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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}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 π-π 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.

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 organisation 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 gallicacid [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 π–π 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-δ-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_2) 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_2 gas and liquid RNH_2 [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, rheology, 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 ($CHCl_3$), dichloromethane (CH_2Cl_2), carbon tetrachloride, *n*-hexane (HEX), *n*-heptane (HEP), cyclohexane (CHX), benzene (PhH), toluene (PhMe), chlorobenzene (PhCl), nitrobenzene ($PhNO_2$), *o*-xylene (*o*-$Ph(Me)_2$), *m*-xylene (*m*-$Ph(Me)_2$), *p*-xylene (*p*-$Ph(Me)_2$), 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 RxI) spectrometer. The ^1H NMR spectra were recorded on an AVANCE DAX-400 (Bruker, Sweden) 400 MHz NMR spectrometer in $CDCl_3$ or C_6D_6 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 gelated 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 Pan analytica X'Pert pro X-ray diffractometer using Cu target (Cu Kα, λ = 1.5418 Å) and Ni filter at a scanning rate of 0.001 s^{-1} 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.

Table 1
Gelation properties of the systems containing SA and different amines in various organic solvents at different mole ratios; The number within the parentheses represents corresponding CGC value (±0.1%, w/v) determined at 25 °C.

Amines	Amine/Anhydride (Mole Ratio)	Gelation properties (CGC ± 0.1%, w/v)								
		Solvent								
		DCM	PhH	PhMe	*o*-Ph(Me)$_2$	*m*-Ph(Me)$_2$	*p*-Ph(Me)$_2$	Ph(Me)$_3$	PhCl	PhNO$_2$
DA	1:1	N	OG (3.8)	TG (3.4)	TG (3.4)	OG (3.1)	TG (3.4)	OG (1.5)	OG (3.6)	OG (4.6)
DDA	1:1	OG (5.2)	OG (1.4)	TG (1.1)	TG (1.1)	OG (1.2)	TG (1.0)	OG (0.9)	OG (2.0)	OG (2.1)
	2:1	N	OG (4.0)	TG (3.6)	TG (5.2)	OG‘ (5.6)	TG (3.8)	WG	OG (7.1)	OG (4.7)
	1:2	N	N	N	N	N	N	N	N	N
TDA	1:1	OG (4.6)	OG (1.3)	OG (1.2)	TG (1.4)	OG (1.3)	TG (1.4)	OG (1.2)	OG (1.9)	OG (2.6)
AN	1:1	OG (3.9)	OG (2.6)	OG (2.7)	OG (2.7)	OG (2.2)	OG (2.1)	OG (1.9)	OG (3.0)	OG (4.7)
	2:1	WG	OG (4.0)	OG (5.7)	OG (5.2)	OG (4.9)	OG (4.7)	OG (3.9)	WG	OG (4.8)
	1:2	N	N	N	N	N	N	N	N	N
4-MAN	1:1	OG (4.8)	OG (4.1)	OG (3.9)	OG (2.9)	OG (3.2)	OG (2.8)	OG (1.5)	OG (3.5)	OG (4.8)
3-MAN	1:1	CF	CF	CF	CF	CF	CF	CF	CF	CF
4-OAN	1:1	OG (4.6)	OG (3.7)	OG (3.7)	OG (3.0)	OG (3.0)	OG (2.4)	OG (1.2)	OG (3.7)	OG (3.7)
4-MOAN	1:1	OG (3.8)	OG (2.6)	OG (2.3)	OG (2.2)	OG (2.2)	OG (2.4)	OG (2.0)	OG (3.4)	OG (3.6)
4-OOAN	1:1	OG (5.0)	OG (3.2)	OG (4.5)	OG (2.9)	OG (3.5)	OG (3.5)	OG (2.6)	OG (3.2)	OG (2.3)

TG = translucent gel; OG = opaque gel; WG = weak gel; N = no gelation; CF = crystal formation; in all the cases the organogels were formed within 5 s of mixing.

The rheology measurements were performed on a Bohlin RS D-100 (Malvern, UK) rheometer using parallel-plate (PP-20) geometry with a constant tool gap of 100 μm. The rheometer is fitted with a solvent trap and peltier device that controls temperature within 25 ± 0.1 °C. An equilibration time of 30 min was allowed before measurements were taken for each sample. All measurements were performed with a matured gel after 10 h of preparation. Oscillatory stress sweep measurements were carried out at a constant frequency of 1 Hz to obtain storage modulus (Gí) and loss modulus (Gíí).

3. Results and discussions

3.1. Gelation behaviour

Gelation tests of the DDA/SA mixtures were initially conducted in cyclohexane (CHX) and benzene solvents at 1:1 mol ratio in screw-capped vials. Gelation did not occur in CHX due to insufficient solubility of SA. However mixing of the two components resulted organogelation in benzene almost instantaneously (within 5 s) at room temperature. It is important to note that gelation of benzene did not occur in the presence of even a small amount of H-bonding solvent (e.g., MeOH) as impurity. This led us to conclude that H-bonding interaction between the components is essential for gelation. Considering the fact that SA has two H-bonding sites (>C=O), we performed the gelation tests also at 2:1 and 1:2 mol ratios (Table 1). The 2:1 DDA/SA mixture led to the formation of weak organogel in benzene solvent instantaneously, but at a much higher concentration. In contrast, the 1:2 mixtures failed to gel benzene and produced a precipitate within 10 min. This could be due to chemical reaction between SA and DDA producing corresponding amide derivative. Therefore, the precipitate obtained from 1:2 mixtures was analysed by NMR spectra and the structure resembled that of corresponding amide derivative (see Scheme S1 under “Supplementary data” for details). This means that in the presence of excess SA the rate of formation of amide derivative is enhanced. It should be noted that when gelation test was performed with the amide derivative, no gelation could be achieved in the solvent at room temperature. This supports our conclusion that gelation of the solvent is due to the formation of hydrogen-bonded complex between SA and DDA molecules. However, the formation of amide derivative competes with the gelation process. In the presence of excess DDA, for example in 2:1 DDA/SA mixture, the rate of gelation over weighs the rate of amide formation thus producing gel at room temperature. Indeed, the formation of the amide product is evidenced by the ^{1}H NMR spectrum of the DDA/SA (2:1) system in C_6D_6 solvent (Fig. S1, Supplementary data), which exhibits peaks (d, c, b) corresponding to the amide derivative at 2.31, 2.56, and 3.40 ppm. The gelation abilities of the 1:1 and 2:1 mixtures were compared by measuring critical gelation concentration (CGC) and the data are included in Table 1. The corresponding anhydride concentration (in mM) is indicated in Table S1 of “Supplementary data”. The results presented in Table 1 reveal that the 1:1 mixture has the highest gelation ability. This means though the presence of excess amine is tolerated, but the CGC value increased, probably due to the increase of solvent polarity.

