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Ting Su,^a Kwon Ho Hong,^b Wannian Zhang,^a Fei Li,^a Qiang Li,^a Fang Yu,^a Genxiang Luo,^a Honghe Gao^a and Yu-Peng He^{*a}

A series of phthalic acid derivatives (P) with a carbon-chain tail was designed and synthesized as single-component gelator. Combination of the single-component gelator P and non-gelling additive *n*-alkylamine A through acid-base interaction brought out a series of novel phase-selective two-component gelator PA. Gelation capability of P and PA, structural, morphological, thermos-dynamic and rheological properties of the corresponding gels were investigated. The molecular dynamics simulation showed that the H-bonding network in PA formed between NH of A and carbonyl oxgen of P altered the assembling process of gelator P. Crude PA could be synthesized through one-step without any purification and selectively gel the oil phase without typical heating-cooling process. Moreover, such crude PA and the gelation process of it could be amplified into kilogram scale with high efficiency, which offers a practically economic viable solution to marine oil-spill recovery.

Introduction

Phase-selective gelators (PSGs)^[1] have drawn considerable concerns due to their potential applications in dealing with oil spill,^[2] which had damaged the ecosystem and the environment irrecoverably. Since Bhattacharya and co-workers published their pioneering findings in this research area in 2001,^[3] quite a number of PSGs were intensively investigated.^[4,5,1f] To meet the overwhelming demand of practical applications, novel PSGs with great gelation capability were indispensable. Recently, two-component PSGs^[6,7] where two individual species interact via covalent or noncovalent forces have shown great advantages.^[8] Among them, two species combined through acid-base interaction brought out a complex which then assembled further to form the fully gelated network have been widely studied. For example, Smith's lab developed several new and efficient dendritic twocomponent systems.^[8a] These systems figure high efficiency, adjustment of gel performance and responsive to chemical stimuli^[8b-g]. However few research on gelation capability of PSGs or two-component PSGs in kilogram scale was presented.

There were three main reasons for this: 1) these gelators couldn't be obtained from easily available and cheap starting materials, 2) tedious synthetic routes, 3) poor gelation capability in large scale process. Such performance limited the application of these gelators. Thus, there is a great need to develop novel PSGs that can be efficiently synthesized by only one-step procedure and maintain a high gelation capability in the scaled-up process.

Among the reported variety structures for gelation, including alkanes,^[4a] amino acids,^[4b,4c] simple modified bolaamphiphiles,^[4d,4e,4f] sugars,^[1c,4g] oligopeptides,^[4g] peptide amphiphiles, ^[4g,4h,4i] dendrimers, ^[4c,4g] C3-symmetric molecules, ^[4c,4g] nucleobases^[4j] etc, to our best knowledge, few easily available phthalic acid derived PSGs have been reported.^[9] In this study, we designed a series of structurally unique two-component phthalic acid derived gelators formed by P and liner aliphatic amine A.^[6d] Research result showed that acid-base interactions between gelators **P** and *n*-alkylamine **A** brought out a new series of two-component gelator PA, while A alone are not capable of gelating these solvents. FESEM morphologies study and X-ray diffraction data showed that the addition of A had changed the assembly manner. Two-component gelator PA has distinct advantages over single-component gelator P as simply changing mole ratio of P and A could tailor the properties of the gel. The optimized mole ratio of P and A was depending on the solvent properties. We also tested the gelation capability of **PA** ($n_P = n_A = 16$) formed by only one-step procedure without any purification, the minimum gelation concentration (MGC) of such crude PA had no significant differences with PA formed by stepwise operation. What's

^aCollege of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Dandong Lu West 1, Fushun 113001, Liaoning, P.R. China. Tel: +862456860548; E-mail: <u>yupeng.he@lnpu.edu.cn</u>,

^bDepartment of Medicinal Chemistry and Institute for Therapeutics Discovery and Development, College of Pharmacy, University of Minnesota, Minneapolis 55414, United States

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more important is that this highly efficient gelation systems can phase-selectively gel the oil phase without normal heatingcooling circle and show superior scale-up gelation ability for the first time.

