Design and physicochemical properties of long and stiff fatty low molecular weight oleogelators

F. Delbecq, R. Nguyen, Elisabeth van Hecke, C. Len

Design and physicochemical properties of long and stiff fatty low molecular weight oleogelators

F. Delbecq[a]*, R. Nguyen[b], E. Van Heck[b], C. Len[c]

[a] Ecole Supérieure de Chimie Organique et Minérale (ESCOM), EA TIMR 4297 UTC/ESCOM, 1 allée du Réseau Jean-Marie Buckmaster, F-60200 Compiègne, France. *E-mail : f.delbecq@escom.fr

[b] Sorbonne Universités, Université de Technologie de Compiègne (UTC), EA TIMR 4297 UTC/ESCOM, CS 60319, F-60203 Compiègne Cedex, France.

[c] PSL Research University, Chimie ParisTech, CNRS, Institut de Recherche de Chimie Paris, 11 rue Pierre et Marie Curie, 75005 Paris Cedex 05, France.

ABSTRACT

Stearic acid and nine other derived long and fatty low molecular weight oleogelators were tested to gelate two different vegetable and edible oils, liquid paraffin and methyl oleate. In these liquids, among all gelator candidates, three of them expressed remarkable Critical Gelation Concentration (CGC) values found in a range of 0.6 and 2 wt % Their gelation ability were apparently dependent on their intrinsic molecular structure and evolved function of their lipophilic balance. To understand the phenomenons reported here, microscopic observations of the gel samples were carried out to study the gel texture. The FT-IR analysis of each sample also afforded detailed information about the molecular assembly of the additives and their potential role in the host liquids. Differential Scanning Calorimetry (DSC) measurements demonstrated the potential for our best oleogelators candidates to form strong gels in the hydrophobic liquids, and the possible direct interactions with the TAGs included in the edible oils. The study of the viscoelastic behavior confirmed also the importance of two long alkyl chains grafted on a small and rigid spacer and the need of a non negligible lipophilic level of these gelators to get a strong and stable gel at the lower concentrations.

Key-words: long fatty oleogelators, self-assembly, oil polymorphism modulation, lipophilic balance

1. Introduction

Lipids and vegetable oils are edible raw materials widely used in the food industry and molecular gastronomy [1-3]. For defined purposes, catalytic hydrogenation of oil products leads to the

formation of fatty solid material displaying improved mechanical and physical properties more suitable for food applications such as processing of margarine or ice-cream. Unfortunately, during the process, a certain amount of trans insaturated fatty acid is generally formed. Nowadays, this category of lipid by-products is known for its undesirable and bad effects on the consumer health such as an elevation of the low-density lipoprotein cholesterol (LDL) and the associated cardiovascular diseases. Besides, trans fatty acids are also suspected to promote endothelial dysfunction and supposed to be also carcinogenic species.

To replace the catalytic hydrogenation process, some alternative strategies could be employed such as the addition of a low molecular weight organogelator (LMWOs) to the liquids, polysaccharide such as ethylcellulose mixed with surfactants [4], or extracted natural products [5]. Usually, at concentrations inferior to 2 wt %, this kind of additive could ensure that oils can get features and rheological properties near to solid material at ambient temperature. Finally, a thermally semi-solid gel stable for several months is formed upon cooling.

Oleogels and especially molecular gels are a solid-like form of soft matter comprised for the majority of liquid and a small amount of a gelator introduced at very low concentration. The formation of a physical gel results from the gelator self-assembly induced by non-covalent forces such as Van der Waals interactions, dipole-dipole or London interactions and more often by hydrogen bonding. Thus, oleogels are now studied as new materials for their physicochemical and organoleptic properties similar to those of fatty material rich in trans saturated fatty acids. In the most recent literature, only a few example of fatty compounds are recognized for their potential to gelate edible oils: lecithin, sorbitan tristearate [6-8], monoacyl glycerides [9, 10], mixture of phytosterol, oryzanol or other steroide-type compounds [11], ricinelaidic acid [12, 13], fatty acids [14, 15], fattyl alcohols [16, 17], 12-hydroxystearic acid (12-HSA) and derivatives [18-22], simple waxes and wax esters [23-26] and lipopeptides [27, 28]. This category of soft materials are typically developed to obtain suitable properties for applications such as ointment in cosmetics, drug delivery system (DDS) [29] or oil spill remediation [30].

Furthermore, for applications in the field of lithium-ion battery or energy, scientists try to make effort to produce aprotic LMWOs able to gelate solvents such as propylene carbonate or liquid paraffin. For this purpose potent 12-HSA or stearic acid based lipopeptides [31] are not suitable materials due to the existence of hydroxyl group or amide functions in their structures, too reactive in presence of lithium metal. Thus, as a passive thermal management system, liquid paraffin gels or solid wax could be useful to modulate the temperature of the batteries in a multi-layered device. Besides, from an industrial point of view, compounds displaying ester functions are easier to produce and cheaper than their amide counterparts.

As depicted on Figure 1, a series of 9 bio-based hydrophobic oleogelator candidates were designed and synthesized in our laboratory. For each compound the self-assembly was investigated in liquid paraffin and edible oil with different techniques such as rheology, FT-IR spectroscopy, differential scanning calorimetry (DSC) and polarized light microscopy. All results were compared to those expressed by stearic acid (SA) that became our reference in this present work.

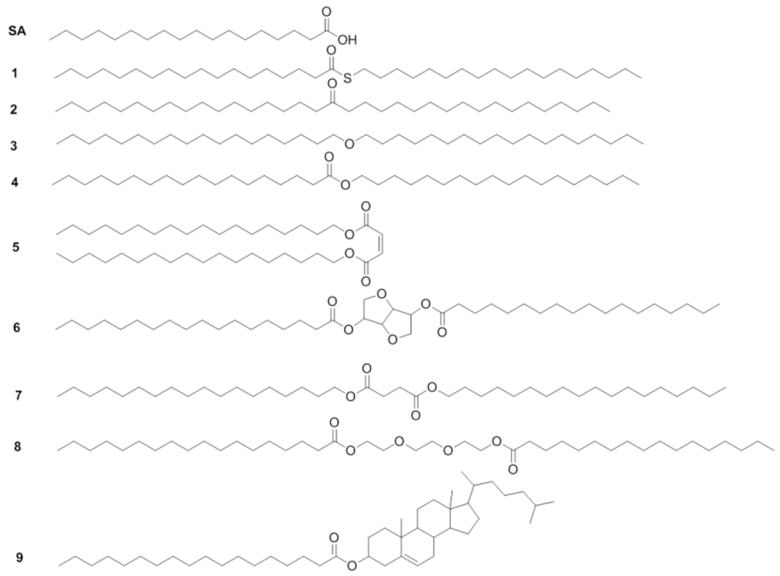

Fig 1. Chemical structure of stearic acid (SA) and and oleogelator candidates 1-9.

