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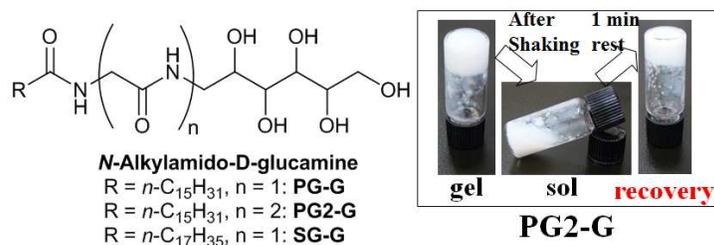
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N-Alkylamido-D-Glucamine-Based Gelators for the Generation of Thixotropic Gels

Yutaka Ohsedo,* Masashi Oono, Kowichiro Saruhashi and Hisayuki Watanabea

Graphical Abstract:



Hydrogels made from new gelators exhibit thixotropic properties, whereas hydrogels formed with structurally similar *N*-alkyl-D-glucamide have a tendency to crystallize.

COMMUNICATION

***N*-Alkylamido-D-Glucamine-Based Gelators for the Generation of Thixotropic Gels**

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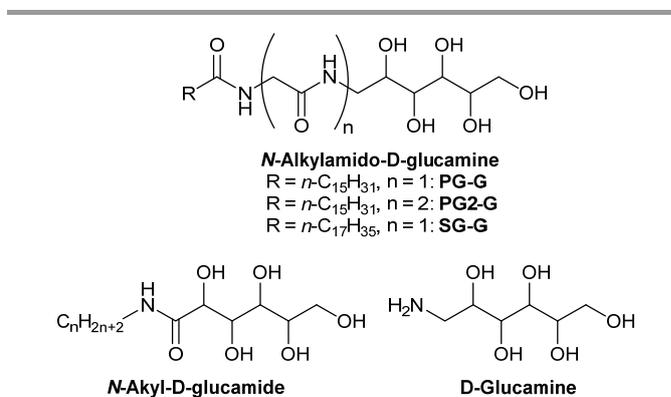
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Hydrogels made from new gelators, composed of the alkyl chain and a D-glucamine moiety linked together with glycine(s), exhibit thixotropic properties, whereas the hydrogels formed with structurally similar *N*-alkyl-D-glucamide, which do not contain the glycine moiety, have a tendency to crystallize and do not show thixotropic behaviour.

Molecular hydrogels made from low-molecular-weight gelators (LMWGs) have attracted attention as new soft matter that feature well-defined chemical structures (comparable to that of polymer gelators) and for their tendency to directly reflect the chemical modification in gelators.^{1,2} While the detailed description of global properties of the gels are under study, physical aspects of molecular gels related to gelation process and the network inside the gels are not fully elucidated. Gels formed with carefully designed LMWGs have found medicinal³ and optoelectronic⁴ applications, and continue to attract researchers in the soft matter due to their potential in human life and society. Stimuli-responsive⁵ and thixotropic⁶ molecular gels have been investigated with an objective to improve the mechanical properties of molecular gels and investigate the relationship between these properties and molecular network in the gel. In particular, thixotropy—mechanically reversible sol-to-gel transitions⁷—of a gel has a potential for utility in industrial applications, such as an additive in healthcare formulations.

N-alkylaldonamides (especially *n*-octyl- and *n*-dodecyl-D-glucamides), structurally simple molecules composed of a polar moiety and an alkyl group, form fibres through an elaborate network of hydrogen bonds and result in hydrogelation.⁸ Several derivatives of *N*-alkylaldonamides exhibit unique nano- and micro-metre scale architectures,⁹⁻¹² however, effective gelation of solvents using the original *N*-alkylaldonamides requires the inclusion of a small amount of a surfactant.¹⁰

The formation of molecular gels with new properties can be achieved by newer methods. For example, it has been shown that mixing two homologs of *N*-alkyl-D-glucamides induces thixotropy in the two-component gel.¹³ Similar mixing induced thixotropy is observed in other organogelators and hydrogelators.¹⁴ Although development of such post-synthesis



Scheme 1. Chemical structures of alkyl-D-glucamine derivatives.

methods for generating functional molecular gels is important,^{15,16} it is necessary to design and synthesize (using simple protocols) novel gelators for promoting the study of gels.