Results and discussion

Design and synthesis of gelators P and PA

We started our work by the synthesis of a series of compound **P** (Scheme1) through a simple procedure using phthalic anhydride and *n*-alkylamines (carbon-chain length from 8 to 18) as starting materials.^[10] Then the gelation ability of compound **P** was tested in several organic solvents and oils (Table 1). The data showed that gelator **P** did not form gel with any protic or polar solvents, but congealed the non-polar solvents selectively. The MGC of **P** ranged from 0.5 to 12.2 (wt%). Particularly, gelation of soybean oil, cyclohexane, paraffin oil and *n*-hexadecane occurred in a relatively low MGC (1.1, 1.9, 0.5 and 1.4 wt% respectively), while gelation performance of **P** were worse in the aromatic solvents.

Fig. 1 showed the gel formed in different solvents when the carbon-chain length was 16 (n_P = 16). It was noteworthy that all of the formed gels were stable for at least two months in our study.

Notably, we discovered that the combination of gelators **P** and *n*-alkylamine **A** ($n_p = n_A$, n is the carbon number of the hydrophobic-chain) in different mole ratios formed a new series of two-component gelators **PA**. For the study of molecular co-assembly, we gradually changed the mole ratio of **P** and **A** from 1:0.2 to 1:1.2, and tested their gelation capability in diesel, paraffin oil, benzene and toluene.



Scheme 1 Synthesis of a series of single-component gelators P.

Table 1 Minimum gelation concentration (wt%) of gelators **P** with different hydrophobic-chain lengths in various organic solvents and oils.^{*a*}

Liquid or oil	n _P =8	n _P =10	n _P =12	n _P =14	n _P =16	n _P =18
benzene	Р	Р	4.3	9.2	6.4	10.3
toluene	Р	Р	4.8	12.2	8.5	6.3
soybean oil	5.0	1.1	1.4	3.1	4.2	5.6
diesel	8.0	4.6	6.3	3.6	3.5	5.6
paraffin oil	Р	3.8	6.5	3.3	1.9	3.3
cyclohexane	3.1	1.9	0.5	1.9	1.2	4.4
lubricant	Р	Р	6.9	11.6	9.8	11.9
n-hexadecane	10.8	1.4	5.0	5.9	2.6	11.6
tetrahydrofuran	S	S	S	S	S	Р
dichloromethane	S	S	S	S	Р	Р
ethyl acetate	Р	Р	Р	Р	Р	Р
chloroform	S	S	S	S	S	S
acetone	S	S	Р	Р	Р	Р
methanol	S	S	S	S	S	Р
ethanol	S	S	S	S	S	S
1,4-dioxane	S	S	S	Р	Р	Р



Fig.1 Gels formed by the gelators P in different solvents ($n_P = 16$): (a) benzene (b) toluene (c) soybean oil (d) diesel (e) paraffin oil (f) cyclohexane (g) lubricant.

For diesel and paraffin oil, gelation performance of PA were extremely regular. The optimized mole ratio of P and A were focused on 1:0.4 in diesel and 1:0.2 in paraffin oil while the hydrophobic-chain length was changed. Under this condition, MGC of **PA** ($n_P = n_A = 16$, **P**:**A** = 1:0.4) in diesel was 0.83 wt%, which was 4 times lower than the corresponding P, and MGC of PA ($n_P = n_A = 16$, P:A = 1:0.2) in paraffin oil was 0.17 wt%, which was 11 times lower than the corresponding P (Table 2). Moreover, MGC of PA in Table 2 were generally lower than 1 wt%, thus the two-component gelators PA showed remarkable property.^[1k,2a,11] gelatinizing Although the gelation performance of PA were relatively random in the case of benzene and toluene as the optimized mole ratio of P and A were changed with both the hydrophobic-chain length and the solvent (Table 3), the gelation ability of PA (most MGC> 1 wt%) was still better than P in both benzene and toluene.

