A hydrogelator derived from polymerisable amphiphilic octadecyl maleamic acid and its potential as a reactor in aqueous copolymerisation reactions†

L. J. Milton Gaspar and Geetha Baskar*

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Octadecyl maleamic acid, a polymerisable surfactant, on coversion to its sodium salt, is shown to exhibit hydrogelation phenomenon. This hydrogelator, consisting of a lamellar structure is further shown to act as an organized reactor for controlled polymerisation reactions in order to generate copolymers with a narrow weight and size distribution.

Gelators are described as species capable of forming network structures in the presence of an entrapped solvent and in turn enhancement in viscosity is exhibited which shows viscoelastic characteristics. Low molecular weight gelators (LMWG) mimicking cell membranes serve as good models in the study of solubilisation and diffusion of materials. They are also known to be potential candidates in drug delivery systems, as templates for development of catalytic and semiconductor materials with directed morphologies. Recent literature has shown that most of the LMWG depict one common amido group in their chemical structure. The presence of non-covalent forces such as H-bonding and van der Waals forces also enables gel formation.[1–6] The chirality and conformations of these gelators vary from β-sheets to helical structures and these control the gelling characteristics.[7] Interestingly, LMWG consisting of free carboxyl groups exhibit 'smart' gel behaviour and they are known to respond to environmental changes.[8] Typical amphiphilic molecules consisting of long tail, rigid segments, spacer groups and hydrophilic segments are also known to exhibit gelling behaviour.[9] Most of the reported LMWG exhibit gelation in organic solvents. Those LMWG capable of gelling water are known as hydrogelators,[10] and in fact those hydrogelators consisting of a polymerisable functional site are very rare. For this study, we have identified the hydrogelation phenomenon in ocatadecyl maleamic acid salt (ODMG) and its potential for generating copolymers with a narrow molecular weight and size distribution.

Octadecyl maleamic acid (ODMA) was synthesized using a reported procedure.[11] Upon neutralization to pH 10.5 using aqueous sodium hydroxide solution, ODMA exhibited a tendency to gelate water as a function of concentration and temperature. It was determined that ODMA performs as a typical hydrogelator capable of gelling water at a concentration as low as 0.75% at 25 °C. The hydrogelation behaviour was observed over the concentration range 0.75–8%. Furthermore, it was observed that ODMA forms a hydrogel only in the presence of sodium or potassium ions. When ODMA was neutralized using organic bases like triethanolamine, it formed a dispersion in water with little tendency to gel, even at concentrations as high as about 8%. We have found that C$_{18}$ is the critical chain length required for significant hydrogelation behaviour in the maleamic acid salt series. It is noteworthy that the lower homologue with a C$_{12}$ chain does not show gelling behaviour and forms micellar solutions under these conditions. The inability of octadecyl succinamic acid salt to form a hydrogel suggests that the typical geometry provided by the π-bond of the maleyl group favours hydrogelation behaviour. The packing characteristics have been established from small angle X-ray diffraction studies (SAXD) on a freeze dried sample of the ODMG hydrogel. The *d*-spacings at 2θ values of 1.45, 2.90 and 4.40° were found to be 60.8 Å, 30.4 Å and 20.0 Å respectively, which are indicative of a typical lamellar structure (Fig. 1). Molecular modeling calculations performed using the cerius^2 package also supported the bilayer arrangement wherein, the total length of the bilayer was estimated to be 61.4 Å, with the C$_{18}$ chain exhibiting a length of 27.4 Å, and the inter-spacing between the two chains being about 6.6 Å (inset Fig. 1). The FT-IR spectrum of a freeze dried hydrogel sample shows absorptions at 1590 cm^{-1} typical of a COO$^-$ group. Furthermore, the absence of a peak at 1710 cm^{-1} confirmed that the hydrogel was devoid of a COOH group. The broad band around 3399 cm^{-1} was typical of NH$_{str}$ in the gel state and a shift of the amide I peak from 1647 cm^{-1} to 1635 cm^{-1} established intermolecular H-bonding in the gel structure. From SEM studies on the freeze dried hydrogel, it was shown that the ODMG hydrogel consisted of uniform fibrillar aggregated structures with a size of about 65 nm (Fig. 2.)