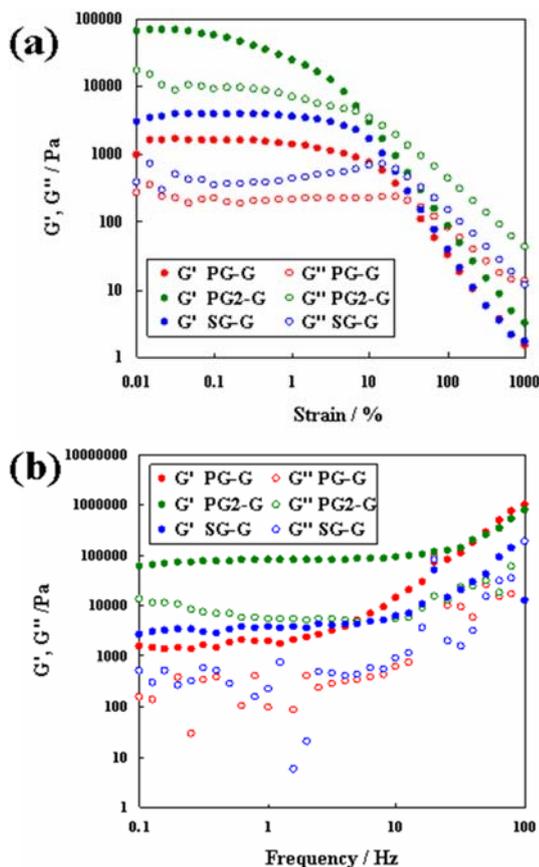
In this report, we describe the creation of new thixotropic hydrogelators (**PG-G**, **PG2-G** and **SG-G**) by ‘inserting’ amino acid residue(s) in *N*-alkylamide-D-glucamines. These molecular gelators, where glycine serves as the linker between polar D-glucamine and hydrophobic alkyl chain, are synthesized by a simple protocol under mild reaction conditions. The amide bonds covalently linking the three moieties in the molecule provide relatively better chemical stability than that of their ester counterparts. The effect of the chemical modification (from *N*-alkylamide-D-glucamine to **PG-G**, **PG2-G** and **SG-G** by introducing the amino acid) on the hydrogelation and the properties of the resulting hydrogel are also evaluated. In a related study, new alkyl ester-D-glucamide type gelators that can gelate various aqueous and organic liquids are evaluated.

PG-G, **SG-G** and **PG2-G** are synthesized by condensation of *N*-glucamine with the appropriate alkyloyl amino acid, which in turn is obtained from a reaction between the appropriate alkyloyl chloride and glycine in an aqueous NaOH solution (see ESI†).¹⁷ The reaction temperature for both the steps of the synthesis is mild. After the completion of the reaction,

Table 1. Critical gelation concentrations (CGCs) of new hydrogelators.

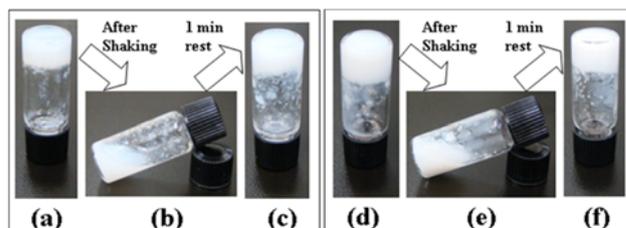
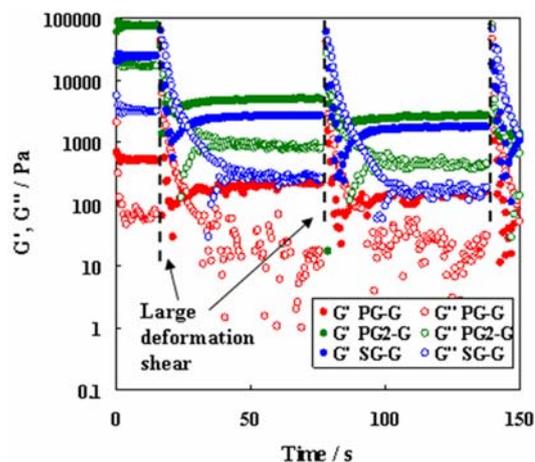
Solvent	PG-G	PG2-G	SG-G
Deionized water	0.5 ^d	3.0 ^d	3.0 ^e
Oxalate buffer ^a	2.0 ^d	2.0 ^d	5.0 ^f
Phosphate buffer ^b	2.0 ^d	1.0 ^d	5.0 ^f
Carbonate buffer ^c	2.0 ^d	2.0 ^d	5.0 ^f
aq.NaCl (1 M)	- ^g	2.0 ^d	- ^g

^apH = 1.68, ^bpH = 6.86, ^cpH = 10.11, ^dturbid gel, ^eclear gel, ^fpartial gel and ^gcrystal from 5.0 wt% solution.