Table 2 Minimum gelation concentrations (wt%) of gelators PA with different mole ratio in diesel and paraffin oil.^a

-						
	1:0.2	1:0.4	1:0.6	1:0.8	1:1	1:1.2
n	Di Pa	Di Pa	Di Pa	Di Pa	Di Pa	Di Pa
8	2.71 S	1.75 S	1.89 S	6.44 S	12.7 S	13.5 S
10	1.74 0.18	1.01 0.31	1.12 0.44	1.38 0.46	2.49 1.05	S 0.75
12	0.97 0.45	0.87 0.79	1.16 0.97	1.43 1.00	1.75 0.89	2.05 1.01
14	1.65 0.25	0.92 0.84	1.00 1.21	2.16 0.68	2.80 0.77	2.96 0.88
16	1.84 0.17	0.83 0.39	2.93 0.61	1.38 0.62	0.92 10.5	1.76 11.3
18	1.97 0.23	1.96 0.43	3.53 0.62	5.60 1.87	3.58 1.04	4.43 1.21

^{*a*}Di = diesel; Pa = paraffin oil; In this table, carbon-chain length of the complementary guest **A** was as same as that of the gelators **P** (n = n_P = n_A); S = soluble. The gelation time^[12] of **PA** (n_P = n_A, **P**:**A** ≥ 1:1) in the diesel was longer than one day (2 hours on the mole ratio of P:**A** = 1:0.4), and crystallization of **PA** in the gel phase could be observed after the gel was placed longer than two days.^[13]

Table 3 Minimum gelation concentrations (wt%) of gelators PA with different mole ratio in benzene and toluene.^{*a*}

	1:0.2	1:0.4	1:0.6	1:0.8	1:1	1:1.2
n	Ве То	Ве То	Ве То	Be To	Ве То	Ве То
8	7.67 4.81	5.14 1.69	5.51 3.18	S S	S S	S S
10	6.70 3.52	2.81 2.47	4.97 9.16	S S	S S	S S
12	2.24 2.28	3.55 2.29	5.71 1.97	4.47 2.49	10.52 S	7.03 S
14	1.98 3.56	2.63 2.78	3.32 2.78	7.77 6.40	10.82 2.40	7.26 2.76
16	1.93 1.92	1.64 2.17	0.71 3.08	2.09 3.35	6.89 4.00	7.38 6.31
18	7.90 8.00	2.79 3.13	5.93 6.01	4.14 3.09	3.62 5.97	4.31 6.41

^aBe = benzene; To = toluene; In this table, carbon-chain length of the complementary guest **A** was as same as that of the gelators **P** ($n = n_P = n_A$); S = soluble.

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^aP = precipitation; S = soluble.

^bn_P is the carbon number of the hydrophobic-chain of the gelators **P**.

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Table 4 Minimum gelation concentrations (wt%) of gelators **PA** withdifferent carbon-chain length of *n*-alkylamine in paraffin oil.

n	n _A=8	n _A =10	n _A =12	n _A =14	n _A =16	n _A =18
n _P = 12	0.43	0.33	0.45	0.47	0.41	0.48
n _P = 16	0.17	0.14	0.16	0.17	0.17	0.20

^a The mole ratio is **P**:**A** = 1:0.2 (optimized mole ratio in the paraffin oil).

The above result was encouraging, since it showed that the gelation capability of **PA** could be changed simply by tuning the mole ratio of the two components.

In addition, we changed carbon-chain length of the non-gelling additive **A** in two-component gelators **PA** ($n_P \neq n_A$) and tested their MGC in paraffin oil (on the optimized mole ratio of **P:A** = 1:0.2, Table 4). It was noteworthy that the gelation property of **PA** were scarcely affected by the carbon-chain length of the non-gelling additive **A**.

For refine oil like benzene, cyclohexane, toluene, diesel and petrol, the formed gel could be melted by heating and distilled to recover the oil.

Thermal stability of gels

Thermal stability of gels formed by gelators **P** and **PA** have been compared through Tgel (gel-to-sol transition temperature), which were measured by differential scanning calorimetry (DSC, Fig. 2).^[14] In diesel, Tgel values were 50.98 °C and 67.83 °C for **P** (n_P = n_A = 16, 10.82 wt%) gel and **PA** (n_P = n_A = 16, **P**:**A** = 1:0.4, 10.82 wt%) gel (Fig. 2a-b). In paraffin oil, Tgel values were 44.64 °C and 61.92 °C for **P** (n_P = n_A = 16, 5.59 wt%) gel and **PA** (n_P = n_A = 16, **P**:**A** = 1:0.2, 5.59 wt%) gel (Fig. 2c-d). **PA** gels demonstrated higher Tgel values then corresponding **P** gels, which indicated that **PA** gels were thermally more stable.



