Reverse thermal gelation of aromatic solvents by a series of easily accessible organic salt based gelators†

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Exploiting crystal engineering and supramolecular synthon concepts, a series of new gelator salts based on primary ammonium dicarboxylate (PAD) salts of azobenzene-4,4′-dicarboxylic acid and primary alkyl amines have been synthesized and characterized by various physico-chemical techniques. Most of the salts were shown to form gels with various solvents. Interestingly, most of the gelator salts possessed rarely observed reverse-thermal gelation (gelation with the rise of temperature) ability of aromatic solvents which may be relevant in developing thermo-responsive materials.

Introduction

Supramolecular synthon, originally coined by Desiraju,¹ is a well-studied and accepted tool in supramolecular chemistry² in general and crystal engineering³ in particular for designing desired supramolecular materials.⁴ By analogy, supramolecular synthon plays the same pivotal role in supramolecular synthesis as synthon does in covalent organic synthesis.⁵ Among the various supramolecular materials that have been synthesized using the supramolecular synthon approach,⁶ low molecular weight organic gelators (LMWGs)⁷ are important due to their various potential applications such as in the field of electrooptics/photonics,⁸ sensors,⁹ cosmetics,¹⁰ structure directing agents,¹¹ conservation of art,¹² drug delivery,¹³ and bio-medical applications,¹⁴ catalysis¹⁵ etc. LMWGs (molecular weight <3000) are supramolecular gelling agents that are able to immobilize a large volume of organic (organogels) and/or aqueous (hydrogel) solvents within a gel forming network—the so called self-assembled-fibriller-networks (SAFINs)¹⁶—formed via supramolecular self-assembly of the LMWG molecules. However, designing a LMWG appears to be a daunting task mainly because of the structural diversity of the gelating agents, lack of molecular level information about the structure of the gel-forming-network and poor understanding of the interactions of the gel-forming-network and the solvents. Nevertheless, there have been attempts to design LMWGs.¹⁷

Microscopic and X-ray diffraction studies revealed that the gel-forming-networks were often crystalline and therefore, have ordered crystal structures; it was, thus, realized that if the structure of the gel-forming-network could be determined, designing LMWGs could become possible. While Weiss et al. showed how the structure of the gel-forming-network could be determined by using X-ray diffraction (combining both powder and single crystal X-ray data), Shinkai et al. proposed a hypothesis based on a structure–property correlation approach¹⁸ that stated that 1-D hydrogen bonding networks (HBNs) were important in gelation whereas 2-D and 3-D networks were not as important. Following this, we have demonstrated that indeed Shinkai’s proposition was based on a logical foundation and since then, we have been investigating the role of 1-D or 2-D forming supramolecular synthons in designing LMWGs.⁷a Among the various 1-D or 2-D forming supramolecular synthons (Scheme 1) that we have successfully exploited in designing a large number of LMWGs, a primary ammonium dicarboxylate (PAD) synthon draws particular attention: the frequently observed HBN from PAD synthons is found to be 2-D. However, we have demonstrated that with the increase in the alkyl chain length of the cationic species, the 2-D HBN undergoes a supramolecular hydrogen bond isomerism leading to the formation of a 1-D nanotubular HBN resulting in gelation (Scheme 1).¹⁹

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Besides, the PAD synthon has been successfully employed in generating various LMWGs wherein the existence of 2-D HBNs (the usual PAD synthon) is observed.20

In this communication, we present the first examples of non-polymeric reverse thermal or heat-set organogels (gel formation with the rise of temperature) derived from a series of PAD salts that were obtained by reacting azobenzene-4,4′-dicarboxylic acid and primary alkyl amines Me–(CH2)n–NH2 (n = 9–15) (Scheme 2).

