



# Instant gels from mixtures of amines and anhydrides at room temperature



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## ABSTRACT

A series of novel two-component organogel systems comprising of amines and anhydrides was developed. These two-component systems in aromatic solvents exhibit instantaneous gelation during mixing at room temperature without the requirement of any external stimulus such as heat, sonication, etc. The corresponding alcohols, however, failed to produce gel under similar condition. The structure-property relationship was investigated. The effect of mixing ratio of the two components as well as the effect of solvents on gelation was studied. A detail characterization of the organogels using electron microscopy, FTIR,  $^1\text{H}$  NMR and X-ray diffraction spectroscopy, differential scanning calorimetry and rheology suggested formation of a hydrogen-bonded complex that induces creation of three dimensional entangled network structures which immobilize the solvent showing macroscopic gelation. The packing of hydrocarbon chains of the amines and  $\pi$ - $\pi$  stacking interaction in aromatic amines were observed to play a decisive role in altering the thermal and mechanical stability of the organogels. The organogels formed by mixing aromatic amines with the anhydride exhibit exceptional thermal and mechanical stability compared to the aliphatic amines.

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## 1. Introduction

Currently, two-component gels have attracted a great deal of interest over single-component molecular gels because of their additional level of functionality, tunability, and control [1–13]. Hanabusa et al. and McPherson et al. first reported the concept of two-component gels in 1993 [12,13]. Hanabusa and co-workers observed that a 1:1 mixture of a pyrimidine derivative and barbituric acid derivative was capable of immobilizing a number of organic liquids after heat-cool treatment. For the reported gel systems, hydrogen-bonding (H-bonding) interaction, [14–18] donor-acceptor interaction, [19–22] and metal-ligand bond formation were shown to be the driving forces for two-component gelation [23,24]. The most common way to achieve two-component supramolecular gels has been via mixing of the components that cannot produce gel individually [25]. Hirst and Smith investigated the self-assembly behaviour of such types of systems consisting of a dendritic peptide and an aliphatic or aromatic diamine [26,27]. It was demonstrated that the length of the diamine spacer and the mole ratio of the components triggered the spatial organization of the dendritic head groups at the molecular level. Not

only dendritic peptides, water-insoluble fatty acids also could achieve hydrogels as a result of mixing with water-soluble primary diamines in ratios ranging from 5:2 to 15:1 [28]. Also, aqueous solution of single-headed cationic surfactant micelles caused increase of visco-elasticity of the resulting mixtures leading to eventual formation of hydrogels upon addition of salts [29]. For example, the addition of sodium salicylate to an aqueous solution of cetyltrimethyl ammonium bromide (CTAB) led to an increase of the viscoelastic properties of the resulting solution. In last few years, two-component gel chemistry has been enriched with melamine. Because of its nine H-bonding sites melamine has been shown to be capable of establishing stable supramolecular complexes and assemblies with other complementary molecules [30–32]. There are a number of reports in the literature on hydrogelation of melamine with riboflavin, uric acid, and gallic acid [30–33]. Pal and co-workers have also reported two-component hydrogel system consisting of melamine and citrazinic acid [34]. The hydrogelation could be achieved just by brief sonication of the mixture in water. More recently, a light responsive two-component hydrogel formation through the supramolecular assembly of anionic azobenzenedicarboxylate and cationic CTAB with a very low critical gelation concentration (CGC) of 0.33 wt% has been reported [35]. On the other hand, Bouteiller and co-workers have proposed a simple concept of a rational design of urea-based two-component

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organogelators that could gel liquids ranging in polarity from silicone oil to acetonitrile [36].

The second category of two-component gels reported in the literature is referred to as co-gels, in which both the components are low-molecular-weight gelators [37–40]. In these cases, mixing of the components causes an increase in the gelation properties, which could not be achieved with the use of only one of the two gelators. For example, Žinić and co-workers have investigated the effect of mixing of homochiral and heterochiral gelators on the self-association process and the properties of mixed gels [39]. It is reported that co-gels of homochiral mixtures show a greater thermal stability and better gelation ability than the co-gels of heterochiral mixtures [39]. Further, Maitra and co-workers have discovered a series of compounds in which  $\pi$ – $\pi$  stacking of the pyrenyl group and H-bonding of the urethane moieties were sufficient to achieve gelation [40]. The packing of the alkyl side chains was also observed to have a decisive role in altering thermal and mechanical properties of the co-gels. Recently, Cornwell et al. showed an innovative approach to produce spatially resolved multidomain multicomponent gels based on low-molecular-weight gelators derived from 1,3:2,4-dibenzylidene-D-sorbitol derivatives which formed gels when pH is lowered in a controlled manner by use of glucono- $\delta$ -lactone. The gel formation from their mixtures triggered by UV irradiation in the presence of diphenyliodonium nitrate as a photoacid was demonstrated [41].

An alternative approach of producing mixed-component gels is by combining one gelator molecule with non-gelling functional molecules [42–46]. The non-gelating functional molecules often add some more functional properties to the gel systems. Recently, Yang and co-workers have reported co-assembly of a peptide-based hydrogelator in the presence of another non-gelling peptide additive [46]. The greater hydrophobicity of the peptide based gelator made the hydrogelator precipitate out within an hour, but the addition of the non-gelling component was found to stabilize the self-assembled nanofibers for more than two months. Gasiorowski and Collier's group reported a mixed-component hydrogel capable of showing immune adjuvant property [47]. They found that incorporation of the functional molecules at the surface of the nanofibers resulted in a much higher activity than those in solution phase.

