Electronic Supplementary Material (ESI) for Soft Matter
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Supplementary information

Metastability in a bicomponent hydrogel of thymine and 6-methyl-1,3,5-triazine-2,4-diamine : Ultrasound induced Vs. Thermo gelation

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Experimental

Gel preparation

6-methyl-1,3,5-triazine-2,4-diamine (**M**) and Thymine (**T**) were purchased from Aldrich, USA and were used as received. The hydrogels were prepared in freshly double distilled water. The gels were prepared by (i) **Heating-Cooling method**: The M and T mixture (1:1 mol ratio) was taken in a 5 ml (dia. = 1cm) glass vial with required amount of water and was sealed with teflon cap. They were heated to make homogeneous clear solution (80^0 C) and cooled at room temperature (30 ^{0}C) to form the gel (ii) **Sonication method**: The bicomponent mixture (1:1 mol ratio) and required amount of water were taken as before and sonicated in a digital ultrasonometre (Takashi Electronic Co., Model: UD80SH-1.3L) at room temperature (30 ^{0}C) for 5-6 minutes to make the hydrogel.

Microscopy

The morphology of the gel was observed through an optical microscope (Leitz, Biomed) under perfectly crossed polarizer and taking the picture through a digital camera (Leica D-LUX 3). The gel samples were taken in a clear glass slide and photographs were taken under perfectly crossed polarizer. The temperature dependent optical micrographs of thermo gel is made at 0.5 %(*w/v*) concentration of the 1:1 M and T mixture, the samples were taken in a 1 mm caped UV cell. To understand the network morphology of the gel more clearly, the hydrogels, produced at 30 ^{0}C, were freeze dried. Then they were observed through an FESEM instrument (JEOL, JSM 6700F) operating at 5 kV after platinum coating.

Rheology

Rheological experiments were performed with an AR 2000 advanced rheometer (TA Instruments) using cone plate geometry in a Peltier plate. The plate diameter was 40 mm, and cone angle of 4 degree. The frequency sweep experiments were made at 25 ^{0}C under controlled stress of 0.05 Pa.

Spectroscopy

The FTIR spectra of pure M, T and the xerogels were recorded using the KBr pellets of the samples in an FTIR-8400S instrument (Shimadzu). The UV-vis spectra of the samples (0.01 %, *w/v*) were recorded on a Hewlett-Packard UV-vis spectrophotometer (model 8453) using a cuvette of 1 mm path length. In fluorescence studies of the hydrogel samples, prepared in a sealed cuvette are carried out in a Horiba Jobin Yvon Fluoromax 3 instrument. Each gel sample in a quartz cell of 1 cm path length was excited at 260 nm wavelength using a slit width of 2 nm for excitation and 5 nm for emission with a 1 nm wavelength increment having an integration time of 0.5 s.

Diffraction Study

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The WAXS experiments of all the samples were performed using a Bruker AXS diffractomer (model D8 Advance) using a Lynx Eye detector. The instrument was operated at a 40 KV voltage and at a 40 mA current. Samples were scanned in the range of $2\theta = 5–40^0$ at the scan rate of 0.5 sec/step with a step width of 0.02^0.

Thermal Study

Differential Scanning Calorimetry (DSC) of the sonicated hydrogel samples in large volume capsule (LVC) pans were performed using a Perkin Elmer Diamond DSC. The instrument was calibrated with Indium before each experiment. The scan rate for the heating processes was 10^0/min. and for cooling, it was 5^0/min. The concentration for the thermal study of the sample was 1 %(*w/v*) and it was made gel by sonication method outside. This gel is then transferred to the LVC capsules. The weights of the samples were checked before and after each run to check any loss of solvent.