2. Experimental

2.1. Materials

Cholesterol (95 %), ethanol absolute (99.5 % extra dry), stearic acid (97 %), octadecyl mercaptan (96 %), isososorbide (98 %), succinic acid and triethylamine (TEA) were purchased from Acros Organics. Other reagents such as 1-octadecanol ReagentPlus (99 %), maleic acid ReagentPlus (≥ 99,0 %), stearoyl chloride (≥ 90 %) and triethylene glycol ReagentPlus (TREG ; 99 %), succinic acid (for synthesis), soy bean oil, dichloromethane analytical standard (CH_2Cl_2), methyl oleate (99 %), rapeseed oil (natural rapeseed oil from Brassica Rapa) and Paraffin (liquid, pure) were obtained from Sigma Aldrich. *p*-toluene sulfonic acid monohydrate (PTSA-98 %) was furnished by Alfa Aesar.

2.2. Organic synthesis

Diester 6 was produced simply by heating at 120°C for one day 2 equivalents of stearic acid in presence of one equivalent of isosorbide and 5-10 % of PTSA. Other esters 4, 8 and the monoester 9 were synthesized by stirring at room temperature, defined amount of the stearoyl chloride in presence of sufficient amount of cholesterol or a diol dissolved in CH_2Cl_2 solution containing TEA. Other compounds, thioesters 1, ketone 2, ether 3 were produced according the procedures found in the literature [32]. Diesters 5 and 7 were both obtained by reaction of maleic or succinic acid respectively with 2 equivalents of octadecanol in presence of 5-10 % of PTSA in neat condition. Then, to isolate each target compound, the crude material was solubilized in CH_2Cl_2 if necessary and the organic layers were successively extracted with aqueous $NaHCO_3$ solution, the two phases were separated, the organic layer was dried on $MgSO_4$ and evaporated under reduced pressure. After being

isolated, all materials were recrystallized from ethanol to afford compounds 1-9 as white crystals. (For the respective ^{1}H NMR charts, see ESI Figure S1)

2.3. Instrumentation

Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Bruker avance III 400 spectrometer equipped with a BBFO probe operating at room temperature using $CDCl_3$ or DMSO-d_6 as solvent.

Differential Scanning Calorimetry (DSC) was conducted on a DSC 8 MC Mettler Toledo using aluminium pans. Scans were conducted under nitrogen atmosphere with a heating rate of 2°C/min in the temperature range of -100 to 150°C.

FT-IR (ATR) spectra were recorded on a FT-IR 4000 Jasco in a range of 600 to 3800 cm^{-1}. Number of scans: 32 or 64.

Viscosity measurements were carried out using a Physica MCR 301 (Anton Paar) rotational rheometer equipped with a double gap measuring system that can regulate the temperature in a range from - 40 to 200°C. Measurements were monitored by Rheoplus software. All experiments were performed at 20°C and the viscoelastic behavior was checked for shear rates ranging from 0.1 to 10 Hz. Two replicates were performed for each sample. Usually, 0.5 g of a selected robust gel sample was uniformly laid between the two discs forming the measuring cone with 2.5 mm of diameter. The storage and loss were plotted as a function of stress at 20°C. The viscoelasticity of each sample was characterized in terms of the elastic modulus (G') and the loss modulus (G'').

Cross-polarized light microscopy observation was carried out on a LEICA DM 2700 M. A drop of melted gel samples has been deposited on a glass microscope slide and the morphology of the gel sampling was observed in real time with a digital camera. Usually, a gel deposit is heated to a temperature slightly superior to its melting point, and then the observation of the resulted drop of liquid is made directly while cooling the glass slide with metal plate thermostated by a water flow system.

For the gel-sol phase transition temperature against gelator concentration measurements, a test tube containing 1.0 g of each selected gel sample was introduced in a thermostated water bath. The temperature increased at a rate of 2°C per minutes.

2.4. Gelation ability examination

The gelation ability of SA and each oleogelator candidate 1-9 was measured in a chosen liquid. In a typical gelation procedure, 10-60 mg of a selected compound was introduced in the liquid (0.94-0.99 g) and 1.0 g of the resulted sample was heated up until a quite clear solution was obtained. Then, the resulted translucent or turbid solution was allowed to return to the room temperature forming a gel in a short period of time. At the higher concentration, the oleogels were stable for up to 6 months.

3. Results and discussion

Usually, when a mixture of fatty alcohols and fatty acids such as octadecanol or stearic acid are added in a triglycerides (TAGs) rich vegetable oil in a sufficient ratio, it is possible to observe the formation of needle-like crystals involved in the rheological behavior variation of an entire gelated system. For example, in edible oil or even in a "TAGs-free" fatty liquid such as liquid paraffin, stearic acid was subject to a self-assembly into a supramolecular structure driven by two additional interactions [33]. First, as illustrated in Figure 2, the fatty acid can form some kind of dimer through a "head to head" packing, then a well-ordered interdigitated network could be generated and reinforced due to the hydrophobic nature of the alkyl tail of SA. Our original idea was to replace here the "head to head" packing stabilized by H-bondings with a covalent and conformationally restricted structure displaying different lipophilicity degrees in order to enhance the physico-chemical properties of the oleogels.

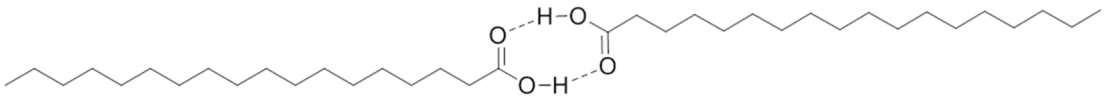

Fig 2. Molecular model of "head to head" packing of generated from SA in oil or liquid paraffin.

3.1. Formation and characterization of various supramolecular gels

In the first stage of our study, the gelation ability of SA and each other oleogelator candidates were examined in four different liquids: liquid paraffin, soybean oil, rapeseed oil and methyl oleate. The gel ability and the respective Critical Gelation Concentration (CGC) of all additives were initially investigated in commercial liquid paraffin as reference and soybean oil and were finally summarized in Table 1.

Table 1. Gelation ability of SA and gelators 1-9 in liquid paraffin and soybean oil.

	CGC (%)	
Gelator	Liquid paraffin	Soybean oil
SA	2	2 (G)-1(PG)
1	4	2
2	0.4	0.9
3	6	4
4	3	2
5	I	I

6	2	2
7	6	6
8	6	6
9	6	6

G : strong gel ; PG : partial gel ; I : Insoluble or recrystallization in the medium.

