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Rapid Communication

A Hetero-network Hydrogel With Self-assembled Nanofibers as Multiple-crosslinkers and Its Liquid-crystal-driven Healing Properties

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ABSTRACT

Hetero-network hydrogels composed of hydrophilic polymers with terminal alkyl chains and nanofibrous self-assemblies were successfully fabricated. The gel formation was not observed in both cases of the self-assemblies in aqueous solution and hydrophilic polymer in aqueous solution. Furthermore the gel-to-liquid crystalline phase transition temperatures of nanofibrous self-assemblies were lowered by addition of hydrophilic polymers with terminal alkyl chains. From these observations, it was considered that the alkyl chains at polymer termini intercalated into the bilayer membrane-based nanofibrous self-assemblies to form cross-linking points. As far as we know, the hybrid hydrogel introduced in this communication is the first example of a hetero-network structure composed of supramolecular assemblies. When the hetero-network hydrogel was crushed by mechanical shearing, these hydrogels recovered by heating at temperatures above their gel-to-liquid crystalline transition temperatures.

The properties of polymer-network hydrogels are essentially dictated by their crosslinking structures. Recently, hydrogel materials with versatile and unique crosslinking structures have been reported [1–9]. Nano-sized objects are promising key materials for promoting the crosslinking of polymer chains into network structures. Inorganic nanoparticles such as clays [1], iron oxides [2], graphene oxide [3], graphene [4] and silica [5] are commonly used as nano-sized crosslinkers because they have a number of reaction sites on their surfaces that allow to connect polymer chains multiply. For instance, nanoclays have been reported to act as nano-sized crosslinking points that connect polymer chains to form hydrogels [1]. We also reported a silica-nanoparticle-crosslinked polymer network that is readily obtained by mixing a water-soluble copolymer containing reactive side chains, and silica nanoparticles in water [10]. In these cases, the reactive sites of polymer chains are anchored to the surface of inorganic nanoparticles via covalent or/and non-covalent bonds, and the nanoparticles act as points for multiple crosslinking. The hybrid hydrogels obtained in this manner exhibited high transparencies, high mechanical strengths and homogeneous swelling properties. Liposomes were also reported to act as nano-sized network junctions to which cholesterol groups at the termini of polymer-chain anchored into the liposomal bilayer membranes [11].

In this communication, we demonstrate the utilisation of self-assembled nanofibers for the multiple-crosslinking of nano-objects. Self-assembled nanofibers are a fascinating class of one-dimensional nanostructure, and are composed of small molecules that spontaneously form aggregates through weak intermolecular interactions involving hydrogen bonds, electrostatic interactions and hydrophobic effects. Consequently, the crosslinking points to connect polymer chains are formed multiple places on nano-objects with extremely large aspect ratios. Such a hetero-network, composed of polymer chains and self-assembled nanofibers, is a novel class of network system for soft materials.

In this study, the double-alkylated amphiphilic glutamide molecule with a pyridinium head group (***G*-Py**$^+$, Fig. 1a) was chosen as the molecular self-assembly tool. ***G*-Py**$^+$ forms nanofibrous, bilayer membrane-based aggregates in water. The water-soluble copolymer (polyethylene glycol (PEG), $M_w = 1.6 \times 10^4$) alkylated with hydrophobic chains at both termini (**C_{18}-PEG-C_{18}**) was synthesised by the esterification of the terminal hydroxyl groups of polyethylene glycol (polymerisation degree = 366, PDI = 3.26) using octadecanoyl chloride. ***G*-Py**$^+$ was dispersed in water by ultrasonication (ASTRASON ultrasonic processor, MISONIX Inc.) at 60 °C for 5 min. After incubation of the aqueous dispersion for 30 min at room temperature (25 °C) and 1 h at 10 °C, then the aqueous solution of **C_{18}-PEG-C_{18}** was added to the