Fig. 2 DSC thermograms of diesel gel of a: **P** ($n_P = 16$), b: **PA** ($n_P = n_A = 16$, **P**:A = 1:0.4), and paraffin oil gel of c: **P** ($n_P = 16$) d: **PA** ($n_P = n_A = 16$, **P**:A = 1:0.2). Top four curves are cooling curves and bottom four curves are heating curves.

Obviously, a key issue in the enhancements of either the gelation capability or thermal stability of **PA** is the presence of **A**. In order to reveal the effect of **A** on the gelators **P**, FT-IR study, FESEM study, X-ray diffraction experiments, molecular dynamics simulation and rheological analysis were carried out.

FT-IR spectroscopy

Self-assembling processes of gelators were known to be driven by secondary forces: van der Waals, hydrogen bonding interaction, π - π stacking, electrostatic, and dipole - dipole.^[15] For the study of these interactions, FT-IR spectra of chloroform solution of P ($n_P = 16$), diesel xerogel of P (n_P = 16), diesel xerogel of PA (n_P = n_A = 16, P:A = 1:0.4), toluene xerogel of PA ($n_P = n_A = 16$, P:A = 1:0.2) and benzene xerogel of PA ($n_P = n_A = 16$, P:A = 1:0.6) were recorded (Fig. 3). The FT-IR spectrum of no self-assembly P (n_P = 16) in chloroform showed transmission bands at 3439 cm⁻¹ and 1722 cm⁻¹, which were non-hydrogen-bonded N-H stretching band and C=O stretching band, respectively (Fig. 3a). The transmission band of P (n_P = 16) diesel xerogel appeared at 3247 cm⁻¹ and 1720 cm⁻¹ respectively (Fig. 3b). The transmission band of **PA** appeared at 3245 cm⁻¹ and 1648 cm^{-1} for diesel xerogel (Fig. 3c), 3308 cm^{-1} and 1711 cm^{-1} for toluene xerogel (Fig. 3d), 3244 cm⁻¹ and 1710 cm⁻¹ for benzene xerogel (Fig. 3e) respectively. These data all declared that N-H stretching bands and C=O stretching bands shifted to lower frequencies. Therefore, intermolecular hydrogen- bonding plays an important role in this gelation systerm.^[16]

Morphologies from Field-emission scanning electron microscope (FESEM)

Field-emission scanning electron microscope (FESEM) was employed to examine the microstructure of organogels (Fig. 4). The FESEM micrograph of diesel xerogel based on gelator **P** ($n_P = 16$) showed lamellar structures of 133 nm thickness and 3.33 µm length (Fig. 4a). Referring to diesel xerogel based on gelator **PA** ($n_P =$



16); c: Diesel xerogel of PA ($n_P = n_A = 16$, P:A = 1:0.4); d: Toluene xerogel of PA ($n_P = n_A = 16$, P:A = 1:0.2); e: Benzene xerogel of PA ($n_P = n_A = 16$, P:A = 1:0.6).



Fig. 4 FESEM images of a: P ($n_P = 16$) diesel xerogels, b: PA ($n_P = n_A = 16$, P:A= 1:0.4) diesel xerogels, c: P ($n_P = 16$) benzene xerogel, d: PA ($n_P = n_A = 16$, P:A = 1:0.6) benzene xerogel.

 $n_A = 16$, **P**:**A** = 1:0.4), flower-like structure with a diameter in the range of 3.1 ~ 3.8 µm was observed (Fig. 4b). It is clear that there are vast tiny platelets branched from the corner of the ball. Such flower-like ball network possibly facilitate the entrapment of more solvent molecules and the branched platelets might bring out better interpenetration to the adjacent balls, therefore **PA**-gel shows higher gelation capability and thermal stability than **P**-gel. It is assumed that the adding of **A** leds to the branching process at the growing of lamellar structure. This could be understood as the result of the unsaturated salt formation.^[17]

Gelator **P** and **PA** formed complete different structure in benzene. From Fig. 4c-d, it is obvious that in benzene gelator **P** and **PA** assemble into fiber stucture. With the combination of **A**, fibers inside **PA** xerogel were much longer (Fig. 4d). This also explain the better gelation performance of **PA** in benzene. And it indicated that solvents had great influence on the assembly way of gelators.

