoline (93#) from Hong Bridge gas station, Harbin. The soybean oil was purchased from COFCO Corporation. The olive oil (extra virgin) was purchased from Spain Moreno. 5S pressing first-class Peanut oil was purchased from Luhua, Shandong, China. Other organic solvents such as chloroform, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), cyclohexane, hexane, and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used as received without any further purification.

2.2. Methods

The oil gelator was prepared through the following procedures. In detail, TDI (0.05 mol) and lauryl alcohol (0.10 mol) were added into 100 mL chloroform and transferred to a 250 mL three neck flask after stirring well. The mixture reacted under mild stirring in water bath at 55 °C for 24 h. After that, the solvent chloroform was removed by air distillation at 90 °C and the concentrated liquid of product was obtained. Then, the concentrated liquid was poured into a glass dish when it was hot and vacuum dried at 150 °C for 12 h. Finally, the product was smashed into white powder after cooling down thoroughly at room temperature.

2.3. Characterizations

FT-IR spectra of the oil gelators were obtained on KBr pallets using Nicolet-Nexus670 instrument with wavelength from 400 to 4000 cm^{-1}. The MS studies were carried out on a LCQ Deca-XP LC-MS instrument operating at positive and negative charge mode by electrospray using carbinol/water = 8/2(v/v) as solvent. Scanning electron microscopic (SEM) images of organogels were obtained using Quanta 200 FEI-Sirion Microscope after vacuum drying and coating with gold with a sputtering coater. The static contact angles (CA) were recorded on a SL200B contact angle testing system at room temperature. The thermal analyses were tested on a DSC-1 differential scanning calorimeter at a heating rate of 5 °C/min, from 25 to 100 °C, with about 5–15 mg sample in nitrogen atmosphere.

2.4. Oil removal rate (M_{rem}) and oil retention rate (M_{ret})

After the phase selective gelation of oil spills on water surface, the oil gels were salvaged and placed in a funnel for 24 h. And the remaining relative clean water was extracted by petroleum ether to measure the residual mass of oil spill (M_{ext}). The oil removal rate (M_{rem}) and oil retention rate (M_{ret}) were determined by the following Equations:

$$M_{rem} = \frac{(M_0 - M_{ext})}{M_0} \tag{1}$$

$$M_{ret} = \frac{(M_{0h} - M_{24h})}{M_{0h}} \tag{2}$$

where M_0 and M_{ext} indicate the total mass and the residual mass of oil spill, respectively. M_{0h} and M_{24h} are the mass of oil gels after just salvage and placing 24 h.

3. Results and discussion

3.1. The preparation of oil gelators

The white powdery oil gelator was synthesized by toluene diisocyanate and lauryl alcohol with the reaction equation shown in Scheme 1.

Fig. 1a shows the mass spectra of the oil gelator. The molecular weight of the gelator is about 546 g/mol and the pseudo molecular ion peaks can be found easily where the peaks of m/z at 545.20 and 547.12 are assigned to M − H, and M + H, respectively. The peak of M + CH$_3$O can be observed in the negative ion mode (Fig. 1a). Fig. 1b shows the IR spectrum. The characteristic peaks of carbamate structure units are very obvious and the peaks around 3292, 1700, 1537 and 1077 cm^{-1} are assigned to N–H stretching vibration, C=O stretching vibration, N–H deformation vibration and C–O stretching vibration, respectively. The characteristic peaks in MS and IR results indicate the successful synthesis of the desired oil gelator product.