3.2. Effect of chemical structure

To study the effect of chemical structure of the anhydride and amine on gelation, the gelation test was also carried out with different anhydrides as listed in Chart 1(a) under the same condition. The results are included in Table S2 (Supplementary data). Interestingly, only SA and GA in the presence of DDA were observed to immobilize benzene. Although DGA possesses similar six-membered ring as GA, yet it failed to gel benzene due to its poor solubility in the solvent. Similarly, failure to gel benzene by MA can be attributed to the formation of amide derivative [53]. Indeed formation of the amide derivative was also confirmed in this work by analysing the precipitate obtained in CH_2Cl_2 solvent. However, formation of a

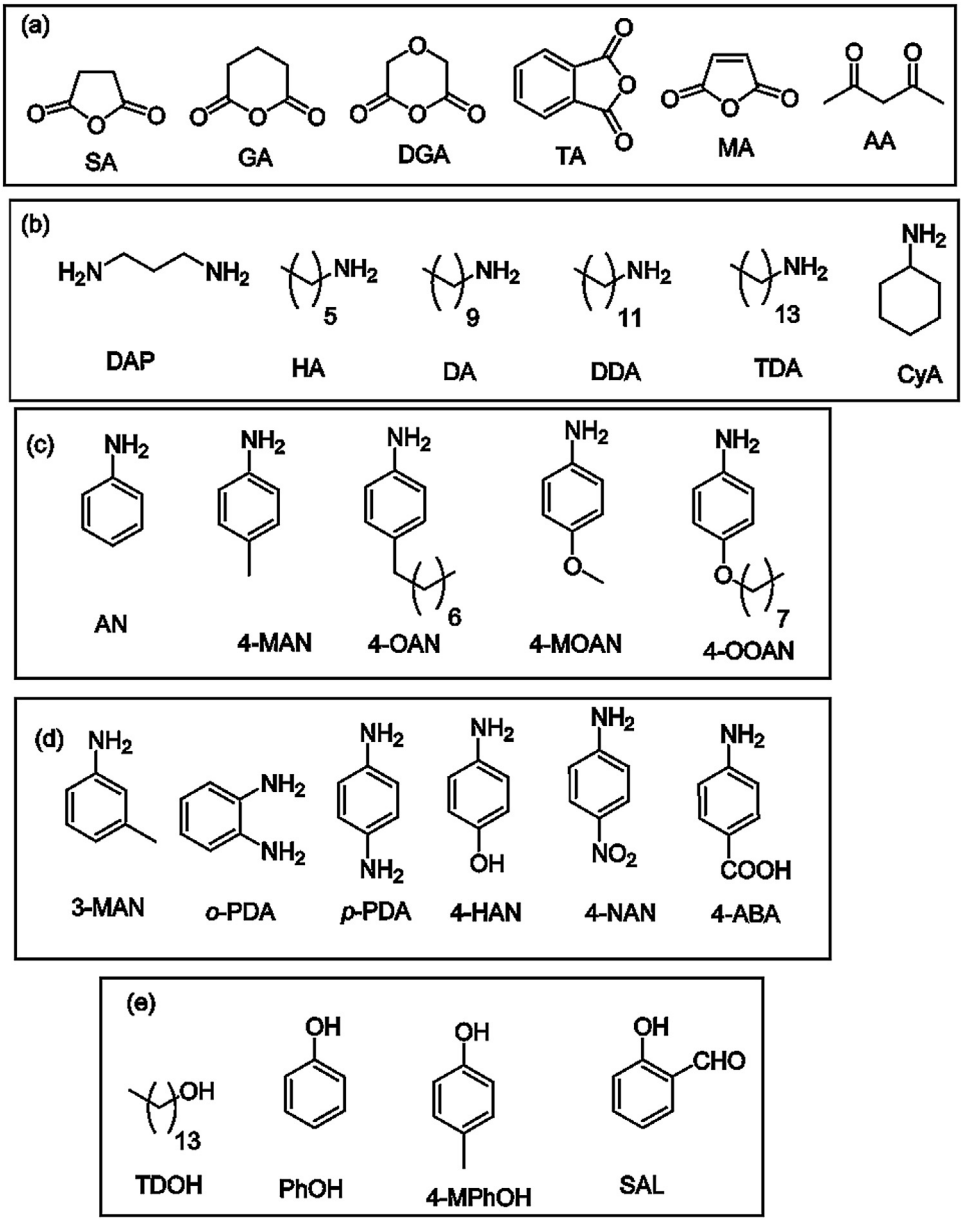


Chart 1. Chemical structure of different (a) anhydrides, (b) aliphatic amines, (c, d) aromatic amines, and (e) aliphatic alcohols and phenols employed for gelation studies.

secondary amide as a result of Michael addition was not observed at room temperature. Since the formation of amide derivative was not observed with SA within the gelation time, MA appeared to be more reactive compared to SA.Considering the fact that the presence of diketone moiety is important, we also performed gelation test using AA in the same solvent in the presence of different amines. However, no gelation but a clear solution was observed even 6 h after the addition of amine. This is not surprising, because first of all both the components are liquid at room temperature. Also it is well known that AA predominantly exists in the enol form, making the carbonyl group unavailable for intermolecular H-bonding interaction. It should also be remembered that the structure of AA is more flexible in comparison to SA.

The gelation test of SA was also monitored with other aliphatic amines having different hydrocarbon chain lengths (C_6 to C_{14}; Chart 1(b)). The results of gelation studies are summarized in Table 1. As expected, HA failed to induce any gelation owing to its shorter hydrocarbon chain length, whereas higher aliphatic amines successfully gelated the solvent with a decreasing order of CGC value in going from HA to DDA. Interestingly, CGC value increased slightly in the case of SA/TDA system in some solvents. The increase of CGC value with the increase of hydrocarbon chain length above C_{12} is also reported by others [54]. This can be attributed to conformational change (bending) of the hydrocarbon chain that reduces van der Waals interactions among the aliphatic chains, thereby disfavouring gelation. In fact, the bending of hydrocarbon chain beyond C_{12} is reported in the literature [55].