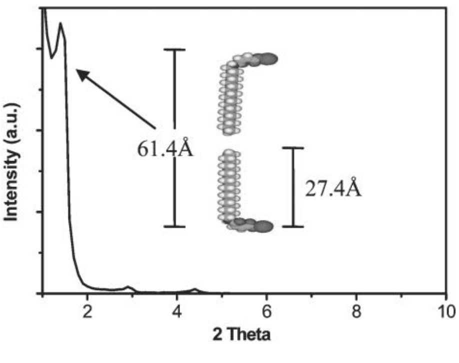

Fig. 1 Small angle XRD spectrum of ODMG gel.

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Industrial Chemistry Laboratory, Central Leather Research Institute, Adyar, Chennai 600 020, India. E-mail: gitsri@hotmail.com; Fax: 91 44 2491 1589; Tel: 91 44 2491 1386
*gitsri@hotmail.com

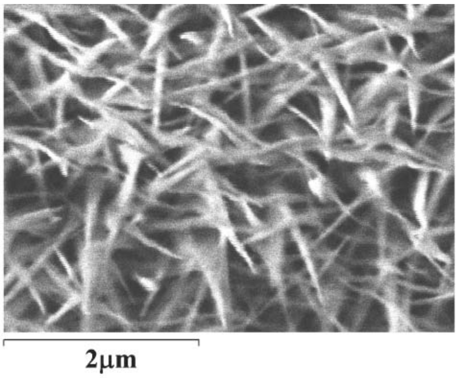

Fig. 2 SEM micrograph of ODMG gel.

The hydrogel transforms to a more viscous solution with an increase in temperature and exhibits thermoreversible behaviour. Specific conductivity estimations performed as a function of temperature suggested reorganization of the gel contributing to a considerable increase in the specific conductivity value. For example, 1% aqueous solution of ODMA showed a sudden jump in specific conductivity from 2.52 mS cm^{-1} to 17.64 mS cm^{-1} on raising the temperature from 52 to 70 °C as shown in Fig. 3. This corresponds to a *ca.* 7 fold increase. Interestingly, typical ^{1}H NMR spectra performed on 1% solution of ODMG in D_2O at temperatures of 30, 40, 50, 60 and 70 °C indicate a sharp increase in intensity values in the temperature range 50–70 °C. The increase in peak intensity of methylene and the end methyl groups of the C_{18} chain demonstrates reorganization corresponding to an increase in the mobility of segments (Fig. 3). The onset temperature of reorganization is around 52 °C which is in agreement with specific conductivity estimations.

Viscosity estimations have been performed on a 1.5% aqueous solution of ODMG as a function of shear rate under ambient conditions using a Brookefield viscometer (Model RVT). It was observed that viscosity decreased from 530 to 196 mPa s on increasing the shear rate from 10–100 s^{-1} (Table 1), indicative of non-Newtonian behaviour characteristic of gel-like materials.

Table 1 Viscosity of aqueous solution of ODMG (1.5 wt%, 25 °C)

Shear rate/s^{-1}	η/mPa s
10	530
20	320
50	234
100	196

In view of the polymerisability characteristics due to the maleyl group and hydrogeling properties, it is important to understand the polymerisation reaction of the hydrogel in an aqueous medium. The scope of micellar assemblies of maleyl surfactants in heterophase aqueous polymerisation reactions has been well documented by Guyot.[12] We show the use of the hydrogelator of ODMG as an emulsifier in an aqueous polymerisation reaction. As maleyl groups are well known for their tendency to undergo copolymerisation reactions rather than homopolymerisation, we investigated copolymerisation reactions using butyl acrylate (BA) as the monomer. In all the reactions a 5% hydrogel concentration of ODMG was maintained and reacted with butyl acrylate in various mole fraction ratios using 1% potassium persulfate as a thermal initiator at 80°C under an inert atmosphere. It was interesting to note that in the presence of butyl acrylate, the hydrogel reorganized into a free flowing emulsion phase. Those polymerisation reactions performed with a feed mole ratio of ODMG > 0.3 m resulted in a low yield of about 15% of low molecular weight polymers. Reported here are two sets of copolymerisation reactions involving 0.88 and 0.74 m butyl acrylate wherein, yields as high as about 95% could be achieved. The polymerisability in other solvents, *e.g.* THF was demonstrated.†