3.2. The phase selective gelation properties

Firstly, the gelling range of the oil gelator was tested. The test method adopted the common heating to dissolve oil gelator and then cooling to gel. The detailed process is as follows. 0.6 g oil gelator was added into a mixture of 2 g organic solvent/oil and lots of water in a sample bottle (diameter $d = 2.5$ cm), and then the system was heated in water bath until the solid oil gelator was dissolved completely. Then the resulting mixture was left to cool down to room temperature in air within 15 min and the sample bottle was inverted to observe whether the organic solution inside could still flow. If no solution flows inside, the gel is formed and recorded as "G". Besides, the critical gelation concentration (CGC) is always another important parameter to evaluate the gelation ability. In a given solvent, gelation occurs when the CGC of the
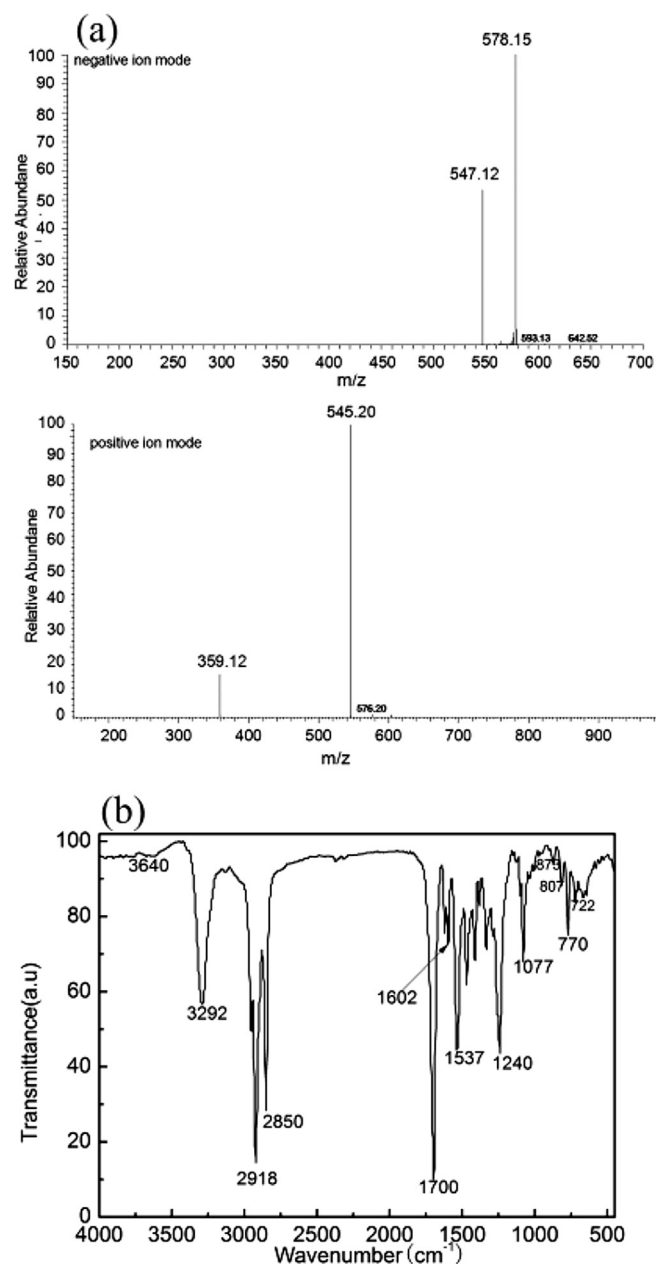

Fig. 1. The secondary mass spectra (a) and the IR spectrogram (b) of the supramolecular oil gelator.

gelator is reached. And the CGC tests were carried out following the same steps above except the addition of oil gelator was increased by trial and error method. The gelation range is summarized in Table 1. The photos of the oil gelator during the gelation process were taken

Toluene-2,4-diisocyanate   Lauryl alcohol   Didodecyl toluene-2,4-dicarbamate
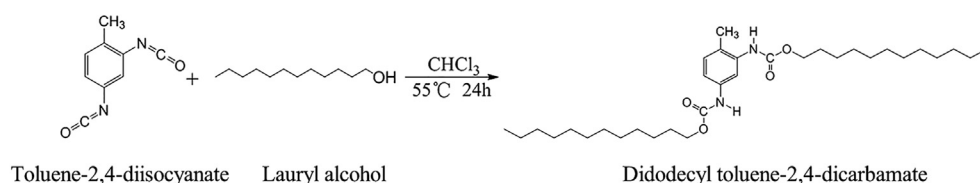
Scheme 1. The reaction equation of the oil gelator (M = 546 g/mol).

Table 1
The phase selective gelation behaviors of the oil gelator.

Solvents	Russian crude oil	Diesel	Gasoline	Soybean oil	Peanut oil	Olive oil	Acetic ether
Gelling behavior	G	G	G	G	G	G	G
Solvents	cyclohexane	hexane	ethanol	methanol	acetone	DMF	THF
Gelling behavior	G	G	I	I	I	S	S