Results and discussion

Azobenzene-4,4′-dicarboxylic acid21 was reacted with the primary alkyl amines in 1 : 2 (acid:amine) molar ratio in MeOH by heating on a hot plate. The presence of a strong band in the range 1589–1587 cm\(^{-1}\) (attributed to \(\text{COO}^-\)) and the absence of 1685 cm\(^{-1}\) (expected for \(\text{COOH}\) in free acid) clearly indicate salt formation. Gelation studies were carried out using 14 selected solvents. It appears that salts having a longer chain length (n = 13–15) are moderate to good gelling agents for both polar and nonpolar solvents (Table S1, ESI†). A typical optical microscopic observation of a 1 wt % ethylene glycol (EG) gel revealed the formation of clusters of crystalline aggregates; the scanning electron microscopy of the same gel also supports such a finding (Fig. 1). Differential scanning calorimetry (DSC) of a selected gel (5.0 wt % DMSO gel of 2.16) revealed a gel–sol dissociation temperature (\(T_{\text{gel}}\)) of 120 °C in the heating cycle whereas the gel formation took place at 94.5 °C. The \(T_{\text{gel}}\) of this particular gel is in good agreement with that obtained by dropping method (\(T_{\text{gel}}\) = 118 °C). It may be noted that there seems to be a phase transition at lower temperature both in heating (36 °C) and cooling (23 °C) cycles (Fig. 2). Table-top rheology22 was employed to measure the thermal stability of the selected ethylene glycol gels of 2.15 and 2.16 (Fig. 3). The plots reveal the steady increase in \(T_{\text{gel}}\) with the increase in [gelator]; this clearly suggests that the gel state is mainly governed by strong intermolecular interactions, such as hydrogen bonding. It is also clear that 2.16 is a stronger gelator than 2.15 indicating the role of alkyl chain in gelation process. Typical rheological response of the 4.0 wt % ethylene glycol gels of 2.14, 2.15 and 2.16 revealed the visco-elastic nature of the gels. Frequency sweep experiments with a constant strain of 0.1% resulted in frequency invariant elastic moduli (\(G'\)) that were nearly one order of magnitude stronger than the corresponding loss moduli (\(G''\)) supporting the visco-elastic nature of the gels (Fig. 4). It can be seen that the strength of the \(G'\) gradually increased with the increase in alkyl chain length of the ammonium moiety of the corresponding gelators indicating the role of alkyl chain length in gelation (Fig. 4).

Fig. 1 The gel of 2.16 from EG; (left) optical micrograph of a1.0 wt % gel; (right) SEM of 0.8 wt % gel.

The reason for choosing an azobenzene moiety was to exploit the well known photo-responsiveness (\textit{trans}–\textit{cis} isomerization under UV radiation) of this moiety23 in producing photo-responsive gels.24 However, when irradiated at 350 nm for 4 h, visual observation (no gel deformation) indicated the photo-inertness of the gels (Ph-Cl/DMSO/EG gels of 2.16). UV-Vis data also indicated that no \textit{trans}–\textit{cis} photo-isomerization took place in the gels. However, when irradiated with UV (350 nm), the corresponding solutions indeed undergo \textit{trans}–\textit{cis} photo-isomerization as expected (data not shown). Although none of the gels turned out to be photo-responsive, a large number of the gels (with aromatic solvents) showed a rarely observed counterintuitive property of being reverse thermal gelators (forming gel at higher temperature);25 all these gels were found to be colloidial suspensions at rt (room temperature). In a typical experiment, when a solution (5 wt % 2.16 salt in chlorobenzene) of the gelator was heated in a sealed tube in an oil bath at about 180–190 °C, the gel formation was observed. However, bringing the temperature down to rt resulted in colloidal suspension usually within about 2 h. A gel, thus formed at high temperature, remained unperturbed for about 2 days when kept in the oil bath at ~55 °C. Microscopic observation revealed the existence of highly entangled assembly of thin fibers in the gel sample at high temperature whereas colloidial particles could easily be seen at rt. (Fig. 5).