Organic salt formation in an organic acid-base reaction was also found to be an interesting way to achieve organogelation and therefore has attracted attention of chemists. Consequently, gelation by mixing L-lysine-based dendrimers with diamines has been demonstrated [48,49]. Dastidar et al. have reported two-component gels produced by mixing cinnamic acid derivative with aliphatic amines (RNH<sub>2</sub>) of varying hydrocarbon chain length [50–52]. Although most reports to date describe two-component gels of either dendrimers or mixing of acids with amines, Weiss and co-workers first reported two-component gels from mixtures of CO<sub>2</sub> gas and liquid RNH<sub>2</sub> [52]. Although a number of two-component systems that gel either organic solvent or water are reported, it is still a challenge to develop a new organogelator to gel a predetermined liquid, which requires an in depth understanding of the structure-property relationship. In fact, there is no report so far, on the spontaneous organogelation by mixing acid anhydride and amines. In the present work, we investigate a series of new two-component gelling system comprising of an aliphatic or aromatic amine and an acid anhydride at room temperature. It is well known that anhydrides are highly reactive towards amines. But to our surprise, we observed an instant transformation of the liquid to a gel when an aliphatic amine was mixed with succinic anhydride in aromatic solvents at room temperature. We have investigated the structure-property relationship by taking different combinations of anhydride and amine (or alcohol) and have examined the nature of the driving force for gelation. The organogels were characterized by a number of techniques, including electron microscopy, rheol-

ogy, differential scanning calorimetry (DSC), and NMR and X-ray diffraction (XRD) spectroscopy.

## 2. Experimental

### 2.1. Materials

Decyl amine (DA), dodecyl amine (DDA), hexyl amine (HA), cyclohexyl amine (CyA), 4-octyl aniline (4-OAN), 4-octyloxy aniline (4-OOAN), diglycolic anhydride (DGA) and propylene carbonate (PC) (Sigma-Aldrich, Bangalore, India) were used without further purification. Aniline (AN), N-methyl aniline, 4-anisidine (4-MOAN), 4-aminotoluene (4-MAN), 4-nitroaniline (4-NAN), 4-hydroxyaniline (4-HAN), 4-aminobenzoic acid (4-ABA), *o*-phenylenediamine (*o*-PDA), *p*-phenylenediamine (*p*-PDA), phenol (PhOH), *p*-cresol (4-MPhOH), *m*-cresol (3-MPhOH), salicylaldehyde (SAL), tetradecanol (TDOH), succinic anhydride (SA), glutaric anhydride (GA), maleic anhydride (MA), phthalic anhydride (PTA), acetyl acetone (AA) were purchased from SRL, Mumbai, India. Chloroform (CHCl<sub>3</sub>), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), carbon tetrachloride, *n*-hexane (HEX), *n*-heptane (HEP), cyclohexane (CHX), benzene (PhH), toluene (PhMe), chlorobenzene (PhCl), nitrobenzene (PhNO<sub>2</sub>), *o*-xylene (*o*-Ph(Me)<sub>2</sub>), *m*-xylene (*m*-Ph(Me)<sub>2</sub>), *p*-xylene (*p*-Ph(Me)<sub>2</sub>), dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol (MeOH), and ethanol (EtOH) were of good quality and were purified and dried whenever necessary.

### 2.2. Methods

The gelation tests were performed in screw-capped glass vials. A solution of each component of desired concentration was made in the solvent. The two solutions were then mixed in known volume ratio in a screw-capped vial at room temperature. The formation of the organogels was confirmed by the tube inversion method [52].

Melting points of the solid samples were measured using the Instind (Kolkata) melting point apparatus with open capillaries. Specific rotation was measured with a digital polarimeter (Jasco P-1020). FT-IR spectra were measured with a Perkin-Elmer (model spectrum Rx1) spectrometer. The <sup>1</sup>H NMR spectra were recorded on an AVANCE DAX-400 (Bruker, Sweden) 400 MHz NMR spectrometer in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> solvents.

Melting temperature of the gels were measured by inverted-tube experiment putting the screw-cap vial containing the gel in a temperature controlled water bath (JULABO, model F12). The gel was slowly heated at a rate of 1 deg/min until the gelled mass starts to flow on tilting of the vial. For selected gel samples, a Perkin Elmer Pyris Diamond differential calorimeter was used to measure melting temperatures. The gel samples were placed in hermetically sealed Tzero lids and pans. The measurements were carried out at a heating rate 5 °C/min under nitrogen atmosphere.

For scanning electron micrographs, the hot sample solution was placed on the aluminium or copper foil, allowed to cool, and air-dried at room temperature. The gel-cast films (xerogels) were further dried in desiccators for 24 h. A layer of gold was sputtered on top to make conducting surface, and finally the specimen was transferred onto the field emission scanning electron microscope (FESEM, Zeiss, Supra-40) operating at 5–10 kV to get the micrograph.

The X-ray diffraction (XRD) spectra were recorded at room temperature on a Panalytica X'Pert pro X-ray diffractometer using Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$  and Ni filter at a scanning rate of 0.001 s<sup>-1</sup> between 2 and 30°, operating at a voltage of 40 kV and current 30 mA. The organogel samples prepared on a glass slide were dried in the air overnight before measurement.

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