G-Gel, I-Insoluble, S-Soluble.
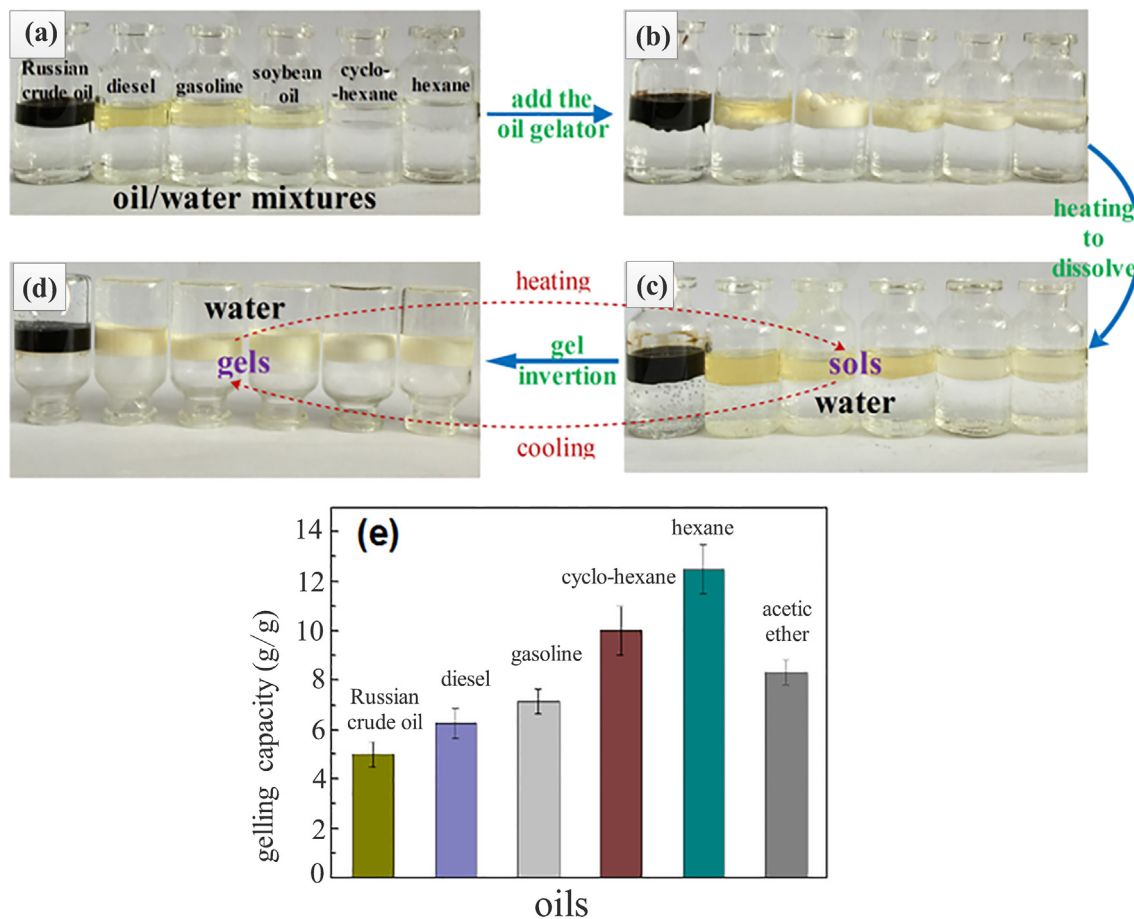
Fig. 2. The photos of phase-selective gelling process and the gelling capacity. (a) oil/water mixtures; (b) after the addition of the white powdery oil gelator; (c) heating until the oil gelators were dissolved to form sols; (d) after cooling in room temperature, the gels were formed within 15 min, and (e) the gelling capacity of the oil gelator for different oils and organic solvents.
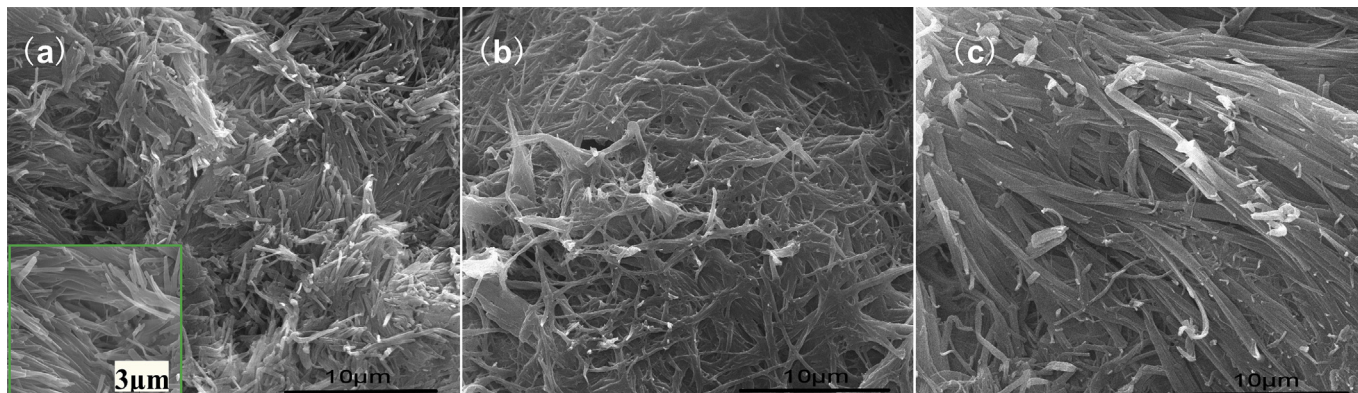

Fig. 3. The SEM images of xerogels from cyclohexane (a), acetic ether(b), gasoline(c).

for many kinds of organic solvents and oils from oil/water mixtures, Fig. 2.