To study the structure–property correlation of the gelation presented herein, we attempted to determine the single crystal structures of the selected gelators namely 2.15 and 2.16. Crystals suitable for single crystal X-ray diffraction (SXRD) were obtained from a MeOH/methyl salicylate (1 : 1 v/v) solution of the corresponding gelator. SXRD data revealed interesting findings. Both the crystals turned out to be 1 : 1 (acid : amine) salts instead of the expected 1 : 2 (acid : amine) salts thereby revealing the structures of 1.15 and 1.16 salts. The structures

![Scheme 2](Image)

Scheme 2 Various organic salts studied herein (the decimal represents the number of C atoms in the amine moiety).

![Fig. 2](Image)

Fig. 2 Differential scanning calorimetry of 5.0 wt % 2.16 gel in DMSO (heating and cooling scan was 10 °C min\(^{-1}\)).
appeared to be isomorphous as revealed from their identical space group and near identical cell dimensions (Table S2, ESI†). The asymmetric unit contains a hydrogen bonded ion pair. The alkyl chain of the cation is found to be adopting an all staggered conformation in 1.15 whereas the alkyl chain in 1.16 is found to be disordered thereby making it difficult to conclude about its conformation. The acid moiety is also found to be disordered in 1.16. The ion pairs are hydrogen bonded via both O–H/O and N–H/O interactions; the monoanionic carboxylate is involved in strong O–H⋯O [O⋯O = 2.602(5) Å; ∠ O–H⋯O = 177(6)°] hydrogen bonding involving carboxylate (COO⁻) and carboxylic acid (COOH) moieties resulting in a1D chain whereas the ammonium moiety forms various N–H⋯O [N⋯O = 2.985(7)–2.790(10) Å; ∠ N–H⋯O = 169.7–110.3°] interactions with the carboxylic acid and carboxylate moieties resulting into an overall 2D network (Fig. 6). Thus, crystallization of 1 : 1 (acid: amine) salts in the crystallization pot of 1 : 2 (acid: amine) salts indicates that during the crystallization process the formation of 1 : 1 salt took place via equilibrium. These results prompted us to make the 1 : 1 (acid: amine) salts and study their gelation properties (Table S1, ESI†). Almost all the salts showed gelation with 1,2-dichlorobenzene; compound 1.16 showed gelation with DMSO and EG but failed to gel 1,2-dichlorobenzene.

\[
\text{R–NH}_2^+ \cdot \text{OOC–COO} \cdot \text{H}_3\text{N–R} \rightleftharpoons 2 \text{R–NH}_2^+ + \text{HOOC–COOH}
\]

\(^1\text{H}\) NMR study of the salts (1.14, 1.15, 1.16) in DMSO-d\(_6\) displayed interesting observation. When the salt under study, for example 1.15, was heated in a NMR tube in DMSO-d\(_6\), the upper layer (A) was found to be gelled whereas the rest appeared to be a clear solution (B) (Fig. 7). \(^1\text{H}\) NMR of the solution phase (B) confirmed the presence of a nonstoichiometric mixture of acid and amine (\(\sim 1 : 0.23\)) whereas that of the gel part (A) displayed the presence of 1 : 2 (acid:amine) salt \(i.e. 2.15\). The fact that the gel part (A) is indeed the salt 2.15 was further confirmed by comparing the FT-IR spectra of 2.15 (bulk) with that of the gel part (A). Similar results are also obtained in the cases of 1.14 and 1.16 (data not shown). These results indicate that the 1 : 1 (acid:amine) salts are not gelators. They appear to gel various solvents because of the formation of 1 : 2 (acid: amine) salts during heating.

Conclusions

Thus, following the supramolecular synthon approach a series of PAD salts derived from azobenzene-4,4'-dicarboxylic acid and primary alkyl amines have been synthesized as potential LMWGs. Contrary to a few reported examples,\(^{24}\) the azo-moiety did not undergo photoisomerization. Remarkably most of the PAD salts reported herein showed reverse-thermal or heat-set gelation of aromatic solvents. Such counterintuitive property (reverse-thermal gelation) wherein a thermal signal is being converted into mechanical signal may find wide range of applications.
applications as new thermo-responsive materials. Further study would be required to understand the process of reverse-thermal gelation of the aromatic solvents.

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Notes and references

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