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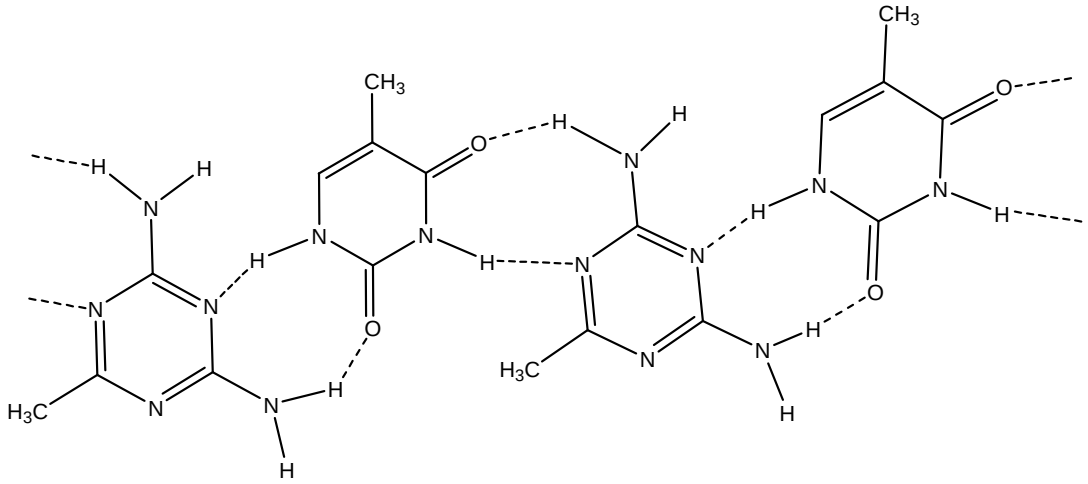

SI Scheme 1: Schematic representation of the H-bonding in MT complex.

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SI **Table 1:** Summary of gelation behaviors in different organic and mixture of organic aqueous solvents (In mixed solvents solvent and water is mixed with 5:1 ratio (*v/v*) :

(A, assembly (i.e. fibres suspended in solution state); VA, viscous assembly (i.e. pre-gel state); P, precipitate; TG, temperature induced gelation; SG, sonication induced gelation)

Solvents	Heat	Sonication	remark	Stability
Dioxane	**A**	P		
Dioxane + water	P	P		
n-decane	P	P		
Acetonitrile	**TG**	P	rapid gelation	Stable
Acetonitrile + water	**TG**	**SG**		Breaks down after few minutes
THF	P	**SG**	Gelation takes some time keeping it undisturbed after sonication	Breaks down after few minutes
THF + water	P	**A**		
DMF	P	P		
DMF + water	P	P		
DMSO	P	P		
DMSO + water	P	P		
Cyclohexane	P	**VA**	Gel is formed after sonicate the hot solution	Breaks down after 10 minutes
Isobutanol	**VA**	**SG**	Gelation takes some time keeping it undisturbed after sonication	Stable for 1-2 hours
Isobutanol + water	P	**SG**	Gelation takes some time keeping it undisturbed after sonication	Stable for 1-2 hours
Benzene	P	P		
o-xylene	P	P		