Surprisingly, the oil gelator prepared in this article could phase-selectively gel and immobilize various fuel oils, edible oils and part organic solvents to form non-transparent gels. From Fig. 2d, the oil gels had high strength and could support the water layer in the upper part of the gels after inverting the sample bottles. Interestingly, the reversible phase transitions between sols and gels can be realized under heating-cooling cycle. It is worth mentioning that the gelation of pure organic solvents including cyclohexane, hexane and acetic ether was easier than the fuel oils and edible oils. Generally speaking, the components of oils are always more complicated than that in pure organic solvents, thus the effective self-assembly among small molecules in oils would be more difficult. It can also be proved by the CGC and the corresponding gelling capacity at CGC (Fig. 2e). The gelling capacity for pure organic solvents was around 10 g/g, while about 5—7 g/g gelling capacity was obtained for different oils.

In order to have a further understanding of the gelling behaviors, the microstructures of some gels were examined using scanning electron microscopy (SEM), Fig. 3. The fine fiber-like microstructures and 3D networks formed by entangled fibers can be observed in the micromorphology of xerogels from cyclohexane (Fig. 3a), acetic ether (Fig. 3b) and gasoline (Fig. 3c). All the tangled networks make contribution to entrap and immobilize the oil phases to form stable gels.

The probable gelling process of the oil gelator in organic solvents or oils is schematically shown in Fig. 4. The bicarbamate groups of the gelator provide the sites of double hydrogen-bonding formation. The aromatic benzene rings and long alkyl chains provide π-π stacking and van der Waals interaction for the aggregation and assembly in organic media. Firstly, the gelator molecules are self-assembled into small fibers through weak non-covalent bond interactions. Then, the small fibers become longer and thicker to form 3D network by aggregation and entanglement, and the 3D networks provide spaces to entrap and immobilize the oil phases effectively to form oil gels.

3.3. Phase transition temperature between gels and sols (T_{GS})

The gels formed by supramolecular gelators through weak non-covalent bonds interactions are general physical gels with the transition between sols and gels under external stimuli. All the gels obtained above have thermal response and the T_{GS} is related to the thermal stability of the gels. For better analysis, the T_{GS} of the gels with different kinds of oils and different dosage of oil gelator were characterized. From Fig. 5, the gels of pure organic solvents had
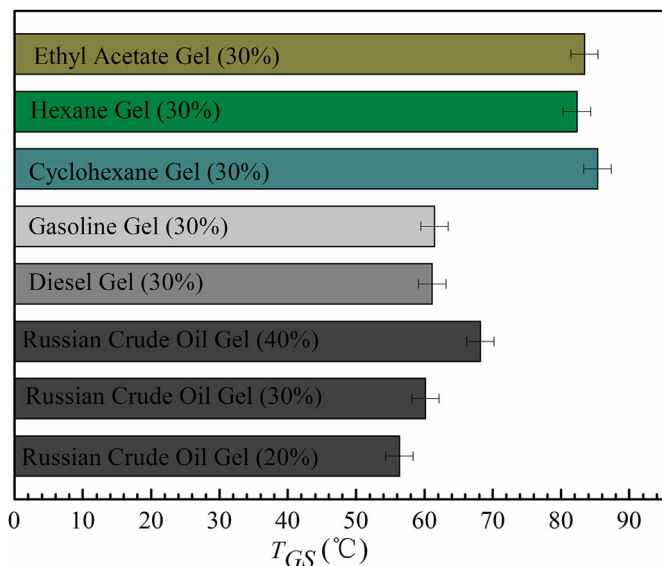

Fig. 5. The sol-gel phase transition temperature (T_{GS}) of gels with different oils or different oil gelator dosage.
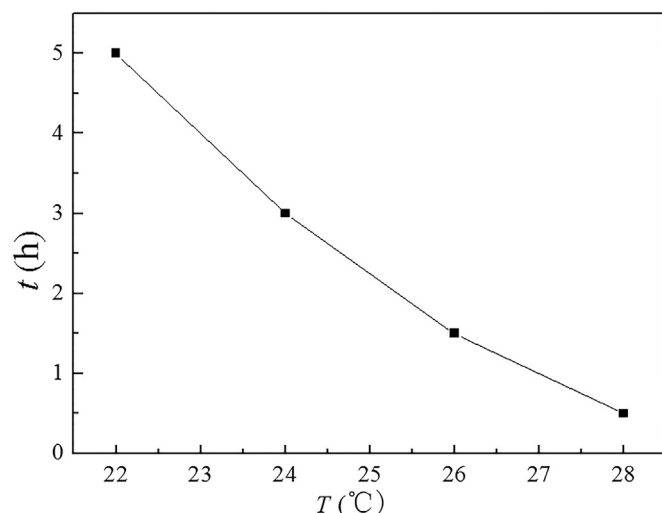