The structural effect on gelation by the two-component systems was also investigated by changing the amine from aliphatic to aromatic. Switching to aromatic amines from aliphatic amines had a dramatic effect on the gelation behaviour. While the aliphatic amines HA and CyA could not instigate any gelation of the solvents, aniline (AN) having the same number of carbon atoms as CyA, could induce gelation instantaneously at room temperature producing an opaque gel. However, as in the case of DDA, the AN/SA system did not produce gel at 1:2 ratio. This signifies that simple structural modification can alter the self-complementary assembly of the gelators. This led us to examine the effect of substitution

onbenzene ring of AN on the self-association and hence gelation process. Therefore, the gelation ability of SA was tested in the presence of a number of substituted AN (see Chart 1(c, d) for structures). The results summarized in Table 1 reveal that the presence of electron donating —CH_3 (4-MAN) and —OMe (4-MOAN) group at the *p*-position of —NH_2 group reduces the gelation ability of the two-component system, and consequently, in the presence of 4-MAN or 4-MOAN the CGC value increased with respect to AN. The effect is stronger in the case of —CH_3. Interestingly, increase of the alkyl chain length (e.g., 4-OAN) has a very little effect on the gelation process as shown by the CGC value, which is almost equal to that of 4-MAN.In contrast, the increase of chain length of the alkoxy group (e.g., 4-OOAN) was observed to reduce the gelation ability of the two-component gel system. This is probably due to the free rotation of the alkyl chain around the C—O bond relative to around C—C bond [56]. The greater flexibility of the alkoxy chain affects self-assembly formation. On the other hand, the amines listed in Chart 1(d) being poorly soluble or insoluble in the solvent did not produce gels. It should be noted here that all the aromatic amines produced opaque gels, whereas aliphatic amines in some cases as discussed above produced translucent gels. The formation of opaque gels in the case of aromatic amines indicates formation of large aggregates that scatter light. The data in Table 1 suggest that the ease of formation of organogels was higher for aromatic amines than that for aliphatic amines, possibly due to π-π stacking interaction. This has been elaborated further below.

The —NH_2 and —OH groups are isoelectronic and both have H-bond donor/acceptor properties. Since both aliphatic and aromatic amines were observed to induce spontaneous gelation on mixing with SA, we also examined gelation abilities of aliphatic as well as aromatic alcohols (see Chart 1(e) for structures) in the presence of SA. Interestingly, none of the alcohols listed in Chart 1(e) could instigate gelation in benzene at any mole ratio. In all the cases, the resulting mixture produced only a clear solution even at a relatively high concentration (0.38 mM for PhOH/SA system). It should be noted that the alcohols did not react to give corresponding ester as the alcoholic oxygen is less basic than the nitrogen atom in amines. For the same reason, the SA/aromatic amine systems have higher gelation ability because the aromatic amines are less basic than aliphatic amines.

In order to examine the role of solvent on gelation process,the gelation tests for the amine/SA systems were performed in a range of solvents, including aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons (e.g., CH_2Cl_2, $CHCl_3$, CCl_4, PhCl etc.) and also in polar solvents, such as propylene carbonate (PC), DMF, DMSO, MeOH, and EtOH. But gelation was not observed in any of the aliphatic hydrocarbon solvents (e.g., HEX, HEP, and CHX) due to insufficient solubility of SA. On the other hand, in polar liquids (e.g., PC, DMF, DMSO, MeOH, and EtOH), gelation did not occur due to interference of the H-bonding solvents. Similar observation was also made in the chlorinated solvents, such as $CHCl_3$ and CCl_4 with the exception of CH_2Cl_2. In contrast, all the aromatic solvents (e.g., PhH, PhMe, *o*-Ph(Me)$_2$, *p*-Ph(Me)$_2$ and *m*-Ph(Me)$_2$, Ph(Me)$_3$, PhCl, and $PhNO_2$ employed transformed into organogels, which means solvent polarity has an important role in the gelation process. It should be noted that the CH_2Cl_2 and $PhNO_2$ organogels broke down after 12 h producing a precipitate. All other organogels remained unaffected for more than amonth, when preserved under the same condition. The lower stability of the CH_2Cl_2 and $PhNO_2$ organogels can be attributed to H-bond donor and acceptor capacity of the solvents, respectively, which facilitates formation of amide derivative.

In order to compare the gelation abilities in different solvents, the CGC values for the 1:1 mixture were determined for all the systems and the results are summarized in Table 1. The gelation abilities of the two-component systems in different solvents can be interpreted by correlating their CGC values with different polarity parameters [57], such as dielectric constant (ε), Kamlet-Taft solvatochromic parameters [58], and Hansen solubility parameters (HSPs) [59]. Although HSPs have been successfully used in rationalizing organogel formation [60,61], we could not correlate the CGC data with HSPs because of the lack of HSP values of a sufficient number of solvents employed in this work. On the other hand, the Kamlet-Taft parameters not only depicts generalised polarity parameters (π*), the H-bond donating (α) and accepting (β) ability of the solvents can also be described by this. The corresponding ε and π* values of the solvents used in this work are listed in Table S3. For both DDA/SA and AN/SA organogel systems, the plot of CGC versus ε and π* parameters are displayed in Fig. 1(a, b). The results demonstrate that though there is no significant correlation between CGC and ε parameter for both the systems, the plot of CGC and π* parameter for DDA/SA, AN/SA, 4-MAN/SA, 4-MOAN/SA shows a linear increase of CGC with π* parameter. The correlation of the CGC values with the π* polarity parameters can be observed with only in aromatic solvents (except PhCl). Since PhCl (β = 0.07) [58] and $PhNO_2$ (β = 0.39) [58] solvents have H-bond accepting ability, they interact with the amine differently as reflected by the higher CGC values. This means H-bonding interactions affect the gelation process. It is interesting to note that for any of the organogel systems, the CGC value is lowest in Ph(Me)$_3$ solvent due to its lowest polarity. In other words, only dispersive and polar interactions are important for the organogelation.

3.3. Driving force for gelation

Since anhydrides are highly reactive towards amines to give amide, there is a possibility of in situ gelation by the amide produced in the reaction medium. However, as mentioned before, the corresponding amide derivative of DDA failed to produce gel at