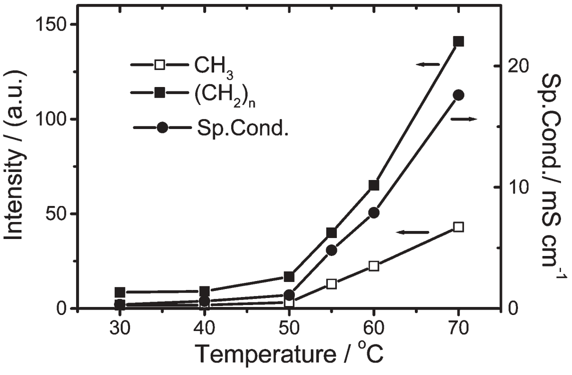

Fig. 3 Plot of ^{1}H NMR peak intensity and specific conductivity *vs.* temperature, 1% ODMA gel at 25 °C.

The copolymers isolated by the solvent precipitation method were characterized for composition from ^{1}H NMR measurements performed on a JEOL ECA 500 NMR spectrometer using $CDCl_3$ as solvent and teramethylsilane as internal standard. The composition of the copolymers was calculated from the ratio of the integral values of the end methyl group of ODMG and BA appearing at 0.86 and 0.93 ppm respectively. The molecular weight of the polymers are estimated on a JASCO Gel Permeation Chromatograph, (model MX-2080-31) with a RI detector using PL gel columns in THF with a flow rate of 1 mL min^{-1}. The molecular weights were calculated with a calibration relative to polystyrene standards. The characteristics of the copolymers and the latex from aqueous emulsion polymerisation reactions are presented in Table 2. The resulting copolymers with a composition almost in line with the feed composition exhibited high molecular weights *ca.* 11–12 × 10^5 with a narrow polydispersity index in the range 1.36–1.41. On the other hand, the solution copolymerisation reactions resulted in oligomers with a broad distribution, (P = 2.56–2.88) of mol. wt in the order of 10^3 (Table 3). It could be argued that the polydispersity index in mol. wt. could be underestimated in the GPC method, especially because of the scope of aggregation due to the ionic sites in copolymers. However, aggregation can be ruled out as tetrahydrofuran was the prefered solvent used for all the copolymers from both the solution and aqueous polymerisation methods.

The particle size estimations were performed using a Malvern particle size analyser at a fixed scattering angle of 90°. The lattices show particle size distribution in the range 70–78 nm with a standard deviation, σ, of 0.12–0.22, indicative of narrow distribution. The zeta potential obtained at a value of −61.9 to −67 mV of the lattices demonstrate the presence of an ODMG component on the surface of the particle. The surface area per molecule of

Table 2 Hydrogelator from ODMG in aqueous copolymerisation reaction: characteristics

Copolymer composition						
ODMA/m	BA/m	Yield (%)	Particle size/nm	Zeta potential/mv	Mol.wt. × 10^5	Poly dispersity
0.12	0.88	96	70	−61.9	11.3	1.42
0.24	0.76	94	78	−67.0	11.8	1.36

Table 3 Solution polymerisation of ODMG and BA, in THF, λ = 365 nm

Copolymer composition				
ODMA/m	BA/m	Yield (%)	Mol. wt. (M_n)	Poly dispersity
0.12	0.88	74	4800	2.56
0.24	0.76	66	4540	2.88

ODMG on the copolymer (*e.g.* 0.88: 0.12m BA: ODMG) particle was calculated to be 0.20 nm^2 from the particle size distribution and the volume of latex; the density of the copolymer particle was estimated to be 1.018 g cc^{-1}.

In this report, we have shown that the ODMG hydrogelator performs as a potential reactor in aqueous polymerisation reactions in the absence of undesirable migrating emulisifier and cosurfactants, typical of most aqueous polymerisation reactions. This provides generation of high mol.wt. functionalised butyl acrylate polymers with a narrow distribution in mol.wt. and particle size.

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