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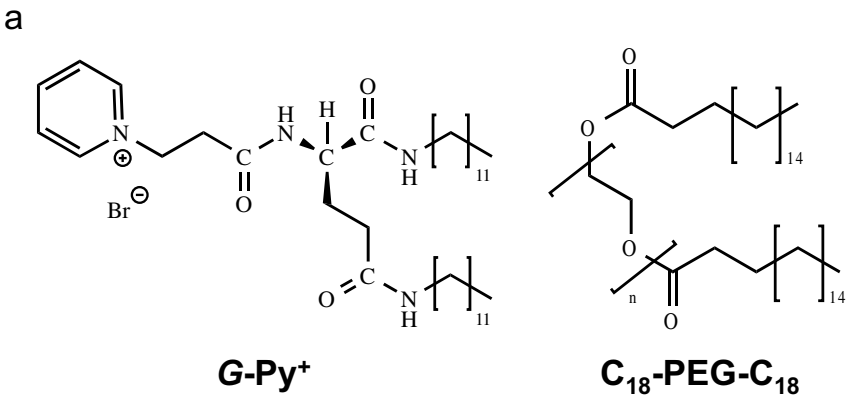

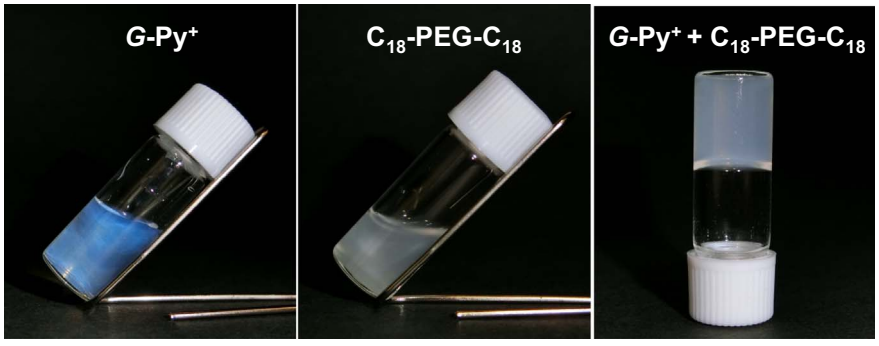

Fig. 1. a) Chemical structures of ***G*-Py**$^+$ and **C_{18}-PEG-C_{18}** and b) photos of hetero network hydrogels composed of **C_{18}-PEG-C_{18}** and ***G*-Py**$^+$. ***G*-Py**$^+$ = 10 mM, **C_{18}-PEG-C_{18}** = 10 wt%, ***G*-Py**$^+$ + **C_{18}-PEG-C_{18}** = 10 mM/10 wt%.

Table 1
Gelation properties of aqueous mixtures of ***G*-Py**$^+$ and **C_{18}-PEG-C_{18}** in various concentrations.

***G*-Py**$^+$ (mM)	**C_{18}-PEG-C_{18}** (wt%)				PEG (wt%)	PEO (wt%)
	0	2	5	10	10	10
0	–	–	–	NG	–	–
2	–	NG	NG[a]	NG	–	–
5	–	NG	NG	NG	NG	NG
10	NG	NG	Gel	Gel	NG	NG
15	–	NG	Gel	Gel	NG	NG
20	NG	NG	Gel	Gel	–	–

Gelation property was evaluated by inversion method at 25 °C. PEG: polyethyleglycol (M_w = av. 1.6 × 10^4), PEO: polyethyleneoxide (M_w = 1.0 × 10^5).
[a] NG: no gelation.