Fig. 6. The curve of relationship between gelling time and ambient temperature.
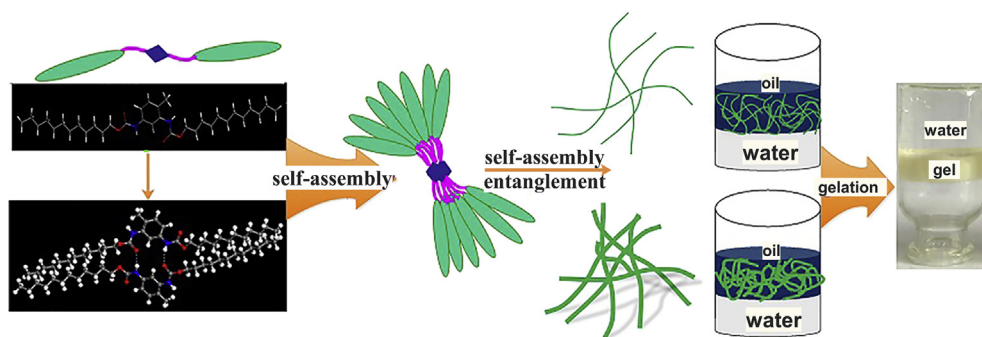

Fig. 4. Schematic representation of probable gelling process for organic solvents and oils. (In molecular structure graph, gray, blue, red and white represent carbon, nitrogen, oxygen and hydrogen, respectively. In other parts, green, blue and pink represent dodecyl, benzene ring and urethane group). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

higher T_{GS} (>80 °C) than oil gels, indicating a higher thermal stability. The higher thermal stability is resulted from easier gelation of pure organic solvents than oils to form more sufficient 3D networks to immobilize organic layers more efficiently. The T_{GS} of oil gels with the same oil gelator content was around 60 °C without significant difference. But for Russian crude oil gels with different oil gelator dosage, the T_{GS} was increased from 56 °C to 68 °C with the increase of gelator dosage from 20% to 40%. More oil gelator can achieve more thorough gelation and obtain oil gels with higher thermal stability. All the tested gels were thermally stable at ambient temperature, indicating the feasibility and practicability of the oil gelators in cleanup or recovery of spilled oil from oil/water mixtures.

3.4. Phase-selective gelation of oil spills from water surface

To simulate the real situation of oil spill, the phase-selective gelation of a thin layer of oils floating on a huge amount of water in flat glass dishes ($d = 12.5$ cm) was tested. Since the common and widely used heating-cooling method in laboratorial phase-selective gelation experiments would be impractical for the cleanup of large-area oil-spills, three possible methods have been tested and evaluated.

Method 1. For convenience, the white powdery oil gelator was added into the oil layer directly. In a typical procedure, lots of water was poured into a flat glass dish ($d = 12.5$ cm) and then 2 g Russian crude oil was poured, with slight agitation to make good dispersion of oil phase. After that, 0.6 g oil gelator was sowed carefully to the surface of oil phase. After repeated tests, the gelling time was found too long to be applied in practice and the gelling time depended on the ambient temperature. From Fig. 6, the gelling time was about 0.5 h at 28 °C, but 5 h at 22 °C and it would be longer at lower temperature. Besides, the strength of oil gels was not enough to salvage easily. So the first method is impractical.

Method 2. For better and faster self-assembly and gelling process, cosolvent was introduced. The suitable cosolvents (THF and DMF) were selected from ethanol, acetone, chloroform, DMF, THF and other organic solvents. A certain amount of oil gelator was dissolved in cosolvent to form a clear and high concentration solution (about 80 wt%) stored at ambient temperature for later use (Fig. 7a). When a part of the solution (about 0.75 g) was sprayed into the oil/water mixtures in a flat glass dish with lots of water and 2 g Russian crude oil, the gelation of the oil layer occurred and was observed within 30 min. Noting the photos in Fig. 7b,c, THF was better than DMF as cosolvent. The oil phase was gelled into semi-solid gels and the gels were strong enough to be scooped out by a spatula from water surface. This method improved the gelling process, such as shorter gelling time, higher gel strength, easier removal and higher oil removal rate (>90%), but organic pollution caused by the introduction of organic cosolvent was unavoidable, indicating possible potential limitations in real oil-spill treatment.