**Fig. 1** Dynamic rheological properties of PG-G (1 wt%), PG2-G (3 wt%) and SG-G (3 wt%) hydrogels; (a) strain sweep and (b) frequency sweep.

purification in both reactions simply involves evaporation of the solvent *in vacuo* and recrystallization in the appropriate solvent; no tedious purification by column chromatography is involved. Elemental analysis confirms the purity of the compounds (see ESI†).

The gelation ability of new *N*-alkylaldonamides are examined in various aqueous solutions to obtain critical gelation concentration (CGC) (Table 1, see photographs of hydrogels in Fig. S1, ESI†). **PG-G**, **PG2-G** and **SG-G** form hydrogels in solutions with a wide range of pH values (2–10) and even in the presence of high NaCl concentration (1 M). While these gelators exhibit moderate CGC values, the hydrogels formed retain their state for over three months. *N*-alkyl-D-aldonamides, lacking the inserted glycine moiety, show poor gel stability in the absence of the additive, sodium dodecyl sulfate. It is likely, then, that the better gel stability observed in case of these glycine-containing LMWGs is due to the generation of amino acid-mediated hydrogen bonding networks

**Fig. 2** Thixotropic tests of hydrogels: (a, b and c) PG-G (1 wt%) hydrogel and (d, e and f) PG2-G (3 wt%) hydrogel.**Fig. 3** Periodic step-shear test results for PG-G (1.0 wt%), PG2-G (3.0 wt%) and SG-G (3.0 wt%) hydrogels.

in these hydrogels. Except in the case of unbuffered deionized water, hydrogelation ability of **PG2-G**, which has a two-glycine-linker, is superior to that of **PG-G**, which has a one-glycine-linker. In addition, the longer-alkyl chain containing hydrogelator, **SG-G**, exhibits an overall inferior gelation property than that of **PG-G**. These results indicate that **PG-G** and **PG2-G** show moderate gel forming properties in various aqueous solutions, even in the existence of salt.

Rheometric measurements of the molecular hydrogels confirm the existence of gel state (Fig. 1), as seen in the case of polymer gels.¹⁸ With increasing stress, the magnitudes of the storage modulus, G' and the loss modulus, G'' , show the transition of the gel state ($G' > G''$) to the sol state ($G' < G''$). In the frequency sweep, gelation is evidenced by the pseudo plateau, where the magnitude of G' is greater than that of G'' . Furthermore, among the three gels, the highest magnitudes of moduli and stability are observed for hydrogels formed with **PG2-G**, indicating that a relatively stiff hydrogel is obtained by introducing the glycine repeat moiety.

Differential scanning calorimetry (DSC) measurements show that similar ΔH values accompany the sol-to-gel and corresponding gel-to-sol transitions (Fig. S1, Table S1, ESI†), suggesting the reversibility of these transitions. The presence of longer alkyl chains (comparing hydrogels formed with **PG-G** and **SG-G**) or the incorporation of a higher number of glycines (comparing hydrogels formed with **PG-G** and **PG2-G**) causes the transitions to take place at higher temperatures; this shift is attributed to the increased interaction between alkyl chains and hydrogen bonding in **SG-G** and **PG2-G**, respectively.

Hydrogels formed with **PG-G**, **PG2-G** and **SG-G** show thixotropic behaviour even when used at concentrations close to CGC (only hydrogels of **PG-G** showed thixotropic behaviour at

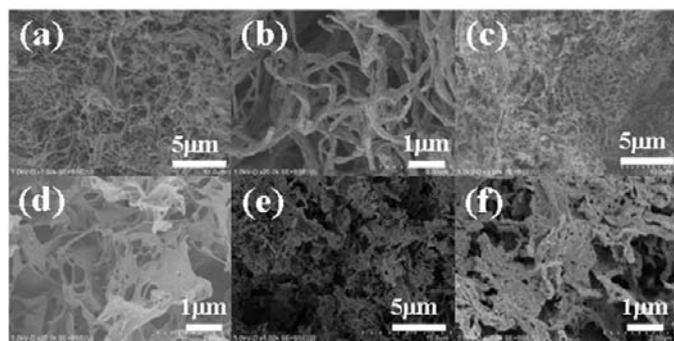


Fig. 4 SEM images of xerogels prepared from the corresponding hydrogels: (a and b) PG-G (0.5 wt%); (c and d) PG2-G (3 wt%) and (e and f) SG-G (3 wt%).