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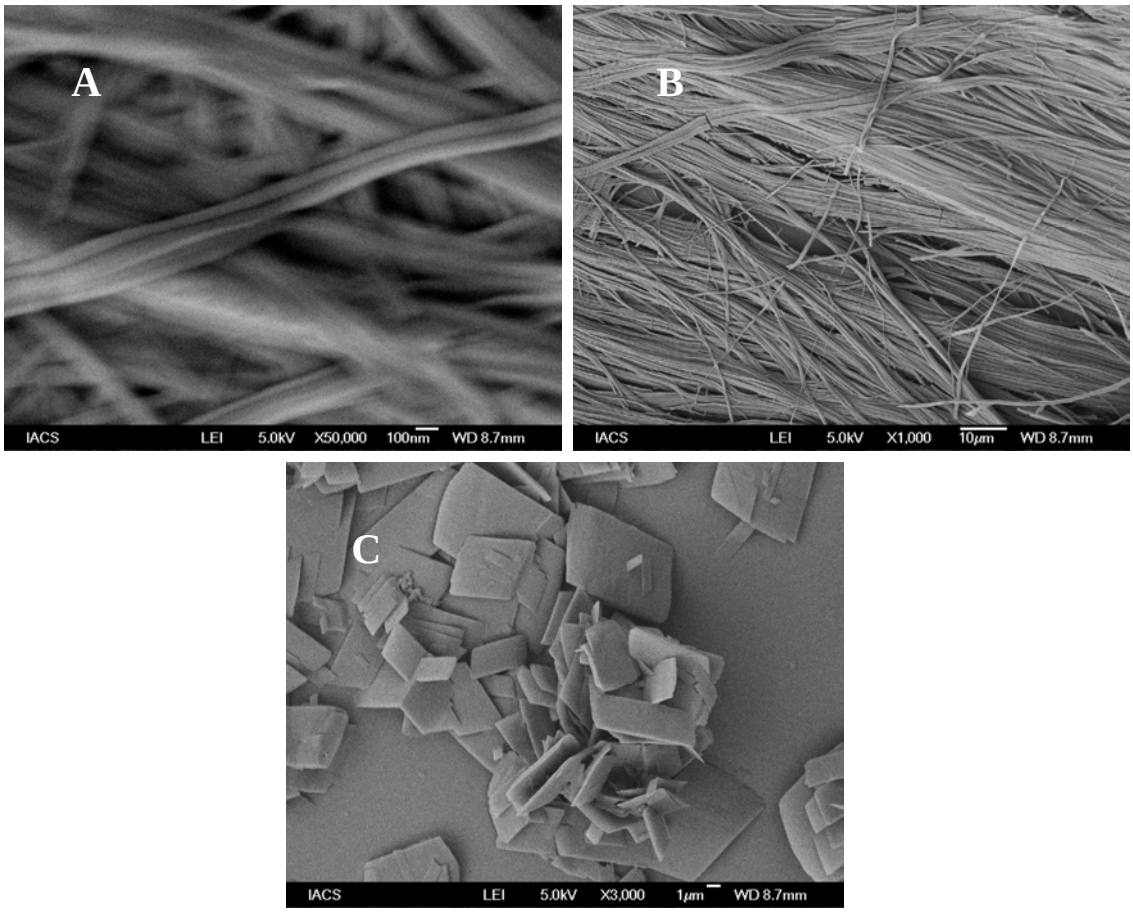

SI Fig. 1: FESEM images of the freeze dried samples (a) S-gel (b) T-gel and(c) the dried crystalline precipitates.

