Alkyl bicarbamates supramolecular organogelators with effective selective gelation and high oil recovery from oil/water mixtures

Yongzhen Wang [a], Songquan Wu [a], Xingru Yan [b], Tao Ma [a], Lu Shao [a], Yuyan Liu [a, **], Zhanhu Guo [b, *]

[a] MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China
[b] Integrated Composites Laboratory (ICL), Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

HIGHLIGHTS

- A series of alkyl bicarbamates supramolecular organogelators were synthesized.
- The driving force for small molecules self-assembly was characterized and analyzed.
- The oil gelator can self-assemble in oils to form different 3D networks.
- Some gelators can phase-selectively gel and recover oil spills from water surface.
- The removal of oils is thorough with high oil removal rate and oil retention rate.

GRAPHICAL ABSTRACT
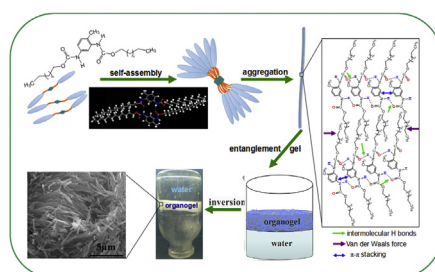
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ABSTRACT

A series of alkyl bicarbamates supramolecular organogelators were synthesized with different structures and lengths of alkyl chains. The driving forces for the self-assembly of small molecules, including the intermolecular H bonding, π-π stacking and van der Waals interactions, played an important role in the formation of different 3D network structures, i.e., fibers, ribbons, sheets, and prisms. And a probable formation process of the gel networks was proposed. Furthermore, the phase-selective gelling performances were investigated for oil removal from aqueous solution. Interestingly, the gelling properties were found to be affected by the length and structure of alkyl chains, while some gelators with intermediate alkyl chain lengths could effectively gel all the tested oils from water surface within 15 min, such as Russian crude oil, diesel, gasoline, soybean oil, peanut oil, olive oil, cyclohexane, hexane and ethyl acetate. Advantageously, fast gelation, high rate of oil removal (>95%) and excellent oil retention rate (close to 100%) were realized in the recovery of oil spills from water surface. This kind of supramolecular gelators demonstrates good potential applications in the delivery or removal of organic pollution from oil/water mixtures.

* Corresponding author.
** Corresponding author.
  E-mail addresses: liuyy@hit.edu.cn (Y. Liu), nanomaterials2000@gmail.com (Z. Guo).

1. Introduction

In recent years, low molecular weight organic gelators (LMOGs) or supramolecular organic gelators have been a subject of

considerable interest due to their wide applications such as sensors, templates, drug delivery (Skilling et al., 2014), tissue engineering (Sagiri et al., 2013), water purification, self-cleaning (Yang et al., 2014), self-healing, oil spill recovery, etc. Many kinds of LMOGs have been reported including sugar derivatives (Jadhav et al., 2010; Man et al., 2010; Mukherjee and Mukhopadhyay, 2012; Prathap and Sureshan, 2012), amino acid derivatives (Basak et al., 2012; Bhattacharya and Krishnan-Ghosh, 2001; Bhattacharya and Pal, 2008; Pal et al., 2007; Suzuki et al., 2006), cholesterol derivatives (Peng et al., 2008; Xue et al., 2009; Zhang et al., 2011a, 2011b), organic salts (Ballabh et al., 2006; Mallia and Weiss, 2014; Trivedi et al., 2003, 2004; Trivedi and Dastidar, 2006), etc. For the phase selective gelation with oils from oil/water mixtures, Bhattacharya et al. provided the first report in 2001 (Bhattacharya and Krishnan-Ghosh, 2001). Thereafter, many attempts and endeavors have been doing. For example, Yan et al. reported dual-responsive two-component supramolecular gels for self-healing materials and oil spill recovery (Yan et al., 2014). Kizil et al. prepared poly(alkoxysilane) reusable organogels for the removal of oil/organic solvents from water surface (Kizil et al., 2015). Chatterjee et al. synthesized D-/L-arabinose based enantiomeric organogelators to be efficient gelators for aromatic solvents and refined and crude oil (Rajkamal et al., 2014). Besides, Mukherjee et al. (Mukherjee et al., 2014), Yu et al (Yu et al., 2014a). and Feng et al (Feng et al., 2014). have also reported some organogelators based on *N*-acetylglucosamine, C2-symmetric benzene and L-phenylalanine for selective gelation of oil from oil/water mixtures.

LMOGs are known to be able to self-assemble into fibrous, tubular, helical or other structures mainly through various noncovalent interactions, including intermolecular H-bonding, π-π stacking, van der Waals interactions, electrostatic attraction, and so on. The formed 3D networks can immobilize organic solvents or oils by capillary force and surface tension. The interactions between solvents and gelators play a key role in mediating organogel formation and ultimately determine the properties of the gels (Shen et al., 2014). Although the gelation mechanism of LMOGs has been studied extensively, it is still difficult to predict the formation of gels from the structure of low molecular compounds (Yu et al., 2014a). Unlike chemical gels (Liu et al., 2011), these physical gels formed by LMOGs can realize reversible sol-gel phase transition under external stimuli, such as heating, mechanical shear, ultrasound (Yu et al., 2014b), light and pH (Shen et al., 2009).