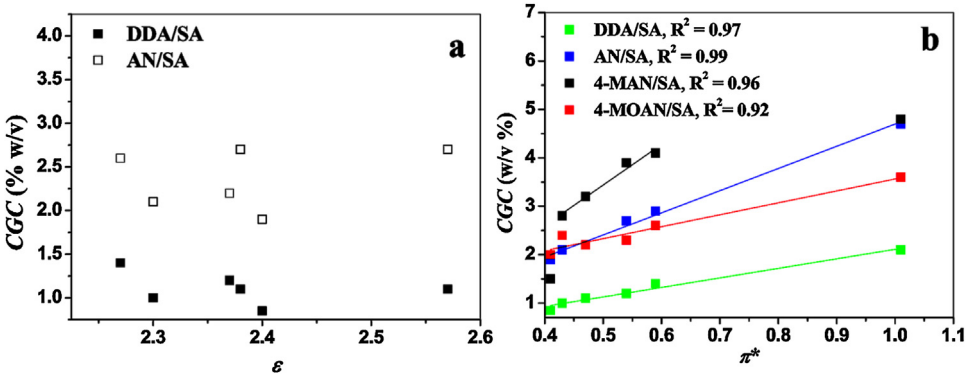
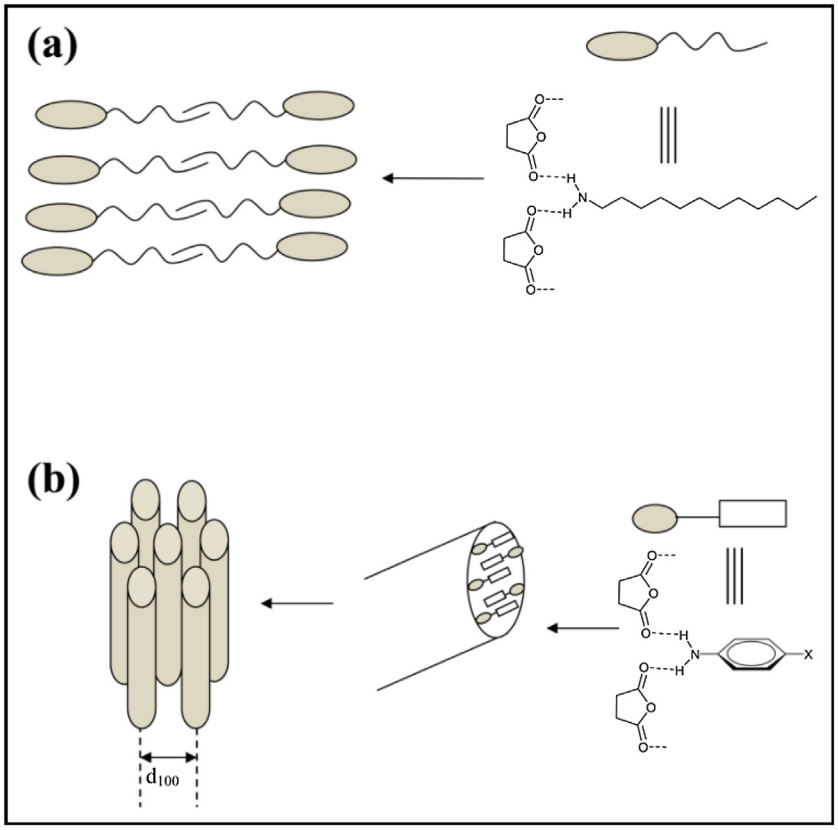


Fig. 1. Variation of CGC value of the gelators with solvent polarity parameters: (a) dielectric constant (ε) and (b) Kamlet–Taft parameter (π*).



Scheme 1. A schematic illustration of 1:1 H-bonded complex of SA with (a) DDA, TDA, 4-OAN, and 4-OOAN and (b) AN, 4-MAN, and 4-MOAN.

room temperature in the same solvent. In fact, gelation could not be achieved with the amide derivative of AN (for details see Supplementary data), even when subjected to heat-cool treatment. Further, it should be remembered that aromatic amines being weaker bases than aliphatic amines cannot react with the anhydride to produce amide. This rules out in situ gelation due to chemical reaction between the amine and SA. Further, it should be noted that the above mentioned gelation takes place almost instantaneously, but the amide derivative is not produced during this short time (~5 s) at room temperature. The stability of the organogels in non-hydrogen bonding solvents over a month suggests that the formation of the amide product is not responsible for gelation. However, an H-bonded complex of the amine and SA can form spontaneously at room temperature as shown in Scheme 1. It should be noted that when the gelation test was performed using N-methyl aniline (a secondary amine) keeping all other parameters same no gelation was achieved. This must be due to the steric hindrance which inhibits H-bonding interaction between the components. Thus it can be concluded that self-association of the components occurs through intermolecular H-bonding and van der Waals interactions producing one-dimensional aggregates (1D), which through entanglement with each other produces a three-dimensional (3D) network structure that immobilizes the solvent. The results of different studies discussed below also suggest this mechanism of gelation. That the self-assembly formation occurs through H-bonding interaction is supported by the fact that the 1:1 mixture AN and SA could not produce gel in the presence of H-bond donating additives, such as 2-aminoethanol (0.082 mM/0.099 mM gelator) and 2-mercaptoethanol (0.071 mM/0.099 mMgelator). Since 2-aminoethanol and 2-mercaptoethanol have H-bond donor functional groups, they do not allow the gelators to orient through intermolecular H-bonding interaction. However, the failure to gel organic solvents by the PhOH/SA system raises question about the role of H-bonding interaction as PhOH is expected to make stronger H-bond than AN. But it should be remembered that H-bonding interaction between two PhOH molecules is much stronger than that between two AN molecules. As a result, PhOH is a solid at room temperature, but AN is a liquid. This means that the H-bonding interaction between SA and PhOH molecules is much weaker than between SA and AN.

In order to show that the gelation is through H-bonded complex formation between amine and anhydride and not through the formation of amides, we have conducted FTIR studies with the organogel of DDA/SA system in *o*-xylene, solid SA, and also with the amide product formed in the reaction between DDA with SA (Fig. S2, "Supplementary data"). The two —C=O bonds of solid SA generate two characteristic infrared absorption bands at 1781 and 1870 cm^{-1}, which are retained in the *o*-xylene gel, but blue shifted to 1815 and 1960 cm^{-1}, respectively. But the solid amide product (Scheme 1) did not show the characteristic anhydride —C=O peaks, instead it showed peaks at 3298, 1650 and 1698 cm^{-1} corresponding to N—H stretching (amide A), C=O stretching (amide I) and C=O stretching vibration of the-COOH group, respectively. These results clearly establish the fact that formation of an H-bonded complex is responsible for the organogelation.

Further, to demonstrate the existence of H-bonding interaction between SA and AN we measured ^{1}H NMR spectra for the AN/SA mixture (1:1) in C_6D_6 at two different concentrations and compared with that of AN. The spectra in Fig. 2(a) show that the NH proton chemical shift for AN in the absence of SA appears at 2.75 ppm (designated as "a") is shifted to 2.38 ppm in the presence of SA (0.024 mM) accompanied by a significant peak broadening. Although the H-bonding interaction cannot explain the upfield shift of the peak corresponding to NH proton, significant peak broadening undoubtedly proved that in the gel state AN and SA self-assembled via H-bond formation. The ^{1}H NMR spectrum (Fig.