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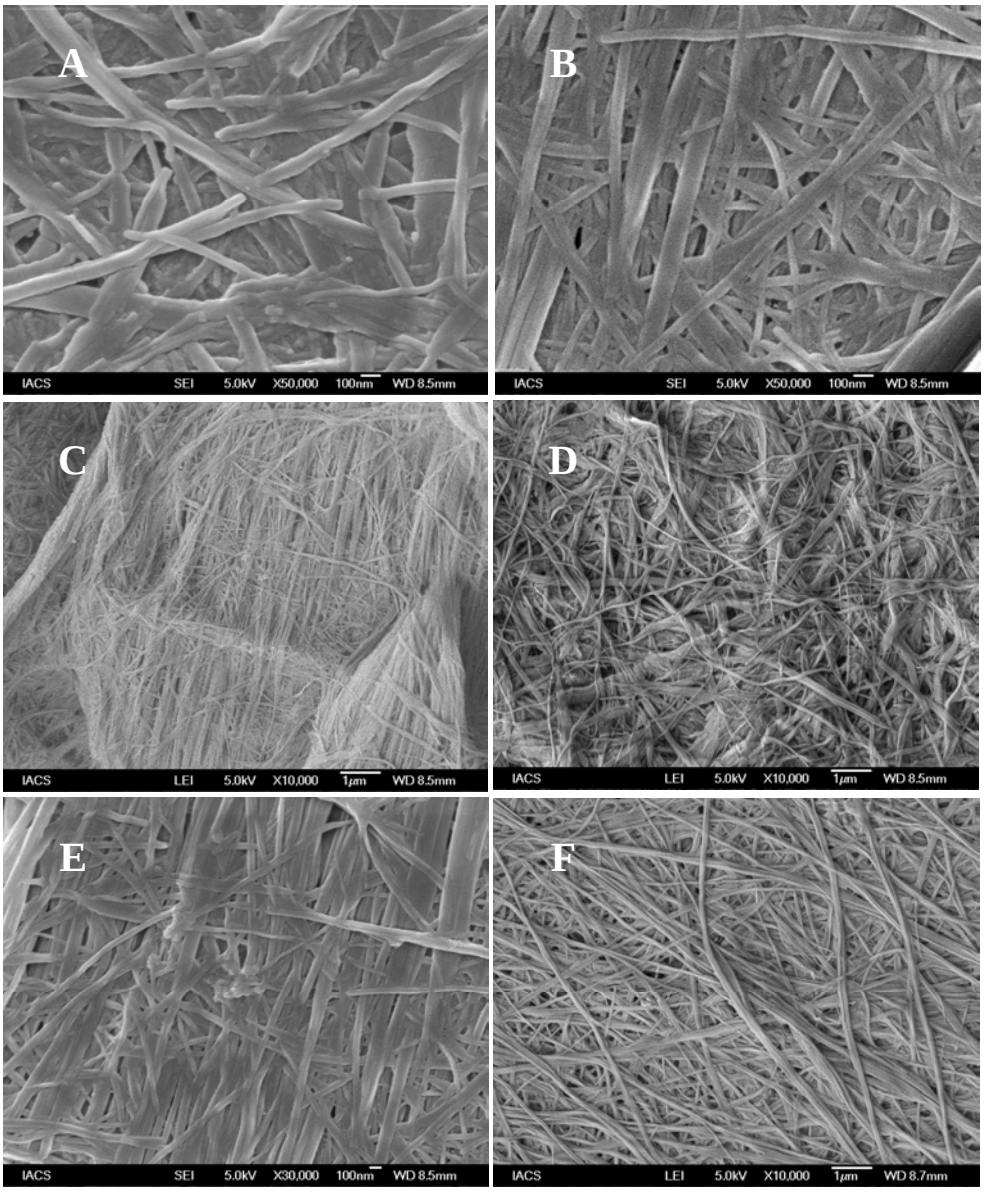

SI Fig. 2: FESEM images of the organogel synthesized with (A) Acetonitrile (b) Acetonitrile & water (c) cyclohexane (d) THF (E) Isobutanol and (F) isobutanol & water. (All the micrographs show fibrillar network morphology characterizing them as gels)

