Synthesis and Self-assembling Properties of Functionalized Glycolipids

Guijun Wang,* Xiaoping Nie, Sherwin Cheuk, Kristopher Williams

Department of Chemistry, University of New Orleans, New Orleans; LA, USA, gwang2@uno.edu

ABSTRACT

Sugar based small molecule organogelators and hydrogelators have potential applications in drug delivery, tissue engineering and as biocompatible materials. Polydiacetylenes exhibit a unique blue to red color transition in presence of heat, pH change and binding to biological agents. We have designed and synthesized a series of monoacetylene and diacetylene containing sugar lipids with various chain lengths, substituents and studied their self-assembling properties in several solvents. Many of the glycolipids synthesized exhibited excellent gelation properties in ethanol or ethanol/water mixture. The systematic study of the chain length to gelation properties can help us to understand the structure requirement for the desired physical properties. These novel functional hydrogelators are useful in forming matrix for macromolecule encapsulation and separation, as sensors and for drug delivery.

Keywords: Self-assembling, supramolecular gels, hydrogelators, organogelators, monosaccharides.

INTRODUCTION

To create functional small molecules that can self-assemble into useful supramolecular structures is important in designing functional materials. Carbohydrates are abundant natural products and biocompatible, therefore, they are used very often in the preparation of advanced materials. Soft materials formed by glycolipids are biocompatible and have potential uses in many biomedical areas and as degradable biomaterials. The self-assembly of small molecules in organic solvents or water to form gels is an interesting behavior of these types of compounds, they are called low molecular weight organogelators (LMWOs) and hydrogelators (LMWHs).[1-3] The gelation process is reversible due to the non-covalent interactions among the molecules. These small molecule gelators can find applications in forming liquid crystal materials, as templates for synthesizing other novel materials, and as matrix for separating peptides and amino acids.[4-5]

Polydiacetylenes exhibit a unique blue to red color transition in the presence of heat, mechanical stress, pH change and binding to biological agents. The polydiacetylene lipids obtained from the crosslinking of diacetylene lipids can result in new stimuli-responsive materials.[5-6] The requirement for effective polymerization of diacetylenes is that the monomers are aligned at specic distances and orientations (Figure 1). In particular, diacetylene lipids that can form hydrogel in aqueous solution are of great interest in designing functional biocompatible materials. This will incorporate both gelation phase transition and the polymer color transition into one system and create highly intelligent novel materials.

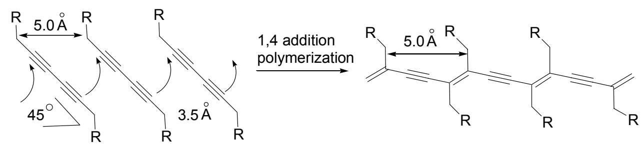

Figure 1. The topochemical 1,4-addition polymerization of diacetylenes.

RESULTS AND DISCUSSIONS

As part of our effort in discovering novel carbohydrate based self-assembling materials, we have designed and synthesized a series of monoacetylene and diacetylene containing sugar lipids with different chain lengths, substituents, and positions of acetylenes and studied their self-assembling properties in several solvents including hexane, ethanol and ethanol/water mixture.[7-8] Many of the glycolipids synthesized (Figure 2) exhibited excellent gelation properties in ethanol or ethanol/water mixture. The positions of the acetylenes and chain lengths affect the self assembling properties significantly. The detail structure and property relationship will be discussed. The systematic study of the chain length to gelation properties can help us to understand the structure requirement for the desired physical properties. As shown in Figure 3, optical microscopy studies showed that the molecules form interesting architectures such as tubules, rods, sheets, and belts. The gels apparently formed cylindrical tubules and perhaps long ribbons that are composed of smaller fibers. In polarized light, they exhibit birefringence, this indicated that the gels are locally crystalline and have liquid crystal like behavior. These are shown in Figure 3b, d, and f. The resulting discetylene containing organogels can be crosslinked and give different colored polymerized gels depending on their structures. One example is shown in Figures 3g and 3h. The ethanol gel turned red after treating with UV light.