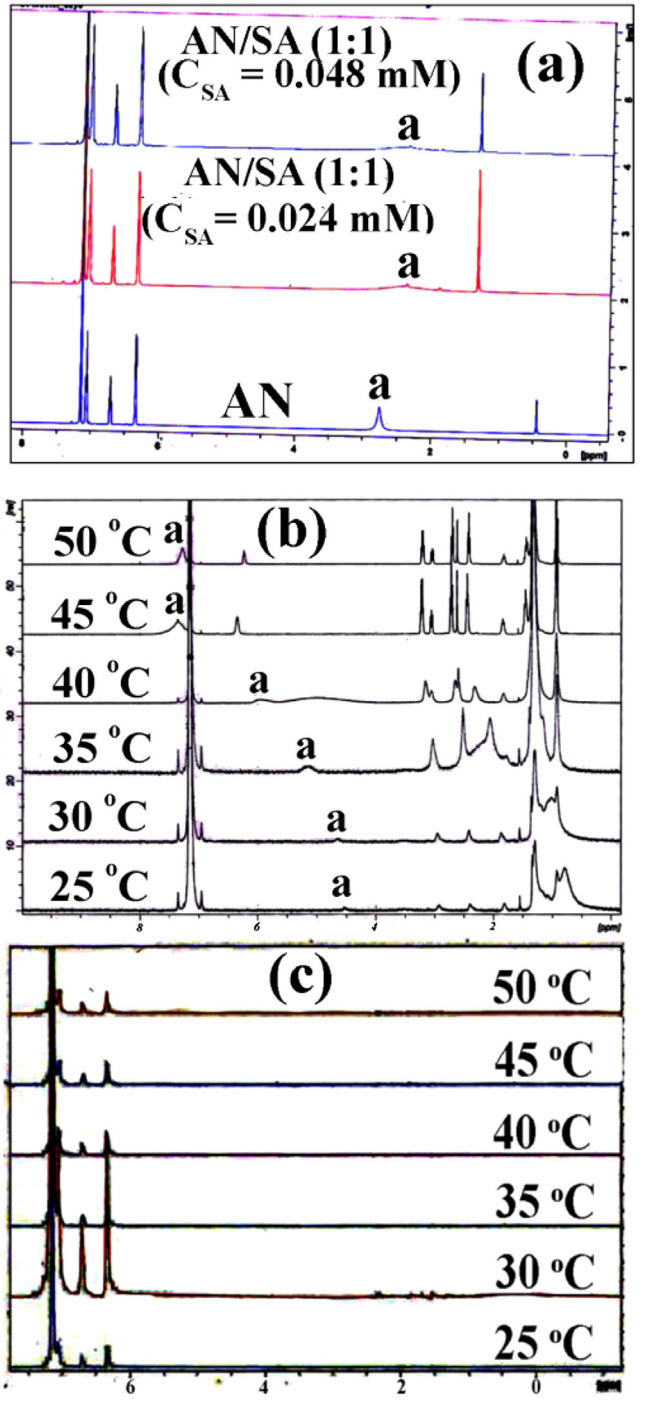


Fig. 2. (a) Concentration dependent ^{1}H NMR spectra of AN, AN/SA (1:1, C_{SA} = 0.024 mM), AN/SA (1:1, C_{SA} = 0.048 mM) in C_6D_6 solvent, (b) temperature dependent ^{1}H NMR spectra of DDA/SA (1:1), and (c) AN/SA (1:1) organogel in C_6D_6 at the respective CGC.

S3, Supplementary data) recorded for the AN/SA organogel in CD_2Cl_2 solvent also showed similar results. In support to our conclusion that the gel networks in these systems are constructed by H-bonding and π-π stacking interactions, variable temperature ^{1}H NMR spectra (Fig. 2(b)) of the gels were recorded for DDA/SA (1:1) and AN/SA (1:1) (Fig. 2(c)) organogels in C_6D_6. At 25 °C, the spectrum of organogels of DDA/SA displayed significant peak broadening of the protons of the amine and anhydride implying the complete participation of all the protons in the gel framework. On raising the temperature to 50 °C, however, the peak becomes sharper accompanied by a downfield shift of the H-bonded (N—H···O=C-) NH protons (designated as "a" in Fig. 2(b)) indicating gradual transformation of the gel into a solution [28]. The plots of peak width at half height ($\Delta_{1/2}$) and chemical shift position (δ_{NH}) as a function of temperature (Fig. S4) exhibit an abrupt change at 45 °C which is taken as the gel-to-sol transition temperature (T_{gs}). Interestingly, in this temperature range, no spectral change is observed in the case AN/SA system (Fig. 2(C)), indicating that the T_{gs} value is much higher than that of DDA/SA organogel. In other words, the former organogel is thermally more stable, which means the intermolecular interactions in the self-assembled structures of AN/SA organogel are much stronger. This is consistent with our hypothesis that the organogels of aromatic amines involve π-π stacking interaction in addition to intermolecular H-bonding and van der Waals interactions. The involvement of π-π stacking interaction of the aromatic amines in the gel state is also indicated by the failure to gel solvents by the CyA/SA system. In the case of CyA, the H-bonding interaction was not sufficient to cause gelation because of its non-planar ring structure, which introduces steric hindrance.

In support of the above conclusion, the gel melting temperatures of the four representative organogels of DDA/SA, TDA/SA, AN/SA and 4-MOAN/SA systems in *o*-Ph(Me)$_2$ solvent were determined by DSC method. The thermograms are shown in Fig. S5. Each thermogram exhibits two endothermic peaks, one sharp peak corresponding to gel melting and a second broad peak at ~142 °C corresponding to solvent evaporation. The T_{gs} values thus obtained decreases in the order 4-MOAN/SA (155 °C) > AN/SA (135 °C) > TDA/SA (65 °C) > DDA/SA (55 °C) showing higher thermal stability of the organogels involving aromatic amines relative to those of aliphatic amines. The enthalpy change (ΔH) associated with the gel-sol transition process also decreases in the order 4-MOAN/SA (101.37 J/g) > AN/SA (38.59 J/g) > TDA/SA (29.25 J/g) > DDA/SA (21.89 J/g). The higher ΔH values for the organogels involving aromatic amines clearly suggest stronger intermolecular interactions in comparison to organogels involving aliphatic amines. This means π–π stacking interaction between phenyl rings is important for the gelation process. The higher ΔH value for TDA/SA organogel compared to that of DDA/SA organogel also suggests increase of van der Waals interaction with the increase of chain length. The π–π stacking of phenyl rings in the self-assembled structures is also shown by the X-ray diffraction (XRD) data of the xerogels as discussed below.