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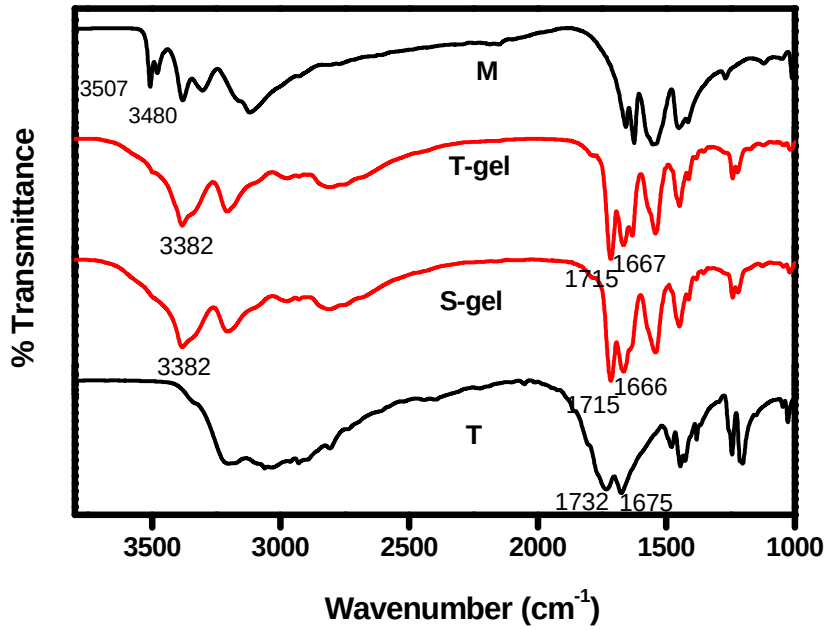
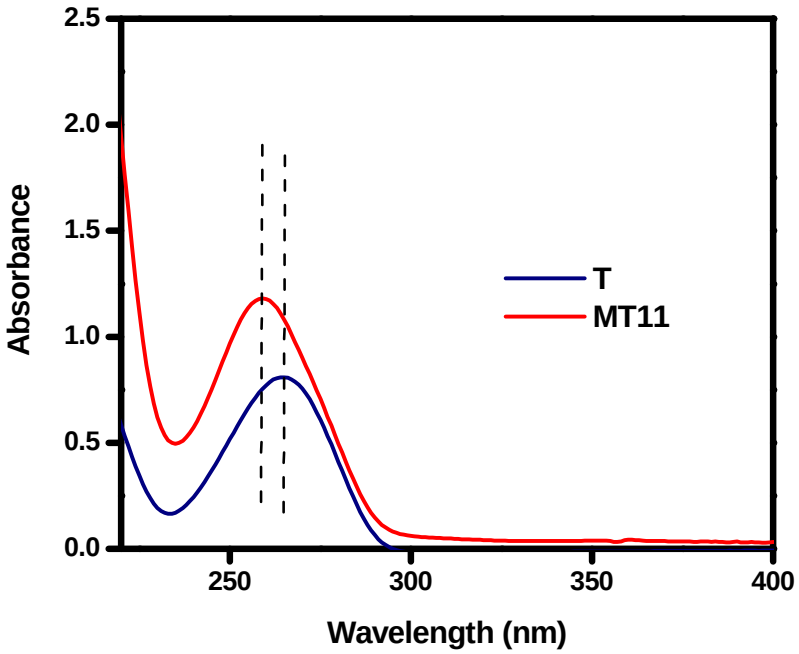


SI Fig. 3: FTIR spectra of the pure components and the dried hydrogels obtained from heating-cooling and sonication method.



SI fig. 4: Normalized UV-vis spectra of the pure M and the MT11 complex at 0.1 %(w/v) in aqueous medium.

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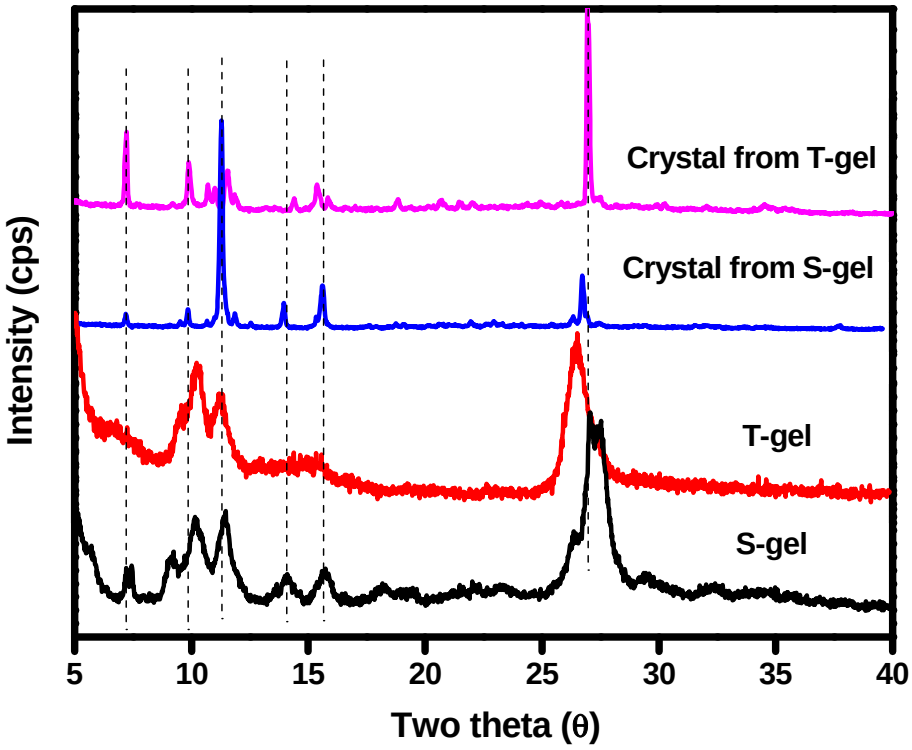