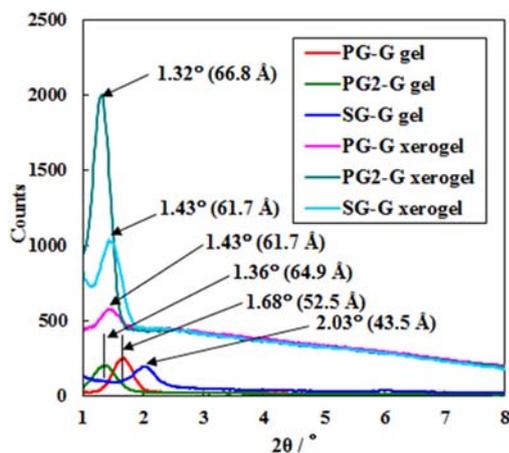


Fig. 5 XRD data of hydrogels and crystals of PG-G, PG2-G and SG-G.

>1.0 wt%). Shaken hydrogels regelated to form stable hydrogels, as shown in Fig. 2 for solutions of **PG-G** and **PG2-G**. Rheometric evaluations of the thixotropic behaviour of hydrogels by step experiment (Fig. 3) show that the magnitude of the recovered G' is greater than G'' after several repeated applications of the deformation shear. The reduction in the magnitude of G' and G'' after each recovery suggests that the network in the hydrogel network is changed (partially destroyed) after each application of deformation shear; however, this change is insufficient to completely breakdown the hydrogels. However, cumulative effect of the applied deformation shear ultimately destroys the hydrogels, and also its ability to recover and rebuild its damaged networks. Relatively more stable plots of modulus are obtained in case of **PG2-G** than the other gelators (Fig. 3). This is attributed to the presence of more sites capable of forming hydrogen bonds (from the two glycines), which can facilitate the rebuilding of the fibrous network in gels. The role of hydrogen bonds of gelators as the driving force of fibre formation was shown by the results of infrared spectra of different states of gelator systems (Fig. S3). To obtain more information about thixotropic behaviour, we conducted the thixotropic hysteresis loop test^{7,19} of our hydrogels (Fig. S4). This test showed that the responses of hydrogels to the repeated applied shear were observed as the peaks of loops and the extent of the response (shear stress) decayed with increasing maximum of shear rate (in **SG-G**, the peak shift was observed probably due to better durability against continuous shear rate change). In addition, the order of the extent of responses corresponded to that of step

experiment above (**PG2-G** ~ **SG-G** > **PG-G**). These results mean that the extent of breaking gels (the extent of decay of response) depends on shear rate and these results coincide with the results of step experiment.

Scanning electron microscope (SEM) images of xerogels, which are prepared by freeze-drying corresponding hydrogels at CGC, show a network structure largely composed of sub-micrometre thick fibres (Fig. 4). Considering that some aggregation occurs during the preparation of the xerogels (during freeze-drying), it is likely that the hydrogels are composed of a network structure made with finer fibres than that observed in xerogels. These networks in molecular hydrogels resemble polymer-like networks and possess thixotropic properties.

X-ray diffraction (XRD) analyses reveal that the peak positions of the hydrogels (Fig. 5) are different from those of the corresponding xerogel sample, and larger than the contour length of the corresponding length of the gelators (optimized by MM2 calculations, Fig. S5, ESI†) except for **PG2-G** (for **PG2-G**, peak positions can be compared between hydrogel and xerogel). It has been shown previously⁷ that *N*-alkyl-*D*-aldonamides molecules form fibre, micelle and lamellar structures based on the bilayer structures of molecules. Considering the contour length of the gelators in the gel state (the XRD results for **PG-G** and **SG-G** showed smaller length than the two contour length of gelators), it is likely that the gelators form interdigitated lamellar based on bilayer structures in fibre (Fig. S6, ESI†) for **PG-G** and **SG-G** (for **PG2-G**, the gelator might form a bilayer structure in fibre). In the xerogel state, it might be probable that the gelator molecules form bilayer structures and the XRD reflection occurs from a periodic structure corresponding length of two gelators.

In conclusion, we have created new family of *D*-glucamine- and alkyl-chain-based hydrogelators by introducing a glycine-linker to connect the two moieties. The tripartite hydrogelators, synthesized under mild reaction conditions, form stable hydrogels with solutions of different pH values. These hydrogels show thixotropic properties, whereas the hydrogel formed with the hydrogelator devoid of the glycine linker, i.e. *N*-alkyl-*D*-glucamide, does not show such behaviour. These results suggest that that the property of a molecular gel can be changed by chemically tuning the gelator molecules, e.g. by introducing a glycine moiety in them. In summary, we have synthesized new hydrogelators that impart thixotropic properties to the gel.

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