3.4. Secondary structures of the organogels

Not only the primary structure as determined by the molecular level recognition events, but also the secondary structure as defined by the morphology of the aggregates is important in understanding complex systems like gels. As mentioned above the gelation abilities of the two-component gels were observed to vary significantly with the chemical structure of the amines and also with the change of solvent property. Therefore, there must be some difference in the aggregate morphologies of the two-component organogels. In order to shed light on the effects of chemical structure and solvent on the microstructure of the aggregates formed in the gel-network, we performed FESEM measurements with the xerogels. The FESEM images of six representative organogels in *o*-Ph(Me)$_2$ solvent are presented in Fig. 3. Fig. 3(A)–(C) depicts the organogels prepared by mixing aliphatic amines of increasing chain length (DA to TDA) with SA. As shown in micrograph 3(B) and 3(C) the 3D network structures of DDA/SA and TDA/SA organogels are constructed by the bundles of belt-like fibers of high aspect ratio and widths of 1–10 μm. The results demonstrated that with increasing chain length of the aliphatic amines the gelators aggregated into well-ordered structure that cross-linked among them helping in arresting the solvent in it.

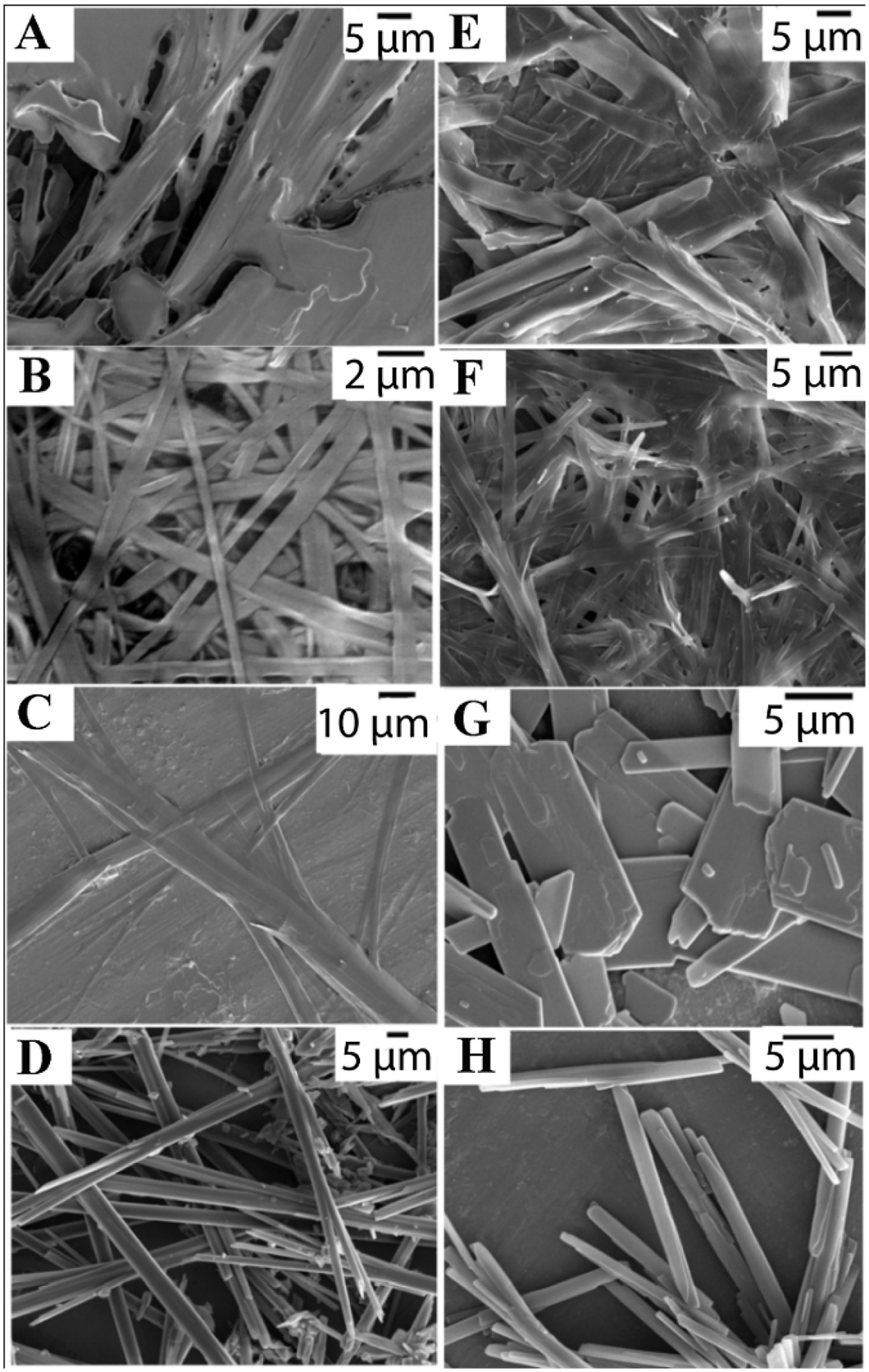


Fig. 3. FESEM images of the organogels of (A) DA/SA, (B) DDA/SA (C) TDA/SA, (D) AN/SA, (E) 4-OAN/SA, (F) 4-OOAN/SA, (G) 4-MOAN/SA, (H) 4-MAN/SA in *o*-Ph(Me)$_2$ solvent. In all the cases the mole ratio of the two-components was 1:1, and all the images were taken at their respective CGC value.

Table 2
Significant XRD peaks of the solid sample and the xerogels.

Compounds	2θ (°)	d (Å)	h: k: l	Remarks
TDA	4.85, 9.79, 14.70	8.20, 9.05, 7.35	1: 2: 3	Lamellar packing
TDA/SA	4.62,9.00, 13.47	19.3, 9.9, 6.6	1: 2: 3	Lamellar packing
4-OAN/SA	5.30, 10.34, 17.57	16.7, 8.6, 5.06	1: 2: 3	Lamellar packing
4-OOAN/SA	4.70, 9.10, 13.52	18.8, 9.7, 6.6	1: 2: 3	Lamellar packing
4-MOAN	13.11, 18.79, 22.07	6.75, 4.72, 4.03	1: $\sqrt{2}$: $\sqrt{3}$	Cylindrical packing
4-MAN/SA	6.75, 11.45, 20.25	13.1, 6.5, 4.4	1: $\sqrt{3}$: 2	Hexagonal packing
4-MOAN/SA	3.64, 6.94, 10.32	24.3, 12.7, 8.6	1: $\sqrt{3}$: 2	Hexagonal packing

On the other hand, the FESEM images of the xerogels obtained in the presence of aromatic amines (Fig. 3(D)–(H)) display straight and stiff ribbons of low aspect ratio. This suggests that the molecules tend to self-assemble in the direction of 1D fiber. A closer look at the images reveals that although similar type of aggregates are observed in the gel network structure, yet the length, width, and density of fibers differ significantly with changing the aromatic amine. Analysis of the network in the xerogel of AN/SA system (Fig. 3(D)) reveals that the ribbons are approximately ~4 μm in width and ~100 μm in length. The gel networks of 4-OAN/SA consist of thick, flexible belt-like fibers (Fig. 3(E)), whereas the image of 4-OOAN/SA (Fig. 3(F)) shows highly entangled fibers. Surprisingly, reducing the hydrocarbon chain length (4-MOAN) the fibers transferred into nice well-ordered plates of width around 5 μm as shown by the micrograph Fig. 3(G). Thus it can be concluded that flexibility of the hydrocarbon chain at the *p*-position of the AN, imparts flexibility to the ribbons.