SI Fig. 5: WAXS patterns of the freeze dried hydrogels and the crystalline precipitates.

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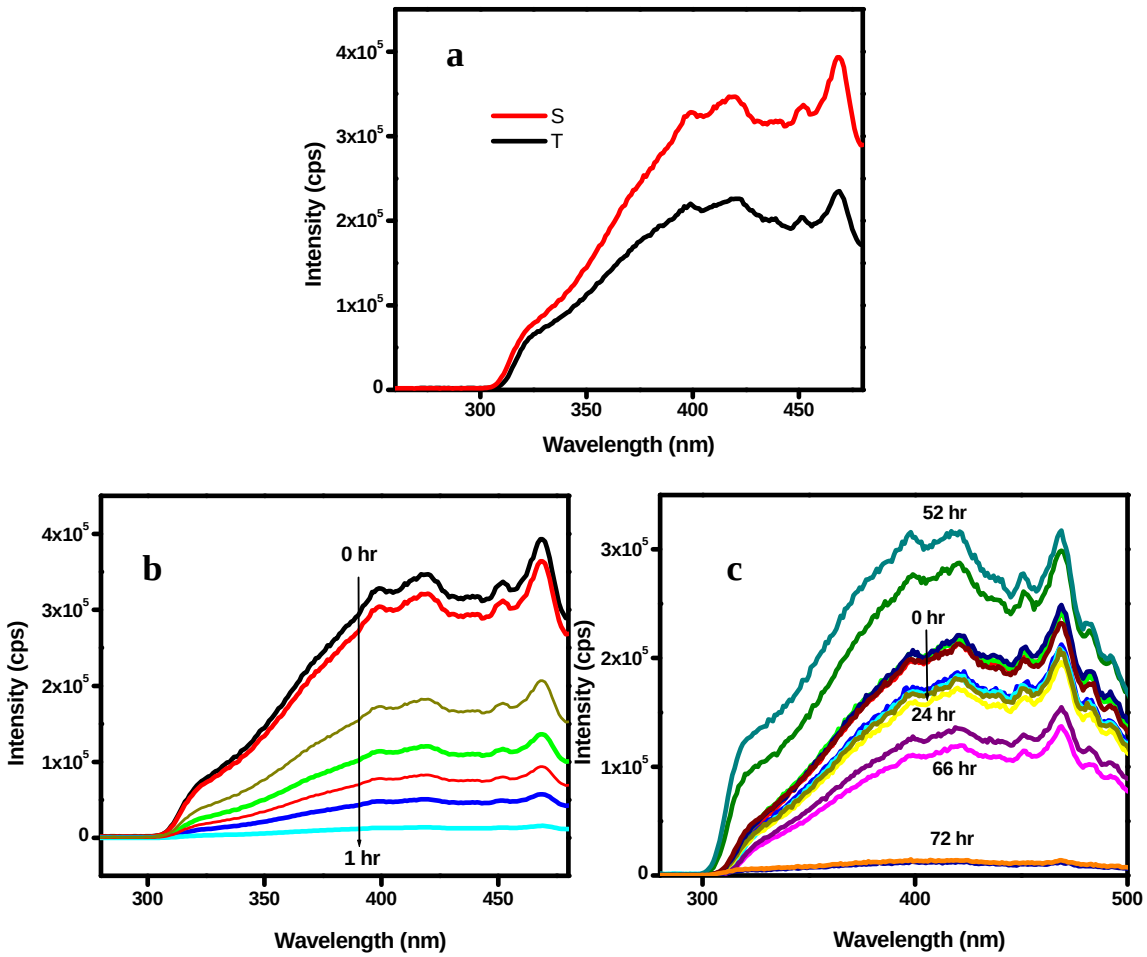

