

Nanostructured Organogel Networks Self-Assembled from Alkylated Isophthalic Acid and Benzimidazole Compounds

Darren A. Makeiff* and Rina Carlini**

*National Institute for Nanotechnology, Edmonton, Canada, darren.makeiff@nrc.gc.ca

**Xerox Research Centre Canada, Mississauga, Canada, rina.carlini@xerox.com

ABSTRACT

Organogel networks from low molecular weight components are a fascinating class of functional nanomaterials, with tremendous potential for a wide variety of commercial applications ranging from medicine, electronics, printing, personal care, and environmental remediation [1]. Here, we discuss the synthesis and characterization of nanostructured organogels from two new classes of amphiphilic compounds: alkylated (1) isophthalic acids (ISAs) and (2) benzimidazolones (BZIs). Both classes exhibit excellent gelator behavior in a variety of nonpolar solvents due to the formation of robust 3D networks of well-defined nanostructured aggregates stabilized by hydrogen-bonding, pi-stacking, and van der Waals interactions.

Keywords: organogels, self-assembly, hydrogen-bonding, soft materials, organic nanostructures

INTRODUCTION

The “bottom up” self-assembly of molecular building blocks into nanostructured materials has attracted significant interest for advanced materials research [1]. Nanostructured materials with controlled size, shape, and function are important for numerous industrial applications. Low molecular weight organogels are a rapidly developing class of such building block materials, in which small molecules self-assemble into hydrogen-bonded assemblies that can form a three-dimensional network capable of rigidifying entire fluids at very low concentrations [1]. Although a large number of organogelator compounds have been reported by many researchers, the rational design and synthesis of new organogelators remains a significant challenge since the gel properties cannot be predicted from the molecular structures alone. We present the design, synthesis and self-assembly of two new classes of amphiphilic organogelator compounds incorporating ISA and BZI functional groups.

RESULTS AND DISCUSSION

The organogelator compounds in Figure 1 were designed to have structures that incorporate a linear or

branched alkyl group R that is attached to a hydrogen bonding ‘head’ group (the ISA or BZI moiety, respectively) by an amide linking group. While isophthalic acids can self-assemble *via* hydrogen-bonding into a variety of structural motifs (tapes, ribbons, lamellae, and cyclic structures) [2], benzimidazolones primarily form hydrogen-bonded chain-like structures [3].

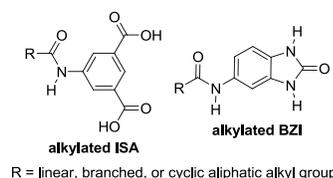


Figure 1. Chemical structures of alkylated ISA and BZI compounds.

Select alkylated ISA and BZI derivatives can gel both polar solvents (e.g. alcohols) as well as nonpolar hydrocarbon solvents (e.g. toluene and cyclohexane). Furthermore, the alkylated ISA derivatives form strong gels at low concentrations (less than 1 wt %), which is beneficial for many diverse applications. The molecular structures of the various ISA-type gelator compounds we have designed and characterized are significantly different from those previously reported [4], and represent novel gel nanostructures [5]. In addition, the BZI-type organogelators we describe here represent a new class of novel gel nanostructures.

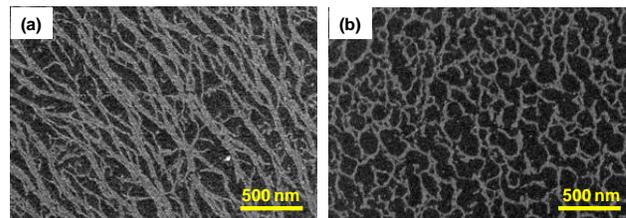


Figure 2. SEM images of aggregates from toluene solutions of (a) alkylated ISA (0.2 mM), and (b) alkylated BZI (2 mM).

Scanning electron microscopy studies of the organogel nanostructures formed from ISA and BZI compounds revealed distinct morphological features. Well-defined one-dimensional fibrillar aggregates were formed when alkylated ISA or BZI derivatives were deposited and dried on carbon-coated copper mesh TEM grids (Figures 2a and b, respectively). The dimensions of

the individual fibrils were 5-10 nm in diameter and reach up to several microns in length.

CONCLUSIONS

Alkylated ISA and BZI compounds were designed, synthesized, and were demonstrated to form interesting 1D nanostructures, which aggregate into 3D gel networks in a variety of organic solvents. The strong ability of these compounds to gel nonpolar and hydrocarbon solvents may be useful in many technological applications, such as environmental remediation.

REFERENCES

- [1] Fages, F. *Low Molecular Mass Gelators*, Vol. 256, 2005 in *Topics in Current Chemistry*
- [2] De Feyter, S.; Gesquière, A.; Klapper, M.; Müllen, K.; De Schryver, F. C. *Nano Letters* **2003**, *3*, 1485-1488.
- [3] van de Streek, J.; Brüning, J.; Ivashevskaya, S. N.; Ermrich, M.; Paulus, E. F.; Bolte, M.; Schmidt, M. U. *Acta Cryst.* **2009**, B65, 200-211. Schwiebert, K. E.; Chin, D. N.; MacDonald, J. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 4018-4029.
- [4] Zafar, A.; Yang, J.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Letters* **1996**, *37*, 2327-2330. Potluri, V. K.; Hamilton, A. D. *J. Supramol. Chem.* **2002**, *2*, 321-326. Rodríguez-Llansola, F.; Escuder, B.; Miravet, J. F.; Hermida-Merino, D.; Hamley, I. W.; Cardin, C. J.; Hayes, W. *Chem. Commun.* **2010**, *46*, 7960-7962.
- [5] Makeiff, D.; Carlini, R. US Patent Application, 2010; National Research Council of Canada and Xerox Corporation.