Molecular packing arrangements from X-ray diffraction data

X-ray diffraction (XRD) experiments were carried out to investigate the molecular packing and orientation of the gelators in the gel state (Fig. 5). Diesel xerogel of **P** ($n_P = 16$) showed two groups of diffraction peaks at $d_1 = 2.87$ nm, $d_2 = 1.42$ nm (1/2), $d_3 = 0.94$ nm (1/3) and $d_1' = 2.51$ nm, $d_2' = 1.25$ nm (1/2), $d_3' = 0.83$ nm (1/3), respectly (Fig. 5a). These results indicated the presence of two sets of lamellar structures in the gel network.^[4e] The extended molecular length of gelator **P** ($n_P = 16$) was 2.62 nm (Fig. 6a, calculated by Material Studio 5.5). Moreover, the XRD response revealed one intense peak in the wide angle region at 2 $\theta = 19.92^\circ$, which may be attributed to the hydrogen bonding distance ~ 0.45 nm.^[18] In the presence of *n*-alkylamine **A**, diesel xerogel of **PA** ($n_P =$ $n_A = 16$, **P:A** = 1:0.4) showed less and low intensity peaks in the small-angle region (Fig. 5b), which indicating more amorphous character.^[19] This is in good coincidence with the FESEM data.

In order to figure out the exact reason for two groups of diffraction peaks in diesel xerogel, XRD experiment was conducted



Fig. 5 XRD spectra of a: **P** ($n_P = 16$) diesel xerogels, b: **PA** ($n_P = n_A = 16$, **P:A**= 1:0.4) diesel xerogels, c: **P** ($n_P = 16$) benzene xerogel, d: **PA** ($n_P = n_A = 16$, **P:A** = 1:0.6) benzene xerogel.

in *n*-hexadecane xerogel of **P** ($n_p = 16$), which showed diffraction peaks at 2.49 nm, 1.24 nm (1/2) and 0.82 nm (1/3). This result indicated that gelator **P** assembled into single set lamellar organization in *n*-hexadecane. Such difference in lamellar structure between **P** ($n_p = 16$) diesel and *n*-hexadecane gel may arise from the complex additions in diesel.^[20] **PA** ($n_p = n_A = 16$, **P:A** = 1:0.4) *n*hexadecane xerogel also presented less peaks in the small-angle region, which was coincide with **PA** ($n_p = n_A = 16$, **P:A** = 1:0.4) diesel xerogel (Fig. S13 in the Supporting Information).

XRD of benzene xerogel of **P** ($n_P = 16$) showed a group of diffraction peaks at $d_1 = 3.91$ nm, $d_2 = 1.97$ nm (1/2), $d_3 = 1.31$ nm (1/3), $d_4 = 0.98$ nm (1/4), $d_5 = 0.78$ nm (1/5), indicating that gelator **P** assembled into single set lamellar organization in benzene. And this periodicity lost in the **PA** ($n_P = n_A = 16$, **P:A** = 1:0.6) benzene xerogel (Fig. 5c-d).

Molecular Dynamics Simulation

From the FESEM micrograph and XRD experiments, we could see that three-dimensional network rather than lamellar structures formed after n-alkylamine A was added. In order to obtain an insight of the gelation process of PA with diesel in a molecular level, a molecular dynamics (MD) simulation of the two components P and A in n-hexadecane molecules was performed using Desmond package^[21]. A novel inverse micelle type **PA**-complex was formed through the H-bonding network among the hydrophilic heads of five P and two A (Fig. 6f and 6g). Representative frames showed that the hydrocarbon tails of PA-complex form efficient hydrophobic interactions (van der Waals interactions) with nhexadecane molecules by aligning themselves parallel to the hydrocarbons (Figure 7). Thus we could concluded that the addition of *n*-alkylamine **A** has changed the self-assembling^[22] way of **P** by forming H-bonding network with P, which leading to a novel balllike structure.