Method 3. Based on the above two methods, a co-congealed solvent may be a good choice for the fast gelling process and the avoidance of organic pollution. After many experiments, we chose
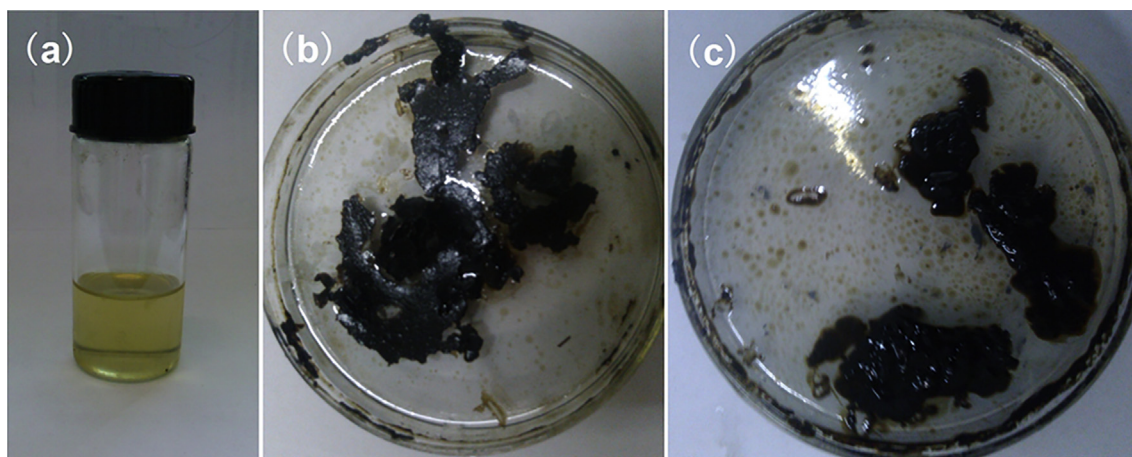

Fig. 7. The photos of phase-selective gelation for Russian crude oils when THF and DMF were introduced as cosolvents. (a) the gelator-THF high concentration solution; (b) the gelling result at 5min after addition of the gelator-THF solution; and (c) the gelling result at 25 min after addition of the gelator-DMF solution.
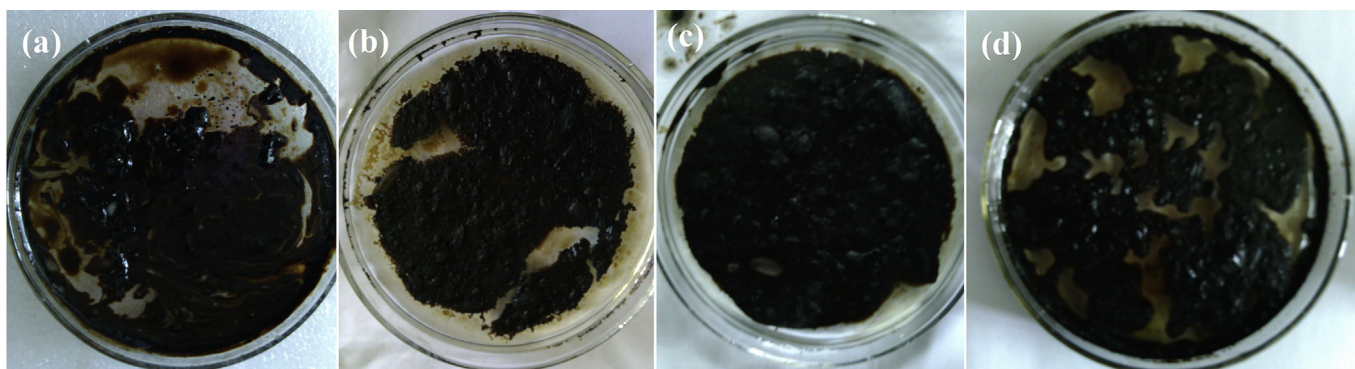

Fig. 8. The results of phase-selective gelation using gelator-gasoline solution of different concentrations: (a) 0.48/1, (b) 1.05/1, (c) 1.5/1, (d) 2/1 (gelator/gasoline, mass ratio).

gasoline as the final co-congealed solvent and it was destined to obtain co-congealed along with the oil in the oil/water mixture to avoid the residual of organic solvent in water. In detail, gasoline and a certain amount of gelator were mixed and heated until the gelator was dissolved completely to form high concentration transparent solution for storage in hot air or water bath (>60 °C) before using to avoid the early gelation of gasoline. Then the solution was evenly sprayed into the oil layer in a flat glass dish with lots of water and 5 g Russian crude oil. However, the concentration of the gelator-gasoline solution had a significant influence on the gelling results. The dispersion of gelator solution in oil phase was poor when the concentration was too high. While too much gasoline was added, fast gelation was not observed because of the dissolution effect of hot gasoline for the oil gelator, when the gelator concentration was very low. Thus, from Fig. 8, the gelation of oil layers was best when the concentration was ranged from 1.05/1 to 1.5/1 (gelator/gasoline, mass ratio).