aqueous dispersion of ***G*-Py**$^+$, and the mixture was heated at 60 °C for 2 h followed by incubation at 25 °C. Although no solution formed a gel on its own, aqueous mixtures of ***G*-Py**$^+$ and **C_{18}-PEG-C_{18}** formed hydrogels as shown in Fig. 1. The gelation properties of the mixtures at various concentrations were evaluated by the inversion fluid method, the results of which are summarised in Table 1. As expected, gelation was observed at higher concentrations of ***G*-Py**$^+$ and **C_{18}-PEG-C_{18}**; the minimum concentration of each component required for gel formation in this study was 10 mM and 5 wt% respectively. The following gelation properties were observed. a) An aqueous solution of **C_{18}-PEG-C_{18}** alone did not form a gel even at 10 wt%. b) An aqueous dispersion of ***G*-Py**$^+$ did not form a gel. c) An aqueous mixture of ***G*-Py**$^+$ with unesterified PEG (without hydrophobic terminal chains) did not form a gel; not even the large molecular weight of polyethyeneoxide (PEO, M_w = 1.0 × 10^5) was effective. These results indicate that the alkyl chains of **C_{18}-PEG-C_{18}** play important roles in gel-network formation through interactions with ***G*-Py**$^+$. Possible interactions may include the insertion of the long alkyl chains of **C_{18}-PEG-C_{18}** into the highly oriented ***G*-Py**$^+$ molecules within the self-assembly. Due to hydrophobic effect, the long alkyl chain may insert into the hydrophobic region of ***G*-Py**$^+$ nanotubular bilayer membrane and thus connecting each other to form a hetero network hydrogel. However, this effect was not observed seriously in the morphological features of the nano-tubular aggregates by transmission electron microscopy (TEM) of the ***G*-Py**$^+$ self-assembly, without or with **C_{18}-PEG-C_{18}**. As shown in Fig. 2a, tubular aggregates were observed in the cast film from aqueous solution of ***G*-Py**$^+$. The inner space of the tubular aggregates of ***G*-Py**$^+$ became unclear by addition of **C_{18}-PEG-C_{18}** (Fig. 2b). This is probably due to the difficulty of infiltration of the staining reagent (uranyl acetate) inside the nanotubes because of the **C_{18}-PEG-C_{18}**-coating layer on the ***G*-Py**$^+$ aggregates. Detailed TEM observations revealed that the diameters of the nanotubular aggregates gradually increased with increasing amounts of **C_{18}-PEG-C_{18}**. The average diameter of the nanotubular ***G*-Py**$^+$ aggregates formed without any additive was 23.1 nm, which increased to 24.7 nm by addition of 10 wt% of **C_{18}-PEG-C_{18}**.

Confocal microscopy was carried out in order to understand the hetero-network structures of these hydrogels, using fluorescein as a fluorescence indicator. Aqueous solutions of ***G*-Py**$^+$, with and without **C_{18}-PEG-C_{18}**, were examined after injection of an aqueous solution of fluorescein. Bright fluorescence images of the fibers were obtained for the aqueous solutions of ***G*-Py**$^+$ without **C_{18}-PEG-C_{18}** (Fig. 2c), indicating that the fluorescein molecules were absorbed onto the fibrous ***G*-Py**$^+$ aggregates. In comparison, dark fibrous shapes on a bright background were observed for the mixture of ***G*-Py**$^+$ with **C_{18}-PEG-C_{18}** (Fig. 2d). This is probably due to the formation of a **C_{18}-PEG-C_{18}**-coating layer on the ***G*-Py**$^+$ aggregates that repel the fluorescein molecules.

Tubular aggregates of ***G*-Py**$^+$ showed gel-to-liquid crystalline phase transitions with peak maxima (T_C) at 32 °C (pre-transition, T_{C1}) and 43 °C (main transition, T_{C2}). These phase transitions were lowered to 29.0 and 39.4 °C, and 29.0 and 36.5 °C by addition of 5 wt% and 10 wt % of **C_{18}-PEG-C_{18}**, respectively, with accompanying endothermic enthalpy decreases (Fig. 3). We reported similar changes in phase transitions when small molecules were added to ***G*-Py**$^+$ aggregates [12]. We