Rheological properties

Rheological behaviour of these organogels can be very important for their practical applications. This is largely depended on the supramolecular aggregation of gelator molecules. Fig. 8a and 8c showed the plots of G' and G'' against strain at a constant



Fig. 6 Possible arrangements of gelator **P** ($n_P = 16$) and **PA** ($n_P = n_A = 16$, **P**:**A** = 1:0.4) in diesel. a) The energy-minimized structure of **P**; b and c) possible arrangements of **P**; d) potential ball-like structure of **PA**; e) selected regions of the XRD pattern of **P** ($n_P = 16$) diesel xerogel; f) MD simulation of **PA** complex; g) H-bonding network in the **PA**-complex.



Fig. 7 Representative frames of the 5 ns MD simulation (1024 frames) of the **PA**-complex in *n*-hexadecane molecules.

frequency of 1 Hz. The storage modulus (G') of these gels decreased rapidly and fell below the loss modulus (G'') after the critical strain region indicated that the oil gels underwent gel (G' > G'') to



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Fig. 8 Rheological studies for the diesel gel of **P** (10.82 wt%, $n_P = 16$) and **PA** (10.82 wt%, $n_P = n_A = 16$, **P**: **A** = 1:0.4) (a) stress sweep, (b) frequency sweep; and for the paraffin oil gel of **P** (5.59 wt%, $n_P = 16$) and **PA** (5.59 wt%, $n_P = n_A = 16$, **P**: **A** = 1:0.2) (c) stress sweep, (d) frequency sweep.

sol (G' < G") change beyond the critical strain. Overall, the mechanical properties of **P** and **PA** gels are very robust and similar, whereas the gels based on single-component gelator **P** are mechanically weaker.

Frequency sweep experiments were taken in the linear viscoelastic region (γ fixed at 0.05%) decided by the strain sweeps experiments. It was showed that the storage modulus (G') was higher than the loss modulus (G") at any given frequency (Fig. 8b, 8d). This observation confirmed the formation of soft solid-like gels.^[23] Also, the two-component gels possessed higher G' values (one order) compared to the single-component gels on the same concentration. These results showed **A**-induced enhancements in the mechanical property of gels which was in line with our expectation.

Applications

It was noteworthy that we also tested the gelation capability of crude **PA** ($n_P = n_A = 16$) formed by only one-step procedure (phthalic anhydride and *n*-alkylamine **A** were stirred together in a glass bottle in a ratio of 1:1.2 and 1:1.4, respectively) without any purification (Scheme 2). To our delight, MGC of such **PA** ($n_P = n_A = 16$) in diesel and paraffin oil (0.90 and 0.21 wt%, respectively) had no significant differences with **PA** ($n_P = n_A = 16$) formed by adding an extra *n*-alkylamine **A** to the pure **P** (0.83 and 0.17 wt%, showed before in Table 2). Thus, such **PA** formed by only one-step procedure is a readily alternative to **PA** formed by stepwise operation in practical applications.

Having established the ability of gelator **PA** to form strong and stable gel in biphase mixture (Fig. S16), we further examined the gelation process without heating-cooling cycle. Since gelator **PA** ($n_P = n_A = 10$, **P:A** = 1:0.4) showed a comparative gelation perfomance and better solubility than **PA** ($n_P = n_A = 16$, **P:A** = 1:0.4), we used it for oil-spill recovery. For the recovery of diesel, petroleum ether (5% ethanol) was used as non-polar gelator carrier (Fig. 9, Video 1).

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To our great satisfaction, the diesel layer was thickened in about 1 minute and could be skimmed off with a sieved scoop. The mass fraction of gelator used was 6 wt% to produce enough gel solidity. Rheological properties of the recovered diesel gel were shown in the supporting information (Fig. S17). Recovery of crude-oil was also tested and the crude-oil layer was thickened within 5 minute (Fig. S18, Video 2). The remained liquor phase was extracted and concentrated, the results showed that neither gelator **PA** nor *n*-decanamine was detectived.

In order to examine the scale-up capability of the target gelators, a kilogram-scale gelation between paraffin oil (1 kilogram, 1.2 L) and crude **PA** was attempted (Fig. 10). The gelation capability of the **PA** was 10.47 wt% (9.1g L-1) in the beaker. Thus, this gelator might be practically viable approach for marine oil-spill recovery.