Next, as shown in Fig. 9 and Fig. 10, the phase-selective gelation and recovery of Russian crude oil and diesel from biphasic mixtures were very obvious and inspiring, when the concentration was 1.05/1. The complete gelation of oil phase was obtained within 15 min and the strength of gel was high enough to recover the oil gels conveniently by a net spoon. Advantageously, both the oil spills and co-congealed gasoline solvent were all gelled and removed to avoid the organic pollution residuals to water. Thus, method 3 can not only achieve fast and excellent gelation but also avoid the secondary organic pollution greatly.

To further evaluate the gelling capabilities of method 3, the oil removal rate and oil retention rate were calculated, including different tested areas such as sample bottle ($d = 2.5$ cm), flat glass dish ($d = 12.5$ cm) and rectangular dish (28 cm × 35 cm). From Fig. 11, for both diesel and Russian crude oil, the oil removal rate could exceed 97% in dozen experiments and the oil retention rate

could be higher than 99% nearly without any oil leak during the salvage and recovery of the oil gels. So the optimal usage method is method 3 showing a good application prospect in the real oil-spill cleanup and treatment.

3.5. Wettability of the oil gelator and gels

The phase-selective gelling abilities were always obtained by adjusting the balance of amphipathic molecules between hydrophily and lipophilicity. Thus, the water contact angle (WCA) and oil contact angle (OCA) of the oil gelator were studied. As shown in Fig. 12, the oil gelator is hydrophobic (114.6°) and superlipophilic (<10°). What's more, the crude oil gel is also hydrophobic (114.1°).