According to these results, the best candidates were apparently the compounds 2 and 6. The first one is a simple long and fatty ketone chemically produced from SA which is structurally close to a natural wax. This compound was expected to exclusively promote hydrophobic interactions in a low polar liquid such as edible oil. The second one is a derivative of isosorbide decorated with two long hydrophobic C18 alkyl chains. Recently, a patent reported the ability of an enzymatically produced mixture of long fatty mono and diesters of isosorbide to modulate the texture and improve the viscosity of oils [34]. In this present work, a coherent decision was made to study only the pure diester derivative. In the case of 2, by replacing the “head to head” packing with a simple carbonyl group, it is possible to enhance the total length and the rigidity of the carbon backbone. Thus, the molecular packing is supposed to be reinforced by dipole-dipole interaction between two nearest and successive carbonyl groups inside the gel networks. On the other hand, for 1 and 4, after replacing the dimeric structure of SA by a thioester function or its simple ester counterparts, it appears possible to obtain gels in liquid paraffin, but at higher concentration of 4 and 3 wt % respectively for 1 and 4. These values were higher than those expressed by SA in the same medium. However in soybean oil, the values were quite similar due to the multi-component nature of the liquid including TAGs and other di- and monoglycerides in various ratios. Other compounds 3, 7, 8 and 9 required higher concentration levels with 6 wt % in average to gelate both liquids. Besides, there were some variations of gelation rates detected with the naked eye and the gel stability was clearly dependent on the nature of the additive itself: for 7 the gelation phenomenon was very fast, by opposite the gelation induced by 9 was slower, especially in the liquid paraffin. Herein, for 9 the introduction of a steroid-type moiety had no positive effect on the gelation ability and expressed higher CGC. For the compound 8, greater CGC and low stability of the gel could be explained by comparison with the conformationally restricted structure of 6. The compound 8 is characterized by its TREG-based and open-ring form which is at the origin of its molecular backbone flexibility. For this main reason, the gelator 8 need being added at the higher concentration, about 6 wt % to afford a strong gel in both studied liquids and after a short period of time, an undesired demixing of two phases is generally observed in the vial. Compared to 2, the long fatty ether 3 also required high concentrations to give gels and the compound 5 recrystallized from its hot solutions to give white needle crystals. Moreover, the gel samples of 3 were easily and mechanically breakable.

On Figure 3, some pictures are given as representative photographs of our best gel samples formed at their lower CGC. As depicted, despite the lower CGC of the sample, as suspected, the gels showed low transparency and they are often opaque even in liquid paraffin.

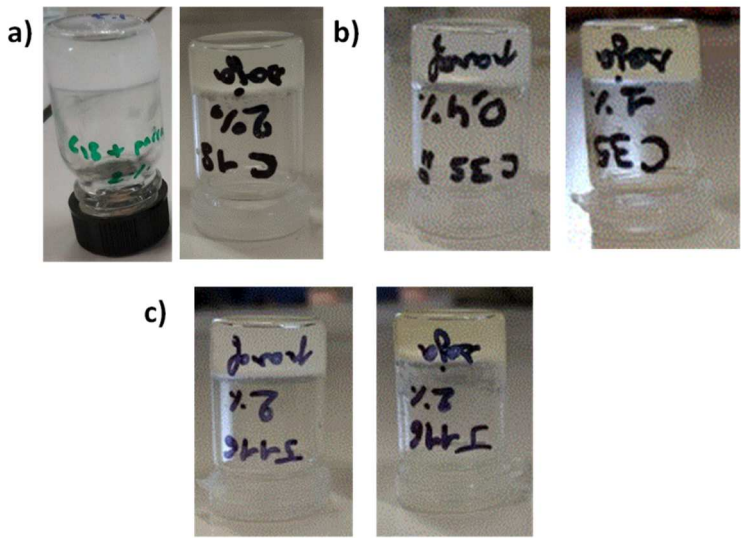

Fig 3. From left to right : (a) gels from 2 wt % of SA in liquid paraffin and soybean oil ; (b) gels obtained from 0.4 and 1 wt % of 1 in liquid paraffin and soybean oil respectively ; (c) gels formed from 2 wt % of 6 in liquid paraffin and soybean oil.

By using our previous best gelator candidates 1, 2, 4 and 6, the tests were extended to two other liquids as reported in Table 2.

Table 2. Gelation ability of gelators 1, 2, 4 and 6 in rapeseed oil (RO) and methyl oleate (MO).

	CGC (wt %)	
Compound	RO	MO
1	2 (WG)	2
2	0.6	1
4	2.5	3
6	4	1

WG : weak gel

As supposed the best candidates remained the gelators 1 and 2. Interestingly, in rapeseed oil (RO) the CGC measured for 6 was higher than the value obtained in soybean oil. For 4, the CGC did not change drastically and was included in a range of 2 and 3 wt % If we consider that compounds 1 and 4 can afford strong gel in a “TAGs-free” hydrophobic liquid such as methyl oleate for concentrations superior to 2 wt % in average, the higher hydrophobic character of 1 could be responsible of its better performance as a texturing agent, but gave weak gels in RO. Besides, when we tried to reduce its

concentration in methyl oleate (MO), a partial gel was generated for concentrations inferior to 2 wt % Later, to remedy to this problem, when 1 was used as gelator in mixtures of RO and MO at different ratio (see ESI, Figure S2), a strong gel was obtained at the constant concentration of 2 wt % in a mixture of RO-MO (9:1, v/v). This phenomenon could be explained by the subtle balance existing here in the poorer TAGs content of the liquid mixture. For 6 and 2, a CGC of 1 wt % was enough to give a strong gel in methyl oleate (see also Figure S2, ESI). As reported before, all physic-chemical properties of a supramolecular gel depend on the solvent polarity of the host liquid. Thus, the mechanical strength, the viscosity and the thermal stability of the materials depend strongly on the characteristic Hansen solubility parameters (HSPs), especially the hydrogen bonding parameters δ_H [35]. On the Table S1 of the ESI, δ_H and others HSP descriptors of edible oils were investigated by means of solubility tests in a large variety of organic solvents (results not shown here) and summarized for all liquids studied in this work. Usually, it is well known that the thermal and structural stability of a physical gel increased with the polarity in parallel with the value of δ_H. Surprisingly, the lower value of δ_H was expressed by MO, but all other liquids showed a similar value of δ_H around 6.0 MPa $^{1/2}$. In regards to these values, it is possible to affirm that MO is surely the most lipophilic liquid and LP is obviously our best second reference for our study in association to SA.

3.2. Gel microstructure observation

The result of the oleogels texture and morphology observations of oleogels obtained in soybean oil from gelators 1, 2, 4 and 6 are given in Figure 4.