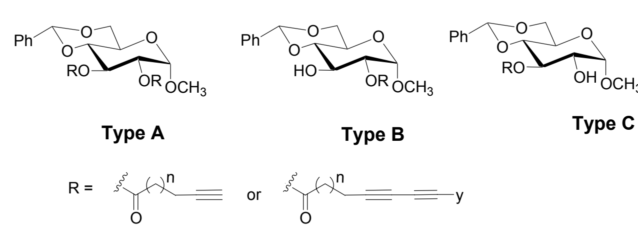

Figure 2. General tructures of the synthesized glycolipids.

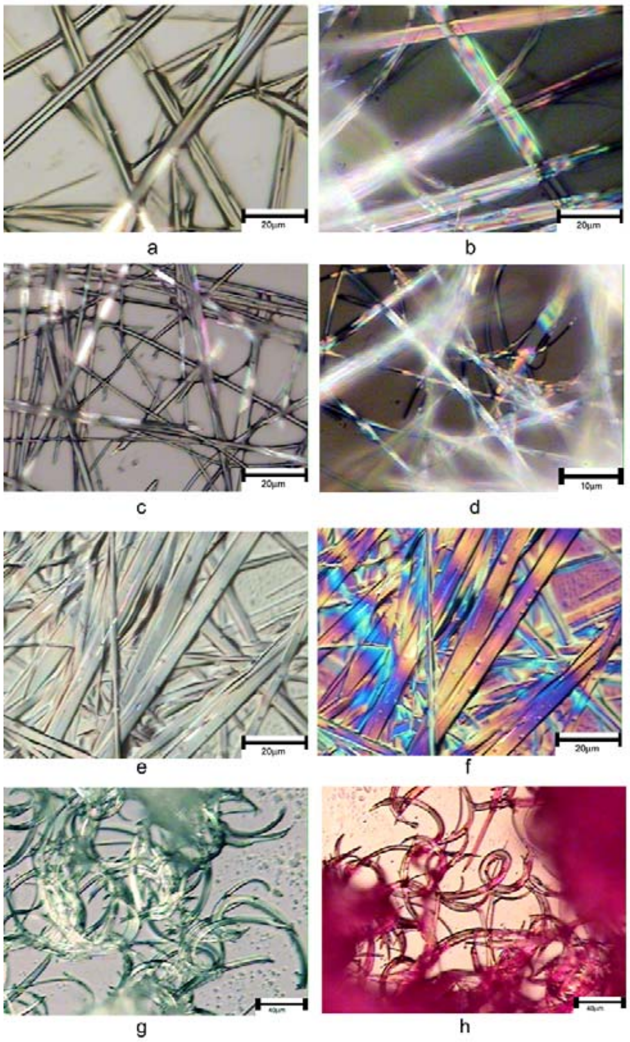

Figure 3. Optical micrographs of the gels formed by several compounds at 10 mg/mL concentration. a, b) type B, n=1. a: bright field image in hexane, b: polarized image of gels in water. c, d) Type C, n=2. c: bright field image in hexane, d: polarized image of gels in water. e, f) Type C, n=2, Y= *n*-octyl. e: bright field image in hexane, f: polarized image e. g, h) Type A, n=5, Y= *n*-decyl, bright field images in ethanol. g: before UV treatment; h: after UV treatment.

These novel functional carbohydrate based organogelators are expected to be useful in forming matrix for macromolecule encapsulation and separation, biosensors, chemosensors and drug delivery.

ACKNOWLEDGEMENT

Financial support for the project is provided by NSF.

REFERENCES

[1] Terech, P.; Weiss R. G. *Chem. Rev.* **1997**, *97*, 3133-3159.

[2] Estroff, L. A.; Hamilton, A. D. *Chem. Rev.* **2004**, *104*, 1201-1217.

[3] Wang, G.; Hollingsworth, R. I. *Adv. Materials* **2000**, *12*, 871-874.

[4] Wang, G.; Hollingsworth, R. I. *Langmuir*, **1999**, *15*, 6135-6138.

[5] Wang, G.; Hamilton, A. D. *Chem. Comm.* **2003**, 311-312.

[6] Wang, G.; Hamilton, A. D. *Chem. Eur. J.* **2002,** *8,* 1954-1961.

[7] Wang, G.; Sharma, V.; Cheuk, S.; Williams, K.; Dakessian, L.; Thorton, Z. *Carbohydrate Research, in press.*

[8] Nie, X.; Wang, G. *J. Org. Chem. Submitted.*