Chapter 14
LOW MOLECULAR-MASS ORGANIC GELATORS

Analyses of the natures of LMOGs and liquids for efficient gelation

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1. Introduction

Several reviews describe the various types of low molecular-mass organic gelators (i.e., LMOGs, gelators that are primarily organic in composition and whose molecular mass is usually less than 2000 Da) and their structural features [1–15]. In this chapter, we provide an in depth survey of organogels, comprised of an organic liquid and low concentrations (typically <2 wt.%) of an LMOG.
The LMOGs are separated into “classes” according to criteria based on molecular structure. The properties of the LMOG networks and, when available, information about the nature of their intermolecular interactions both with other gelator molecules and with those of the liquid, are presented. The intent of this chapter is to demonstrate the versatility of the molecular structures that self-aggregate into 3-dimensional fibrillar networks (SAFINs) as well as the properties of the liquid components that promote or inhibit gel formation. In many examples, the properties of the gelators and their liquids are correlated with micro- and macro-properties of their gels. Other aspects of several of the gel systems within this chapter are discussed in greater detail in other chapters. Also, the gelation properties of LMOGs leading to hydrogels and those gelators based on carbohydrates, steroids, and porphyrins are not included here for the most part because they are described in Chapters 15 and 18.

LMOG organogels are usually prepared by warming a macroscopically phase-separated gelator in an organic liquid until the mixture becomes a solution or sol, and then cooling the solution/sol to below a characteristic gelation transition temperature, \( T_g \). Empirically, \( T_g \) is the temperature below which flow no longer is discernible over long periods. It depends on the concentration of the gelator, the properties of the liquid, and, in some cases, the protocol for cooling the solution/sol. For a more rigorous rheological definition of a gel and \( T_g \), see Chapters 5 and 8.

Unlike many chemical gels, such as cross-linked polymers where the network is maintained through covalent bonds that must be broken if the system is to revert to a sol or solution, most physical gels of LMOGs are thermally reversible. The forces responsible for the formation of their immobilizing networks can be London dispersion interactions, hydrogen bonding, aromatic (\( \pi-\pi \)) interactions, ionic or organometallic coordination bonding, or (almost always) a combination of these. The interconversion between the gel and solution/sol phases depends only on the disassembly and assembly of the constituent molecules; in both phases, the chemical composition is unchanged unless disassembly is concurrent with a form of chemical equilibrium, as in the case of coordination bonding.

2. Classification of Organic Gelators

It is not yet possible to select \textit{a priori} a molecule that can gel definitively a selected liquid. Many discoveries of organic gelators have been fortuitous, usually occurring as a result of observations during the workup of a reaction mixture. As an aid to defining strategies for the molecular design of new organic gelators, examples of known LMOGs are grouped by structure, starting from the simplest and increasing in complexity.