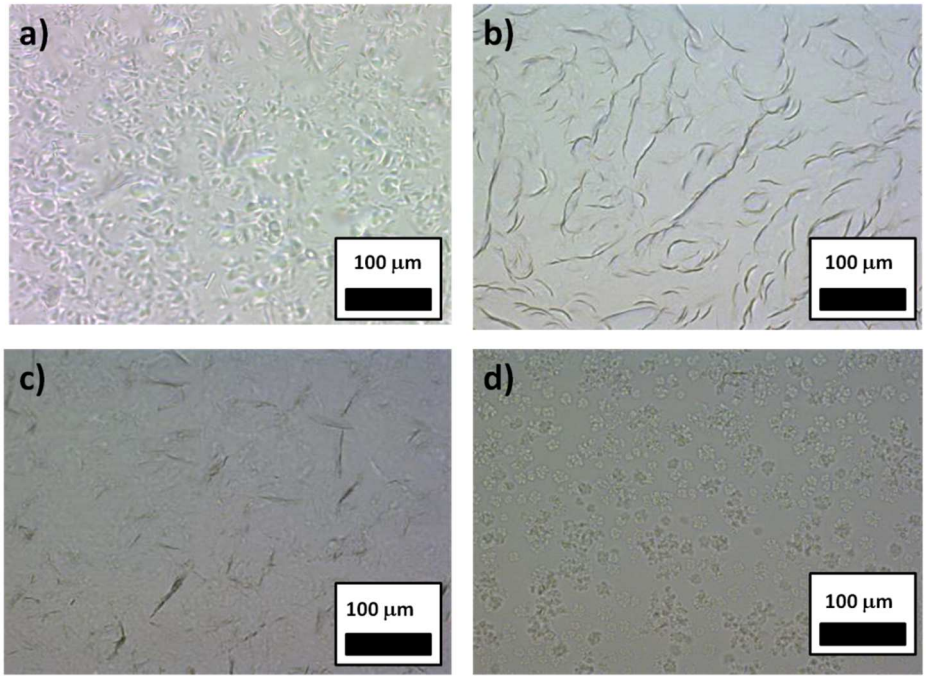

Fig 4. Polarized light micrographs of gel from : a) 2 wt % of 1 in soybean oil ; b) 1 wt % of 2 in soybean oil ; c) 2 wt % of 4 in soybean oil ; d) 2 wt % of 6 in soybean oil. All concentrations were set up near to the respective CGC of each gelator.

On the photographs, compared to 1, the gelator 4 is able to give in all liquids used in this work some kind of elongated fiber-like crystals of 50 μm of length source of the hardness and elasticity of the sample. On the other hand, the gelator 1 has a behavior relatively close to those expressed by 6 proven by the generation of a finer network able to entrap the liquid in its physically stabilized microstructure. In fact, the gel matrix shows well dispersed spherulitic crystalline units, even if the shape of the crystals generated from 6 differed visually from those obtained with 1. In the case of 6, the recrystallization phenomenon appeared to be very slow on the microscope. It is well known that spherulitic structures have more time to diffuse at a low cooling rate and they are able to fuse with more compatible elements or the nearest already nucleated species. Then, this mechanism leads to the formation of huge clusters immobilizing the liquid. More interestingly, by using 2 in all liquids reported in this work, apparently the gelator could self-assemble into broad and twisted fiber-like structure. This shape is known as a typical feature of a self-assembled fibrillar network (SAFiN) often observed with lipopeptides [36] employed as low molecular organogelators in organic solvents such as toluene. It is also comparable to the behavior of 12-HSA and its derivatives [37].

Obviously, other additional interesting comments can be made for the not very powerful gelators 3, 7, 8 and 9 (pictures not shown here). In case of 3, the microscopic observation showed tiny fibers that never grew anymore during the cooling. For 7, the sample morphology was characterized by large platelet-like structures easy to separate under mechanical frictions. In the case of the TREG derived gelator 8, despite the formation of the expected spherulitic structures in the edible oils, we obtained the same morphology pattern in liquid paraffin. In parallel to the higher CGC expressed by 8 in both liquids reported in Table 1, it is possible to imagine that the nuclei formed by gelator shows some difficulties to interact with the TAGs found in the soybean oil. In case of 9, by returning progressively to room temperature, the microscopic observation confirmed the presence in the hot medium of insoluble droplets of the gelator turning into spherulites and slowing down their curses before being immobilized in a gel matrix. For 9, this phenomenon should be interpreted exclusively as a multi-steps and more complicated process. In summary, to obtain the most suitable matrix leading to the formation of an oleogel, our study proved that a good gel texture requires common long fiber of needle-like structures able to incorporate a large volume of the liquid components of oils such as non crystallizable fatty esters. It is important to bear in mind that for the edible oils, the crystal growth is clearly dependent on the mass transfer of the TAGs from the liquid to solid interface under the influence of an additive but also of the removal of heat generated by the recrystallization process. The additive must play the role of a promoter of nucleation seeds that is subject to some conditions reported in the next paragraph.

3.3. FT-IR analysis

In the ESI, as depicted on Figure S3, for pure liquid paraffin, the characteristic signals of symmetric and anti-symmetric CH_2 vibrational modes were located respectively at 2934 and 2852 cm^{-1}. Once the gels were formed from the addition of 1, 2, 4, and 6 at their CGC, the signals are expected to evolve into a sole broad band observed usually between 2923 and 2852 cm^{-1} except for 4 showing the second

peak located at 2848 cm^{-1}. Besides, in liquid paraffin, the scissor mode of CH_2 groups appears as a strong doublet of two peaks located at 1458 and 1466 cm^{-1}. In addition, the difference of intensities of these peaks indicated us that a $\beta 1'$ inclined lamellar structure could be representative of the gel networks with a more intense peek found at 1463 cm^{-1} (see Figure S3d, ESI). Interestingly, for 6 in LP the ratio was inverted. Furthermore, the additional rocking band was observed at 721 cm^{-1} for all samples, evidence of long "polymethylene chains". All results are compatible with a typical orthorhombic perpendicular subcell leading to the formation of the robust liquid paraffin gel samples. In fact, this situation is said to be ideal when researchers try to develop new compounds as new nucleation agents acting as modulator of crystallization kinetics in the vegetable oils.

In order to complete our study, the spectra of Figure S4 of the ESI could be useful. We compared the previous gels samples with rapeseed oil gels obtained using the same previous gelators introduced at their respective CGC. Thus, two distinct bands were clearly observed at 2852 and 2923 cm^{-1}. This minor variation of the wave number often appeared from enhanced Van der Waals interaction between the nearest hydrophobic chains. Besides, the characteristic bands of CH_2 scissor mode were also observed at 1456 and 1463 cm^{-1} associated to the CH_2 rocking bands recorded at 721 cm^{-1} for both 1 and 6. Curiously, the rapeseed oil gel of 2 gave a broad signal for the methylene rocking band. Compared to liquid paraffin gel samples, the signal strength of both signal were in their best ratios that could confirm the creation of a parallel lamellar structure and the gel assembly can first evolve independently of the TAGs present in the liquid [38-41].

3.4. Results of the DSC analysis

Further oleogel samples formed in liquid paraffin (LP) and rapeseed oil (RO) were prepared and tested at their CGC or at superior values for being evaluated by DSC in a range of temperature set up between -90 and 100°C. Some representative features of the thermograms of gel samples of 1, 2 and 6 were given in the ESI, on Figure S5. The cooling rate of 2°C/min remained unchanged for all experiments and the results are reported in the following Table 3.

Table 3. Summary of all exo- and endothermic events measured for both liquid paraffin and rapeseed oil gels generated from the addition of gelators 1, 2, 4 and 6 at concentrations leading to the formation of strong gels in both liquids.