3.5. X-ray diffraction spectra

In order to explore the molecular packing and the gelation mechanism, we measured the XRD spectra (Fig. S6–S10) of the xerogels of 4-MAN/SA, 4-OAN/SA, 4-MOAN/SA, 4-OOAN/SA and TDA/SA obtained from *o*-Ph(Me)$_2$ solvent. The corresponding data are summarized in Table 2. For comparison purposes we also recorded the XRD spectra of 4-MOAN and TDA in the crystal state (Figs. S11, S12). The XRD spectra of TDA/SA, 4-OAN/SA and 4-OOAN/SA organogels exhibit sharp and periodic peaks with d spacings almost in the ratio of 1: 2: 3 corresponding to (100), (200) and (300) planes, demonstrating lamellar organisation and is consistent with the molecular packing as shown in Scheme 1(a). The XRD spectra of 4-MAN/SA, 4-MOAN/SA, 4-OAN/SA, and 4-OOAN/SA xerogels exhibit a peak at 2θ value between 24.25° and 26.22° corresponding to *d* spacing ca. 3.6 Å, which is closely equal to the typical π-π stacking distance of 3.5 Å between the aromatic rings [62,63]. This is consistent with the distance between phenyl rings (3.6 Å) in the crystal phase of 4-MOAN the XRD pattern (Fig. S11) of which also exhibits a peak at 2θ = 24.22°. It is interesting to note that, the characteristic peak is absent in the XRD spectrum of TDA/SA xerogel as well as of TDA crystal (Fig. S12). However, the XRD pattern of TDA/SA xerogel shows sharp reflections with *d* spacing ratio of 1: 2: 3, suggesting lamellar packing. The large interlayer *d* spacing in the cases of TDA/SA (19.3 Å), 4-OAN/SA (16.7 Å), and 4-OOAN/SA (18.8 Å) is less than twice the molecular length of TDA (17.7 Å), 4-OAN (16.2 Å) and 4-OOAN (18.8 Å), respectively. This suggests a large degree of interdigitation of the hydrocarbon chains in the bilayer. Such interdigitated arrangement of molecules, however, is not observed in the 4-MAN/SA and 4-MOAN/SA organogels because of the very short hydrocarbon chain. However, the diffraction pattern of 4-MOAN/SA xerogel exhibits reflections with *d* spacings which are in the ratio of 1: $\sqrt{3}$: 2: $\sqrt{7}$, indicating a hexagonal column packing in the gel state as shown in Scheme 1(b). A similar hexagonal column packing of molecules is observed with 4-MAN/SA organogel. It can be generalised from the packing modes that molecules consisting of long alkyl chain have a tendency to self-assemble in lamellar fashion due to interdigitation of the alkyl chains forming the bilayer. But lack of alkyl chains in the cases of 4-MOAN and 4-MAN forces the molecules to self-assemble to a columnar hexagonal close packing structure, where the benzene rings are oriented toward interior of the column so that efficient π-π stacking interaction can occur.

3.6. Rheology

Although visual observation confirmed the formation of organogels, the rheological experiments with the gels were carried out in order to determine the true gel behaviour and to determine the mechanical strength of the gel network. The rheological measurements were done for all the two-component gels of *o*-Ph(Me)$_2$ solvent, and the results are presented in Fig. 4(a–j). The frequency-independent behaviour of the storage moduli (G′) and loss moduli (G″) is consistent with a true gel. All the gels were prepared and stored under the same condition to measure the yield stress (σ_y) value at a constant frequency, f = 1 Hz. For all the organogels, the amplitude sweep measurements provide us information that the G′ value is greater than the corresponding G″, confirming their behaviour as an elastic material and above a critical stress (σ_y) value the gel starts to flow which means breaking of the gel structure. The frequency sweep measurements in some cases display a significant dependency of G′ on frequency. This might be due to the relaxation and lifetime of the bonds during network formation between the gelator molecules actually determines the dependency of dynamic moduli with the frequency. When these bonds have permanent character, either a very small dependency of G′ value on frequency or a frequency independent behaviour is observed. On the other hand, if the newly formed bonds possess a temporary character, a striking frequency dependency of G′ is observed [64]. From the results of rheology measurements it can be concluded that the two-component gels formed by AN possesses higher mechanical strength than that of aliphatic amines (e.g., DDA) at 1:1 mol ratio. This result is consistent with the difference between their gelation abilities as discussed above and confirms the presence of π-π stacking interaction.

We also investigated what effect a substitution in the aromatic ring can have on the self-association process. Surprisingly, it was found that gels formed by 4-OAN/SA have very low σ_y value (~3 Pa) in comparison to DDA/SA organogel. This difference in the mechanical properties can be attributed to the efficient packing of the long alkyl chains (C_{12}) in the molecular level. However, the weakening of the organogels caused by the incorporation of C_{14} alkyl chain is a result of the less tight packing of the hydrocarbon chains due to bent structure of TDA. The same study was also carried out with the gels 4-OOAN/SA system. These organogels also appeared weak with a very low σ_y value (~5 Pa) because of weak π–π stacking interaction due to more free rotation of the alkoxy chain as discussed above. In support of our conclusion that weakening of the gel strength is caused by the long chains, the σ_y values were measured for the gels formed by 4-MOAN/SA system where the long chain has been replaced by the —OMe group. As expected, this gel displayed greater strength as indicated by the