Scheme 2 Synthesis of two-component gelator PA via one-step procedure ($n_P = n_A = 16$, phthalic anhydride: A = 1:1.4).



Fig.9 a) Petroleum ether (5% ethanol) solution of gelator PA ($n_P = n_A = 10$, P:A = 1:0.4) was spread over a diesel/water mixture (20 mL:400 mL). b) Gelation of the diesel layer in about 1 min. c) Removal of the diesel gel with a sieved scoop. d) The removed diesel gel.



Fig. 10 Gelation of 1.2L paraffin oil with the crude product.

Experimental

Synthesize of single-component gelator P

All alkylamines, solvents were purchased from well-known commercial sources and were used without further purification, as appropriate. 1.07 g (7.2 mmol) of phthalic anhydride and 65 mL acetone (solvent) were introduced into a 150-mL round-bottomed flask. Then 6.6 mmol of *n*-alkylamine **A** was added slowly with rapid stirring. After the completion of addition, stirring was continued for 6h at room temperature. The crude product was recrystallized from water/ethanol mixture to give the mono-alkylamide phthalic acid **P** with yield from 67% to 76%.

Gelation Studies

The gelation propensity of **P/PA** was initially investigated in paraffin oil. For evaluation of MGC, a known amount of **P/PA** in paraffin oil was heated to 85-90°C, which resulted in a clear solution. The resulting clear solution on spontaneous cooling transformed into gel within 1-2 min. The organo-gelation propensity of **P/PA** has been checked systematically by gradually increasing the amount of the paraffin oil. In that way the minimum concentration of the gelators that required to immobilize 1 mL of paraffin oil, i.e, MGC value was determined. The above measurement was carried out three times and the average MGC value has been reported.

Characterization

NMR spectra were recorded on Agilent Technologies 400/54 Premium Shielded instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. High resolution ESI mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. FTIR measurements were carried out in a Perkin Elmer Spectrum-GX Spectrometer using KBr pellet, respectively. Gels were carefully mounted on the glass slide and dried for a few hours under vacuum before imaging. The samples were then coated with platinum vapor and analyzed on a Hitachi SU-8010 microscope operated at 1 kV. Gels were analyzed using a Rigaku D/MAX-RB instrument. The X-ray beam generated with a rotating Cu anode at the wavelength of K α beam at 1.5406 Å was directed toward the film edge and scanning was done up to a 2θ value of 48°. Differential scanning calorimetry (DSC) was carried out by using a TA DSC-TGA. A volume of 0.5 ml of P diesel gel (10.3 wt% as example) was placed into a screw-capped vial. The sample vial was placed into the DSC apparatus together with an empty sample vial as reference. Each sample was heated to melting to remove the anisotropic history. The heating-cooling-heating cycle from 0 °C to 100°C was performed at a rate of 5°C min⁻¹. Rheological measurements were performed with a hybrid rheometer (TA instrument DHR-2) equipped with steel coated parallel-plate geometry (25 mm diameter). The gap distance was fixed at 1mm. All measurements were done at 25°C. Firstly, a stress sweep at fixed frequency (1 Hz) was performed to determine the linear regime of

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the sample. Secondly, a frequency sweep experiments was carried out from 0.01 Hz to 10 Hz at a constant strain of 0.05%.

Conclusions

We have successfully designed and prepared a novel twocomponent gelation system derived from phthalic acid (MGC < 1 wt%). MD simulation showed the additive **A** changed the selfassembling way of gelator **P** by forming H-bonding network in the acid-base complex, which bring out better gel properties comparing to the simple-component gelation system. Unlike other previously reported two-component gelation systems, we can readily modify the mole ratio of gelator **P** and additive **A** to control the gelation capability of **PA**. Especially, the obtained two-component gelation system has a high two phase selectivity between aqueous and organic solvent, this process could be finished without heatingcooling operation. Furthermore, the gelation process can be progressed in a kilogram scale, which is reported for the first time and thereby showed to be an alternative solution for practical oil spill recovery.

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Acid-base interaction in the cooperative assembly enhanced the gelation capability dramatically, which lead to an efficient kilogram-scale gelation.

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