	LP				RO	
Gelator	Tc (°C)	Tm (°C)	Tc_1	Tm_1	Tc_2	Tm_2
1[a]	31.8	41.5	-41.5	-16.4	39.1	45.9
2[b]	45.9	58.2	-54.1	-45.8	48.1	61.3
4[c]	27.1	35.7	-54.2	-18.3	38.8	45.8
6[d]	34.2	57.7	-53.8	-17.9	34.1	52.3

Gelator concentrations in both LP and RO: a) for 1 (4 wt %) ; b) for 2 (2 wt %) ; c) for 4 (3 wt %) ; d) for 6 (2 wt %).Tc_1, Tm_1, Tc_2, Tm_2 were all expressed in °C.

Without surprise, in a lipophilic and "TAGs-free" liquid such as liquid paraffin, the gelators could be considered as a simple low molecular weight gelators (LMWGs), confirmed by the sole successive exothermic and endothermic event seen on their thermograms. The LP gel samples obtained with the gelator 2 appeared to be the most stable for temperature superior to 50°C and it gives the higher value of recrystallization temperature of 58.2°C. This result could explain for 2 the non usual aspect of the gel texture given in Figure 3b by a low rate of the gelation process. The same phenomenon was observed for 6 with comparable value of undercooling (Tm-Tc), but this time with the formation of network made of thinner fibers. Interestingly, despite the incorporation of a sulfur atom and its resulting improved lipophilic character compared to the ester 4, 1 showed a Tc value of 31.8°C in LP where it seems to be more soluble than 2 and 6 due to its lower undercooling, that could explain its higher CGC. For 1, the increase of Tc_2 and Tm_2 values could be coherent with the direct influence of the medium composition on the gelator behavior. In the case of 4, the gel state was comprised in the narrowest range of temperature. When 4 was compared with SA, if the acid was introduced at 2 wt % in liquid paraffin, both values of Tc and Tm were recorded respectively at 24.8 and 41.2°C. This result was directly closed to those of 4 when measured in the same liquid. It is also well-known that both enthalpy peaks of melting and recrystallization increase linearly with the gelator concentration. Herein, for a 4 wt % liquid paraffin gel sample of 4, Tm reached a value of 37.5°C remaining inferior to the above Tm value of SA. It is important to notice that liquid paraffin gels made from the addition of gelators 3 and 7 at 6 wt % of concentration gave similar feature for their thermograms with the current Tc and Tm bands located in a typical range of temperature from 40 to 50°C.

RO is known to be oil rich in erucic acid with a specific crystallization behavior due to the exact nature of its TAGs composition [42]. Usually, when a native oil sample is cooled at a temperature inferior to -20°C, it should crystallize in α form at temperatures near to -60°C and could be converted in a β' form upon slow heating rate [43-45]. However, after the incorporation of one of our gelator, when the measurements were carried out between 0 and -80°C, only two thermic events Tc_1 and Tm_1 were recorded for each RO gel samples of 1, 2, 4, and 6. Usually, these peaks were recorded in association to the supposed normal peaks Tc_2 and Tm_2 of gelators included in the liquid. If we consider the initial position of the Tc_1 peak on each thermogram, it is possible to imagine the crystallization of the TAGs under typical α form inside the gel cavities formed from the gelators at the ambiant temperature. Surprisingly, there was no additional exothermic peak under 0°C possibly attributed to any β' form. Due to the supercooling effect, the phenomenon is stopped at some kind of nucleation state, maybe to the presence of the gelator able to mimic the structure of TAGs. Our mimetic and lipophilic gelators may delay the melting of the aggregates except for 2. Due the higher value of Tc_1 for 2, it is easy to admit that the gelator has less affinity for the TAGs compared to the other candidates. In fact, nothing indicates us that for temperatures superior to 0°C, the aggregates of gel incorporates or not in their composition more or less of the TAGs present in the oil. In addition, by replacing RO by SO, the resulted gel samples of 6 (4 wt %) and 2 (2 wt % of concentration) gave respectively Tm values of 53 and 65°C. Obviously, it seems to be evident that using our gelators, the oil nature does not affect the gelation process for a range of temperatures comprised between 0 and 70°C.

3.5. Viscoelastic behaviour

The same previous oleogel samples were also tested to measure their viscoelastic behavior and confirm the semi-solid nature of these soft matters [46]. In order to confirm the gelation ability of each gelator 1, 2, 4 and 6, their corresponding gel samples in liquid paraffin and rapeseed oil were employed for testing their rheological properties. In LP, all samples were observed as strong elastic gels throughout the entire frequency range with higher G' systematically upper than G'' and always parallel with the respect of the angular frequency. The details of all experiments were depicted on two different graphics a and b of the Figure 5.

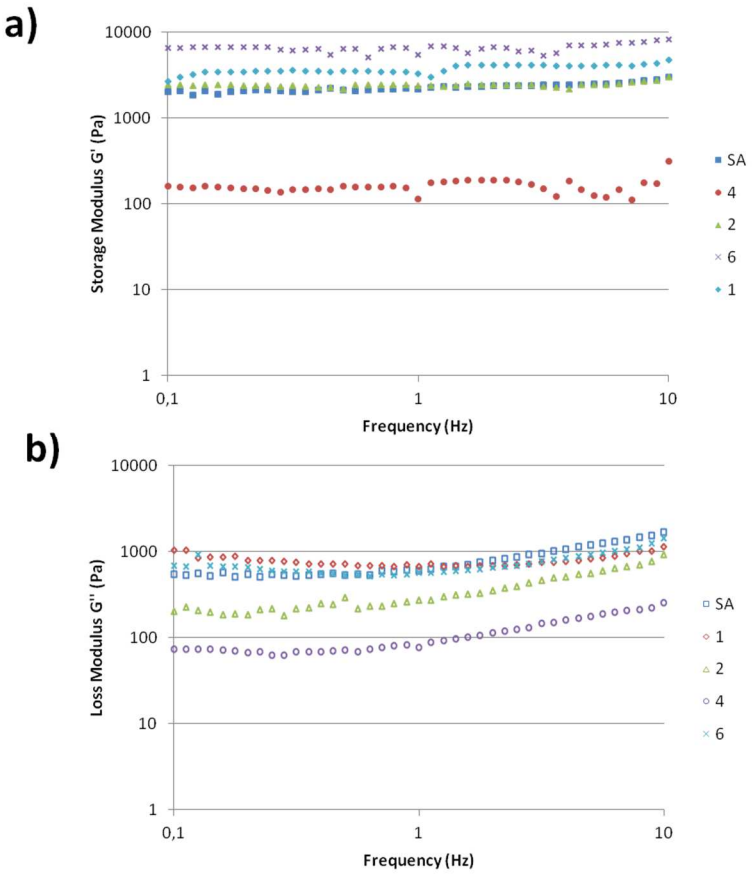

Fig. 5. Angular frequency dependence of (a) the storage moduli (G') and (b) the loss stimuli (G'') of LP gels at their optimum concentrations : SA (2 wt %) ; 1 (4 wt %) ; 2 (2 wt %) ; 4 (3 wt %) ; 6 (2 wt %).