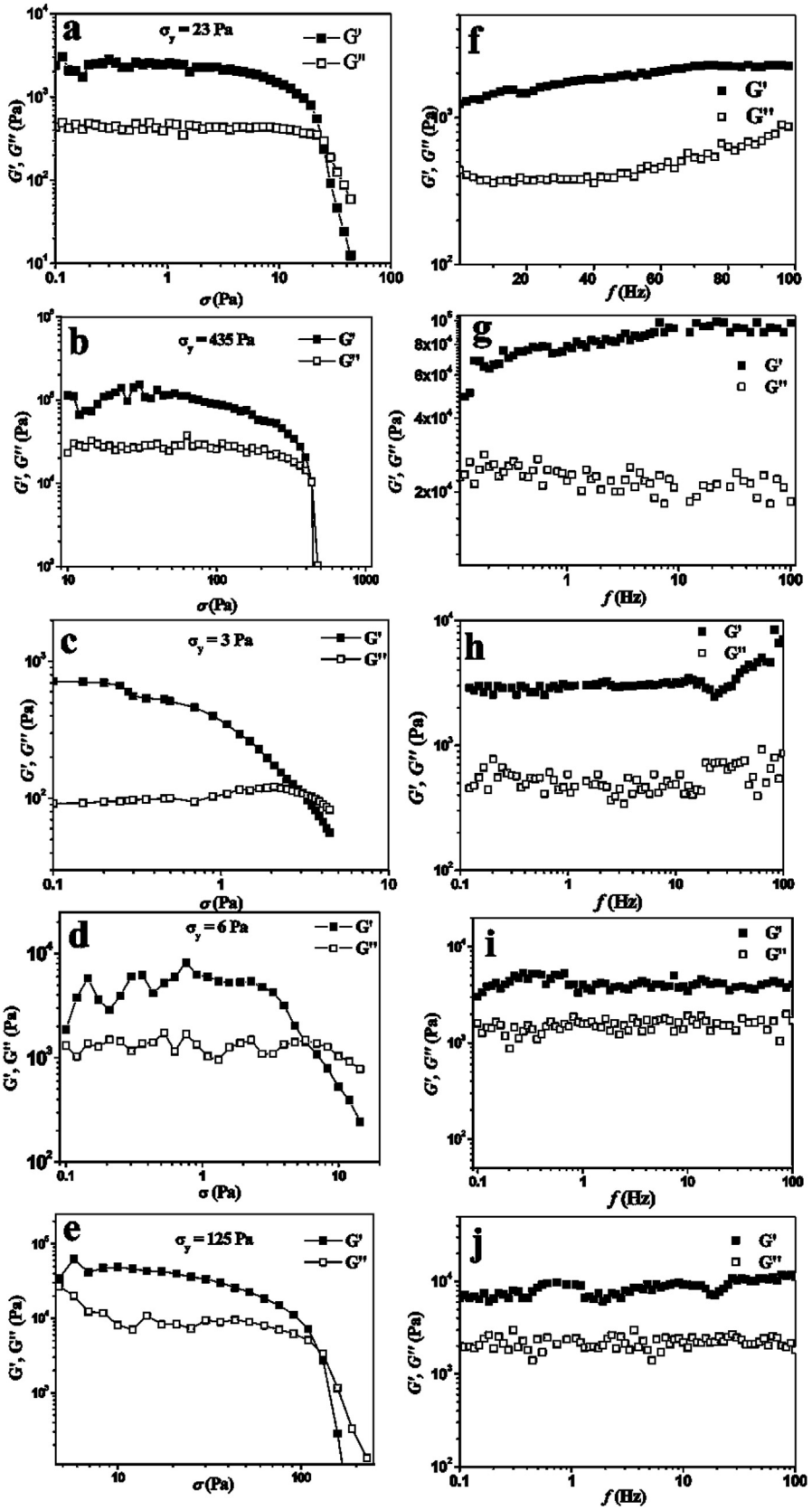


Fig. 4. Variation of G′ and G″ with shear stress (σ) for the organogels in *o*-Ph(Me)$_2$ solvent formed by the two-component systems (1:1) at CGC: (a) DDA/SA, (b) AN/SA, (c) 4-OAN/SA, (d) 4-OOAN/SA, and (e) 4-MOAN/SA; Variation of G′ and G″ with frequency (f) for the organogels: (f) DDA/SA, (g) AN/SA, (h) 4-OAN/SA, (i) 4-OOAN/SA, and (j) 4-MOAN/SA.

higher σ_y value (123 Pa). Indeed when the storage moduli (G′) of different organogels at a given frequency (e.g. 10 Hz) are compared (see Fig. S13 of Electronic Supplementary data) it is observed that the viscoelasticity of the two-component organogels decreases in the order AN/SA > 4-MOAN/SA > DDA/SA > 4-OOAN/SA > 4-OAN/SA. This agrees very well with the measured σ_y values of different organogels. All these observations undoubtedly suggest that the organogel formation by mixing amines with anhydrides demands not only a subtle balance of solvophobicity, but also requires π–π stacking interaction. These results are consistent with the thermal stability of the organogels.

4. Conclusions

In this paper, we present the gelation properties of mixtures of succinic anhydride and both aliphatic and aromatic amines in various organic solvents at different mole ratios. These gels are produced in the gelation medium instantaneously at room temperature through H-bond formation between simple, non-gelating building blocks. For all mixtures, the gelation ability was observed to be highest at 1:1 mol ratio. We have demonstrated that by varying the chemical structure of the individually non-gelating starting components the gelation behaviour of the resulting H-bonded complex can be controlled. For example, we have shown how substituents at different positions in the phenyl ring of AN can alter the gelation ability. Although the pK_a value of these aromatic amines decreases in the order *p*-PDA (6.08) > 4-HAN(5.50) > 4-MOAN (5.29) > 4-MAN (5.08) > 4-OAN (5.02) >3-MAN (4.67) > AN (4.63) > *o*-PDA (4.47) > 4-ABA (2.32) > 4-NAN (0.98), [63] the gelation efficiency in a given solvent for example, benzene increases in the order AN = 4-MOAN > 4-OAN > 4-MAN. This means that there is no correlation between acidity of the $-NH_2$ and gelation efficiency of the two-component system. Indeed, 4-NAN having lowest pK_a (0.98) [65] value failed to gelate any solvent in the presence of SA. In other words, gelation efficiency solely depends on the molecular structure of the amines as well as of the anhydride. Thus introduction of H-bonding functional group (e.g., −OH, COOH, $-NO_2$, etc.) in the *o*-, *p*-, or *m*-position of the phenyl ring of aniline destroys the gelation ability of the mixture. In the case of aliphatic amines with similar pK_a values, the gelation ability of the mixture increased with the increase of hydrocarbon chain length due to the increase of van der Waals interactions. Introduction of long hydrocarbon chain at the *p*-position of AN also increased its gelation ability. We have shown that the aromatic amines are efficient gelators in the presence of anhydride due to π-π stacking interaction, which also made the organogels thermally and mechanically more stable than those of aliphatic amines. Thus, we have developed a series of new two-component gelling systems comprising of simple amine and anhydride. The organogels in non-hydrogen bonding solvents were found to be stable for a few months when preserved under the same condition. The novelty of the supramolecular gels is that they are formed spontaneously and instantly on mixing without the requirement of any external stimulus, such as heat, sonication, etc. Moreover, the modular nature of the gel formation and easy availability of the various building blocks make this a straight forward method to construct complex materials, eliminating the need for long and difficult synthetic procedures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfb.2016.08.026.

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