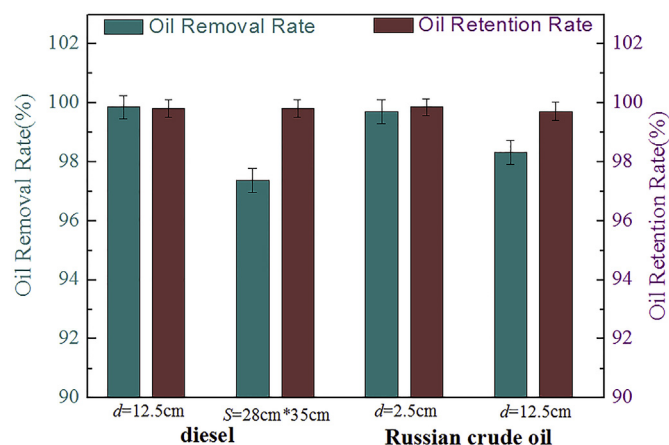**Fig. 11.** The oil removal rate (M_{rem}) and oil retention rate (M_{ret}) of the oil gelator for Russian crude oil and diesel at different tested areas.
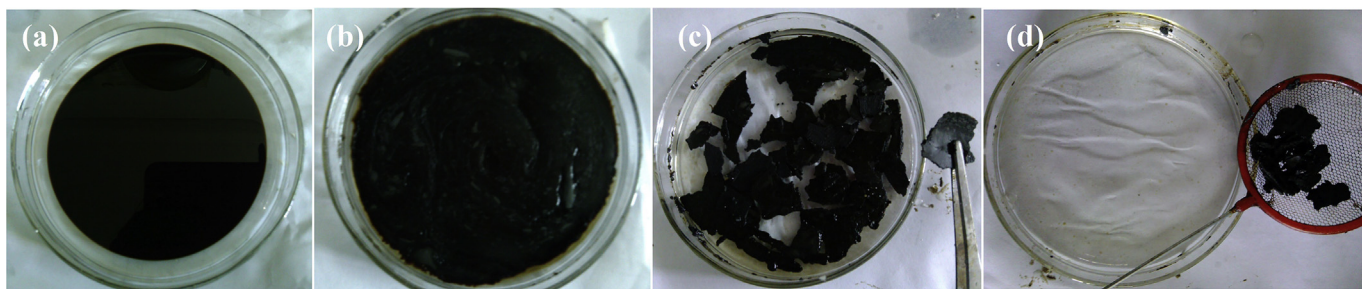
Fig. 9. Phase-selective gelation and recovery of Russian crude oil from oil/water mixture. (a) mixture of 5 g Russian crude oil and lots of water, (b)(c) selective gelation of the crude oil layer after addition of the gelator-gasoline solution at 15 min (crude oil gel floating on water), (d) the clean water surface and crude oil gel after salvage with a net scoop.
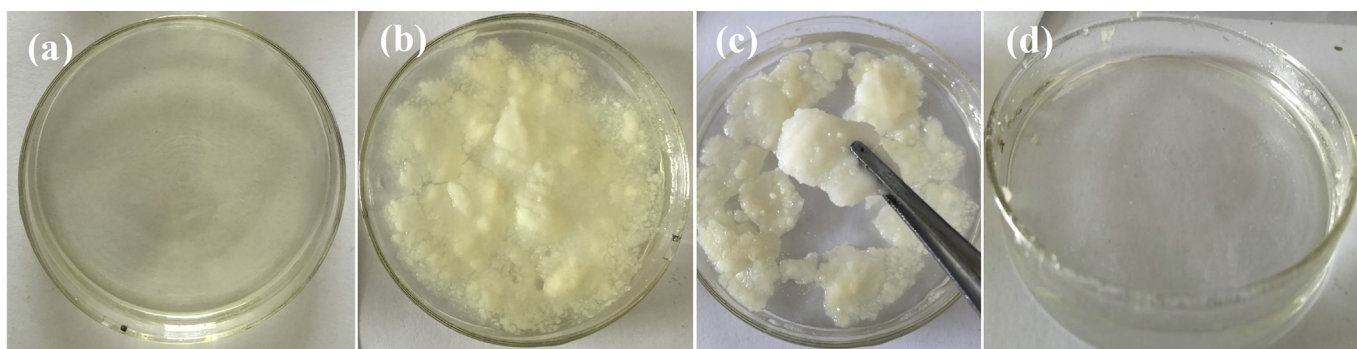
Fig. 10. Phase-selective gelation and recovery of diesel from oil/water mixture. (a) mixture of 5 g diesel and lots of water, (b)(c) selective gelation of the diesel layer after addition of the gelator-gasoline solution at 15min (diesel gel floating on water), (d) the clean water surface after salvage of diesel gels.
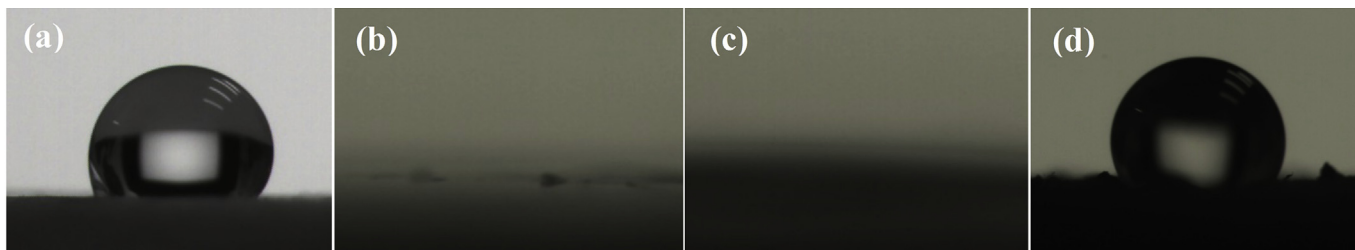
Fig. 12. The contact angle of oil gelator with (a) water, (b) cyclohexane, (c) gasoline and (d) the water contact angle of the Russian crude oil gel.

Thus, the gels can retain on water surface steadily and the strength of oil gel could increase as the time goes because of the further self-assembly and entanglement of 3D network. The hydrophobicity of the oil gels provides enough time for the salvage and recovery of the gels.

4. Conclusion

An effective phase-selective oil gelator based on TDI was synthesized. Interestingly, the oil gelator can gel various organic solvents and oils (commercial fuel oils and edible oils) from oil/water mixtures and self-assemble into fiber-like entangled microstructures to immobilize oils to form thermal stable and responsive gels. The optimal conditions for using the gelator to recover the spilled oil was taking gasoline as co-congealed solvent to achieve fast and effective gelation, almost without secondary organic pollution. Advantageously, the gelling process was fast (<15min) and the oil removal rate (>97%) and oil retention rate (>99%) were very high. Besides, the gels were thermally stable at room temperature providing enough time to recover the gels floating on water surface. With such advantages of good phase-selectivity, short gelling time, thorough and convenient recovery of oil gels, etc, the gelator may have a broad application prospect as an effective oil solidifier in oil spill cleanup.

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