When introduced at the same CGC, 1 and SA had almost the same behavior and gave constant values of G' representative of the elasticity of the material at all frequencies. Also added at 2 wt %, the gelator 6 confirmed its best performance to provide the more robust gel in LP with the higher values of G' located just under 10000. However, 4 gave intermediate values of storage modulus, even if a concentrated sample of 4 wt % was employed during these experiments. Unfortunately, when the gelator 4 was added at a concentration superior to its CGC, it gave values of G'' starting from 100 and increasing progressively from angular frequency of 1 Hz but remained too low. Regarding the values of G'', for all above samples, they evolved in a range found between 100 and 1000. Surely, it is possible to affirm that the type of morphology of the gels, especially for 2 and 6, is a decisive factor to get strong gels in oil or liquid paraffin. From these results, the gelators 1, 2 and 6 were chosen to

measure by the same manner the viscoelastic behavior of rapeseed oil samples. The rheological properties of the oleogels in rapeseed oil were compared in Figure 6.

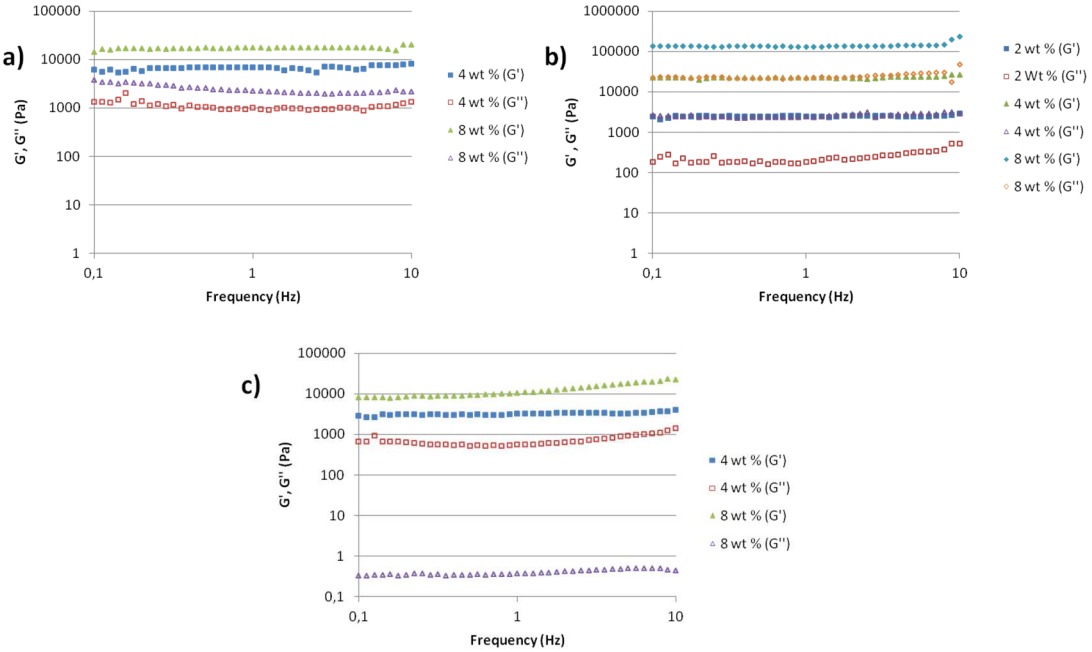

Fig.6. Angular frequency dependence of G' and G'' for rapeseed oil gels at different concentrations (wt %) of gelators: (a) 1 ; (b) 2 and (c) 6.

As before, the storage modulus is independent of the angular frequency and remains much larger than the loss modulus. First, according to the graphics, in all cases by enhancing the concentration of each gelator, both values of G' and G'' increase in the same way. Surprisingly, by focusing on the 4 wt % gel samples, in comparison to the previous results, the result was inverted and the best candidates became the gelator 2. This result is in line with with the lower CGC obtained with 2 in this liquid. Furthermore, in case of the gelator 1, for a concentration superior to 2 wt %, the compound is able to give a stronger gel than a gel produced in RO from 6 when added at the same concentration. This result could explain why the gelator 6 afforded rapeseed oleogels of high brittleness. This result could also be connected to both lower value of Tm and undercooling expressed by 6 in rapeseed oil compared to those of 2.

3.6. Influence of liquid nature on gelation rates and Tm of gels

For specific applications, it should be interesting to be able to modulate the melting temperature of our gel samples, especially in case of LP gels. Indeed, these gels could become good precursors for phase change materials (PCMs) in lithium ion batteries instead of paraffin waxes composites [47, 48]. During the discharge, the battery requires a rapid and efficient heat dissipation system with a Tm found in a range of temperature between 45 and 50°C. In Figure 7a, the Tm of LP gel samples from gelators 1, 2, 4 and 6 were recorded in function of their increasing concentrations. In LP, at different concentrations of gelators 2 and 6, each Tm never exceeded 80°C despite the supersaturation of the medium. In case of 1, the gel concentrations varied from 4 to 8 wt %, but from 6 wt % Tm was observed near to 53°C. However for all concentrations, LP gel samples of 4, showed the lower Tm

values, always inferior to 52°C. From a kinetic aspect, for all LP gel samples of 1 and 2, the gelations rates were higher but almost similar to those expressed by LP gel samples of 4 and 6 obtained at their higher concentrations of 9 and 6 wt % respectively. As a potent component of a passive thermal management system, the best and most rapid gelating candidate seems to be gelators 1 with the lowest CGC included in the adequate rate of temperature.

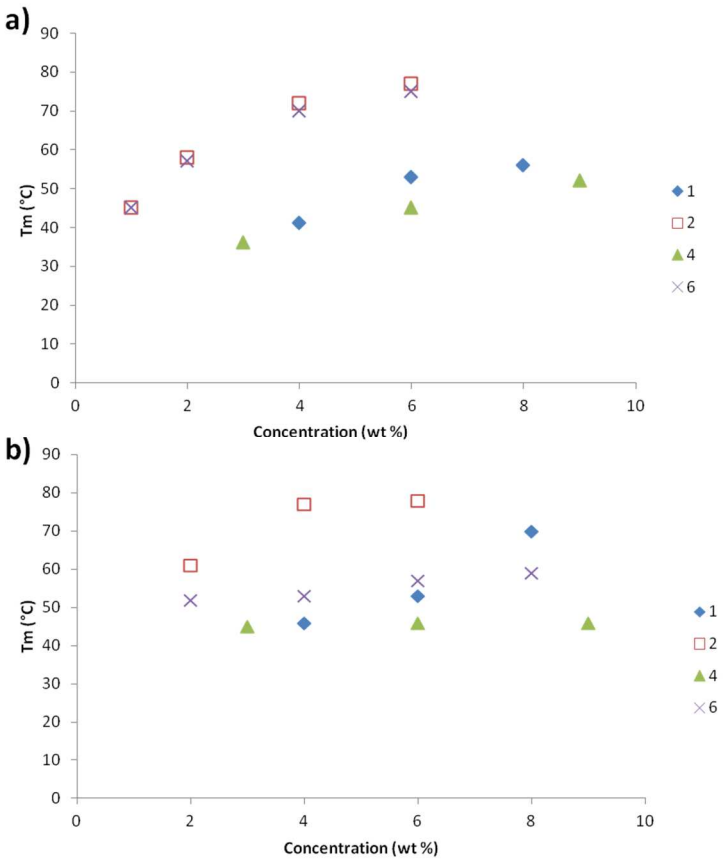

Fig. 7. Plot of Tm against gelator concentrations in: a) LP ; b) RO.