Among LMOGs, carbamates, an important kind of self-assembly organogelators, may include aromatic ring, alkyl chains, urethane group as well as other hydrogen bonding groups in their structures. In 2005, Moniruzzaman and Sundararajan reported the example of carbamate LOMGs involving carbamate/benzonitrile gels and the morphology of their xerogels. Afterwards, Khan et al. (Khanna et al., 2009; Khan and Sundararajan, 2011, ; Khan and Sundararajan, 2013) studied the influence of double hydrogen bonds and alkyl chains on the gelation and crystallization behavior of carbamates and reported that the sheets, eaves trough, tubes and oriented fibers could be formed through self-assembly. However, most of the studied carbamates LMOGs were mainly based on linear isocyanate matrixes, such as hexamethylene diisocyanate (HDI) and octadecyl isocyanate. Toluene diisocyanate (TDI) based bicarbamates supramolecular oil gelators and their applications in selective removal of oil spills from oil/water mixtures have been reported rarely.

In this paper, a series of alkyl bicarbamates supramolecular organogelators with different lengths or structures of alkyl chains were prepared by toluene diisocyanate and corresponding alcohols. And they can be self-assembled to form different 3D structures driven by H bonds, van der Waals interaction and π-π stacking, etc. The influences of the length and structure of alkyl chains on the supramolecular self-assembly driving force and the phase-selective gelling properties were tested and analyzed systematically. The feasibility of these alkyl bicarbamates LMOGs as effective gelators for removing organic solvents and oil spills from the water surface was tested.

2. Experimental

2.1. Materials

Toluene diisocyanate (TDI) (>98%) containing 80 wt% toluene-2,4-diisocyanate and 20 wt% toluene-2,6-diisocyanate was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI) and used as received. Alcohols: n-butanol (AR) was purchased from Bodi chemical Co., Ltd, Tianjin, China. n-hexanol (AR) was purchased from Guangfu Fine Chemical Research Institute, Tianjin, China. n-octanol (AR) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. n-nonanol, *n*-cetanol, *n*-octadecanol, *n*-docosanol (AR) and cyclohexanol (GC) were purchased from Aladdin. n-decanol, *n*-lauryl alcohol, *n*-tetradecyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. n-undecanol (98%) was purchased from Alfa Aesar. And all the alcohols were used without any further purification. Oils for gelling tests: Russian crude oil was received from Daqing Oil Field Co. Diesel (0#) and gasoline (93#) were purchased from Hong Bridge gas station, Harbin. Soybean oil was purchased from COFCO Corporation. Olive oil (500 mL, extra virgin) was purchased from Spain Moreno. 5S pressing first-class Peanut oil was purchased from Luhua, Shandong, China. Other solvents included acetone, chloroform, carbon tetrachloride, cyclohexane, hexane, and ethyl acetate, etc.

2.2. The synthesis of alkyl bicarbamates organogelators

The TDI derived alkyl bicarbamates were obtained through the following process. TDI (0.05 mol) and corresponding alcohol (1.0 mol) were added into 100 mL appropriate organic solvent (acetone, chloroform or carbon tetrachloride) and transferred to a 250 mL three neck flask after stirring well. The mixture reacted under mild stirring in a water bath at 50–70 °C for 24 h. After that, the solvent was removed by air distillation at 80–95 °C and the concentrated liquid containing products was obtained. Then, the concentrated solution was poured into a glass dish when it was hot and vacuum dried at 150 °C for 12 h to remove the residual unreacted TDI. Finally, the product was smashed into powder after cooling thoroughly at room temperature. For convenience, each of them has been designated as nCTDI gelator (alkyl toluene-2,4/2,6-dicarbamate) (Wang et al., 2014), where n denotes the number of carbon atoms in the alkyl side chains.

Besides, in order to analyze whether the π-π stacking interaction exists or not in the self-assembly, a compound was synthesized with *n*-lauryl alcohol and 1,6-hexamethylene diisocyanate (HDI) replacing TDI, refer to Fig. S2 for the details, and the product was called 12CHDI (dodecyl hexamethylene dicarbamate) organogelator (Wang et al., 2014).

2.3. Characterization

The characterizations were mainly operated on 12CTDI gelator showing the best gelling properties. The FT-IR spectra of the products and gels were recorded on KBr pellets using Nicolet-Nexus 670 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 the positive and negative charge mode by electrospray using carbinol/water = 8/2 (v/v) as solvent. ^{1}H NMR spectra were carried out on an ADVANCE III instrument operating at