On the other hand, in order to investigate the impact of the medium itself on both Tm and gelation rate, we pursued our study by using RO. Then, on Figure 7b, the Tm of LP gel samples of 1 increased progressively in parallel with the concentration of the gelator to reach a final value of 70°C at 8 wt % For 2, despite the triglyceride based nature of RO, the same evolution of Tm was observed. Like for LP gels, gels from 1 and 2 are the most rapid to form, followed by 4 and 6 in this order, independently of their concentration. Curiously, for 4 and 6, we observed a slight increase of the Tm values, but respectively closed to 46 and 53°C. If we compare the gelators 1 and 4, obviously the enhanced hydrophobic character of the sulfur containing compound can afford the most robust gel from edible oils. In fact, it is recommended to bear in mind that the additives may interact directly with the triglycerides to induce or accelerate their recrystallization in the edible oils promoted by the hydrophobic nature of a nucleating agent.

4. Conclusion

After a short survey, three linear and rigid long fatty and hydrophobic gelators were identified for their good performances to gelate edible oils and other lipophilic liquids at low concentrations.

Exclusively based on strong hydrophobic interaction these molecules expressed remarkable gelation ability in various kinds of hydrophobic liquids. One of them, a thioester derivative could also become a promising candidate as organogelator of liquid paraffin to create new type of thermal management system for lithium ion batteries. In the edible oils, their gelation abilities were not only directly connected to the oil composition and their capacity to incorporate the TAGs in the generated supramolecular aggregates. In the next stage of our study, we intend to use our best oleogel candidates loaded with hydrophobic drugs such as prednisolone for testing their stability and their aptitude to release the bioactive material in-vivo condition.

Supplementary data

Supplementary data (^{1}H NMR charts of each gelator 1-9, photographs of additional gels samples, experimental values of HSPs of each studied liquid, FT-IR spectra, and DSC thermograms) associated with this article can be found in the online version, at…

References

[1] A. R. Patel, K. Dewettinck, Edible oil structuring: an overview and recent updates, Food Funct. 7 (2016) 20-29.

[2] A. R. Patel, A colloidal gel perspective for understanding oleogelation, Current opinion In Food Science 15 (2017) 1-7.

[3] A. P. B. Ribeiro, M. H. Masuchi, E. K. Miyasaki, M. A. F. Domingues, V. L. Z. Stroppa, G. Marangoni de Oliveira, T. G. Kieckbusch, Crystallization modifiers in lipid systems, J. Food Sci Technol 52 (2015) 3925-3946.

[4] M. Davidovich-Pinhas, Oil structuring using polysaccharides, Current Opinion in Food science 27 (2019) 29-35.

[5] N. Nagavekar, A. Kumar, K. Dubey, R. S. Singhal, Supercritical carbon dioxide extraction of kokum fat from Garcinia indica Kernels and its application as gelator in oleogels with oils, Ind Crop Prod 138 (2019) 111459.

[6] E. J. Perez-Monterroza, H. J. Ciro-Velasquez, J. C. Arango Tobon, Study of the crystallization and polymorphic structures formed in oleogels from avocado oil, Rev. Fac. Nac. Agron. 69 (2016) 7945-7954.

[7] V. K. Singh, K. Pal, D. K. Pradhan, K. Pramanik, Castor Oil and Sorbitan Monopalmitate Based Organogel as a Probable Matrix for Controlled Drug Delivery, J. Appl. Polym. Sci. 130 (2013) 1503.

[8] H. Si, L-Z. Cheang, J. Huang, X. Wang, H. Zhang, Physical Properties of Soybean Oleogels and Oil Migration evaluation In Model Praline system, J Am Oil Chem Soc 93 (2016) 1075-1084.

[9] A. L. Martinez, M. A. Charo-Alonso, A. G. Marangoni, J. F. Toro-Vazquez, Monoglyceride organogels developed in vegetable oil with and without ethylcellulose, Food Res Int 72 (2015) 37-46.

[10] Z. Meng, L. Yang, W. Geng, Y. Yao, X. Wang, Y. Liu, Kinetic Study on the Isothermal Crystallization of Monoglyceride Organogels, The Scientific World Journal (2014).

[11] A. Bot, Y. S. J. Veldhuizen, R. den Adel, E. C. Roijers, Non-TAG structuring of edible oils and emulsions, Food hydrocoll 23 (2009] 1184-1189.

[12] M. Zhang, R. G. Weiss, Insights into the Gelating Abilities of Ricinelaidic Acid and its Ammonium Salts : How do Stereochemistry, Charge, and Chain Lengths Control Gelation of a Long-Chain Alkenoic Acid ? ChemPhysChem, 17 (2016) 4059-4067.

[13] A. G. Marangoni, N. Garti, Edible Oleogels Structure and Health Implications (Book-elsevier) (2011) 81.

[14] K. Uvanesh, S. S. Sagiri, K. Senthilguru, K. Pramanik, I. Banerjee, A. Anis, S. M. Al-Zahrani, K. Pal, J Effect of Span 60 on the Microstructure, Crystallization Kinetics, and Mechanical Properties of Stearic acid Oleogels : an In-Depth Analysis, Food Sci. 81 (2016).

[15] H. M. Schaink, K. F. van Halssen, S. Morgado-Alves, D. Kalnin, E. van der Linden, Crystal network for edible oil organogels : Possibilities and limitations of the fatty acid and fatty alcohol systems, Food Res. Int 40 (2007) 1185-1193.

[16] F. R. Lupi, D. Gabriele, V. Greco, N. Baldino, L. Seta, B. de Cindio, A rheological characterization of an olive oil/fatty alcohols organogel, Food Res International 51 (2013) 510-517.

[17] A-L. Fameau, S. Lam, A. Arnould, C. Gaillard, O. D. Velev, A. Saint-Jalmes, Smart Nonaqueous Foams from Lipid-Based Oleogel, Langmuir 31 (2015) 13501-13510.

[18] F. M. Alvarez-Mitre, V. A. Mallia, R. G. Weiss, M. A. Charo-Alonso, J. F. Toro-Vazquez, Self-assembly in vegetable oils of ionic gelators derived from (R)-12-hydroxystearic acid, Food Struct. 13 (2017) 56-69.

[19] J. F. Toro-Vasquez, J. Moralez-Rueda, A. Torres-Martinez, M. A. Charo-Alonso, V. A. Mallia, R. G. Weiss, Cooling Rates effects on the Microstructure, Solid Content, and Rheological Properties of Organogels of Amides Derived from Stearic and (R)-12-Hydroxystearic Acid in Vegetable Oil, Langmuir 29 (2013) 7642-7654.

[20] M. Zhang, R. G. Weiss, Self-Assembled and Molecular Gels Derived from Long-Chain, Naturally-Occurring Fatty Acids, J. Braz. Chem. Soc. 21 (2016) 239-255.

[21] M. A. Rogers, A. G. Marangoni, Kinetics of 12-Hydroxyoctadecanoic Acid SAFIN Crystallization Rationalised Using Hansen solubility Parameters, Langmuir 32 (2016) 12833-12841.

[22] M. Zhang, S. Selvakuvar, X. Zhang, M. P. Sibi, R. G. Weiss, Structural and solubility Parameter Correlations of Gelation Abilities for Dihydroxylated Derivatives of Long-Chain, Naturally Occurring Fatty Acids, Chem. Eur. J 21 (2015) 8530-8543.

[23] A. R. Patel, K. Dewettinck, Comparative evaluation of structured oil systems: Shellac oleogel, HMPC oleogel, and HIPE gel, Eur. J. Lipid Sci. Technol 117 (2015) 1772-1781.

[24] L. S. K. Dassanayake, D. R. Kodali, S. Ueno, K. Sato, Crystallization Kinetics of organogels Prepared by Rice Bran Wax and Vegetable Oils, J. of Oleo Sci. 61 (2012) 1-9.

[25] S. Hong, H-J Kim, S. Park, S. Lee, J. Lee, J. Lee, Effects of or Metal-Chelating Antioxidants on the Oxidative Stability of Organogels of Beeswax and Grapeseed Oil Exposed to Light Irradiation, J Food Sci. 83 (2018) 881-891.

[26] I. Tavernier, C. D. Doan, D. Van De Walle, S. Danthine, T. Rimaux, K. Dewettinck, Sequential crystallization of high and low melting waxes to improve oil structuring in wax-based oleogels, RSC Adv 7 (2017) 12113-12125.

[27] G. Bastiat, J-C. Leroux, Pharmaceutical organogels prepared from aromatic amino acid derivatives, J. Mater. Chem. 19 (2009) 3867-3877.

[28] M. Suzuki, H. Saito, M. Shirai, K. Hanabusa, Supramolecular organogel formation triggered by acid-base interaction in two-component system consisting of L-lysine derivative and aliphatic acids, New J. Chem. 31 (2007) 1654-1660.

[29] C. Ren, F. Chen, F. Zhou, J. Shen, H. Su, H. Zeng, A low-cost phase-selective organogelator for rapid gelation of crude oil at room temperature, Langmuir 32 (2016) 13510-13516.

[30] C. M. O'Sullivan, S. Barbut, A. G. Marangoni, Edible oleogels for the oral delivery of lipid soluble molecules: Composition and structural design considerations, Trend Food Sci.Technol. 57 (2016) 59-73.

[31] F. Delbecq, Supramolecular gels from lipopeptide gelators: Template improvement and strategies for the in-situ preparation of inorganic nanomaterials and for the dispersion of carbon nanomaterials, Adv Colloid Interface Sci. 209 (2014) 98-108.

[32] R. Nguyen, J. Castello, I. Pezron, D. Luart, E. van Hecke, C. Len, Efficient Synthesis, Calorimetric and rheological studies of Symmetrical Bio-Based Fatty Ethers, I&Ec Research 56 (2017) 10329.

[33] S. S. Sagiri, V. K. Singh, K. Pal, I. Banerjee, P. Basak, Stearic acid based oleogels: A study on the molecular, thermal and mechanical properties, Mater. Sci. Eng. C 48 (2015) 688-699.

[34] K. Stensrud, S. Baseeth, S. R. Jadhav, J. I. Lee, L. Wickland, Structuring and gelling agents, Patent WO 2015/095472 (2015).

[35] M. A. Rogers, Hansen Solubility Parameters as a Tool in the Quest for new Edible Oleogels, J. Am Oil Chem Soc 95 (2018).

[36] F. Delbecq, Y. Masuda, Y. Ogue, T. Kawai, Salt complexes of two-component *N*-acylamino acid diastereoisomers : self-assembly studies and modulation of gelation abilities, Tetrahedron Lett. 53 (2012) 6588-6593.

[37] F. Delbecq, N. Kaneko, H. Endo, T. Kawai, Solvation effects with a photoresponsive two-component 12-hydroxystearic acid-azobenzene additive organogel, J. Colloid Interface Sci. 384 (2012) 94-98.

[38] H-W. Li, H. L. Strauss, R. G. Snyder, Differences in the IR Methylene Rocking Bands between the crystalline Fatty Acids and n-Alkanes : Frequencies, Intensities, and Correlation Splitting, J. Phys. Chem A 108 (2004), 6629-6642.

[39] R. N. A. H. Lewis, R. N. Mc Elhaney, Membrane lipid phase transitions and phase organization studied by Fourier transform infrared spectroscopy, Biochimica et Biophysica acta 1828 (2013) 2347-2358.

[40] F. Kaneko, J. Yano, K. Sato, Diversity in the fatty-acid conformation and chain packing of cis-unsaturated lipids, Curr Opin Struct Biol. 8 (1998) 417-425.

[41] A. C. T. Teixeira, A. R. Garcia, L. M. Ilharco, A. M. P. S. Goncalvez da Silva, A. C. Fernandes, Phase behavior of oleanolic acid/stearyl stearate binary mixtures in bulk and at the air-water interface, Chem Phys Lipids 160 (2009) 45-57.

[42] K. Kawamura, The DSC thermal analysis of crystallization behavior in high erucic acid rapeseed oil, J. Am. Oil Chem Soc. 58 (1981) 826-829.

[43] Y. Cegla-Nemirovsky, A. Aserin, N. Garti, Oleogels from Glycerol-Based Lyotropic Liquid Crystals : Phase Diagrams and Structural Characterization, J Am oil Chem Soc 92 (2015) 439-447.

[44] M. Abes, S. S. Narine, Crystallization and phase behavior of fatty acid esters of 1,3-propanediol I: Pure systems, Chem Phys Lipids 149 (2007) 14-27.

[45] F. R. Lupi, V. Greco, N. Baldino, B. de Cindio, P. Fischer, D. Gabriele, The effects of intermolecular interactions on the physical properties of organogels in edible oils, J. Colloid Interface Sci. 483 (2016) 154-164.

[46] H. Pehlivanoglu, M. Devirci, O. S. Toker, Rheological properties of wax oleogels rich in high oleic acid, Int J food prop (2017).

[47] Z. Zhang, Y. Li, Experimental study of a passive thermal management system using copper from paraffin composite for lithium ion batteries, Energy Procedia 142 (2017)2403-2408.

[48] J. Zhang, X. Li, F. He, J. He, Z. Zhong, G. Zhang, Experimental Investigation on Thermal Management of Electric Vehicle Battery with Paraffin/Expanded Graphite Composite Phase Change Material, Int. J. Photoenergy, (2017), Article ID 2929473.

Graphical abstract

Design and physicochemical properties of long and stiff fatty low molecular weight oleogelators

F. Delbecq[a]*, R. Nguyen[b], E. Van Heck[b], C. Len[c]