SI Fig. 6: (a) Photoluminescence spectrum of S-gel and T-gel and kinetic study of the transformation of the (b) S-gel and (c)T-gel .

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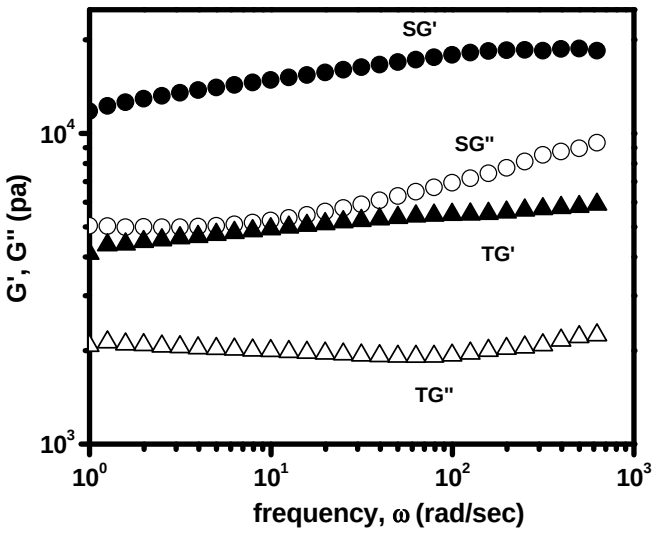
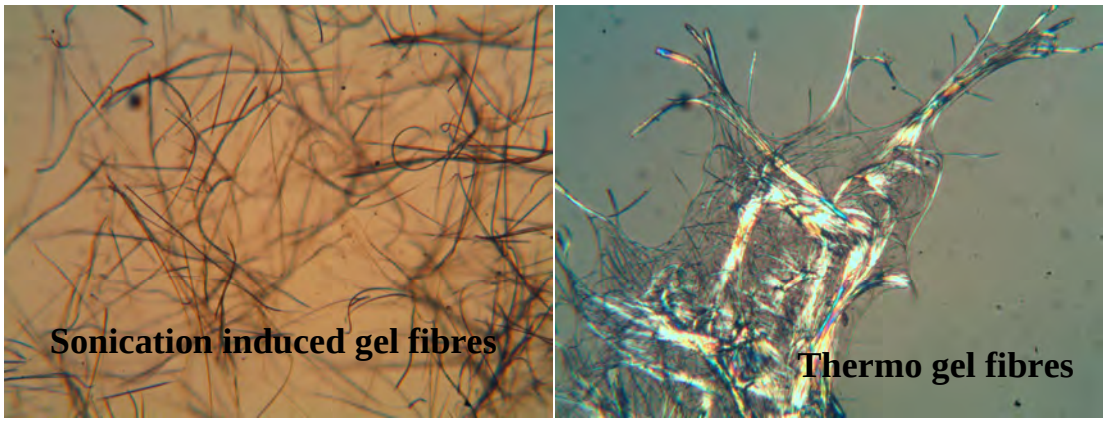


SI Fig. 7: Frequency dependent rheological experiment of the hydrogels at 2 %(*w/v*) at a constant stress of 0.05 Pa.



SI Fig. 8: Polarized optical micrographs of the MT hydrogel fibers made in glass slide.

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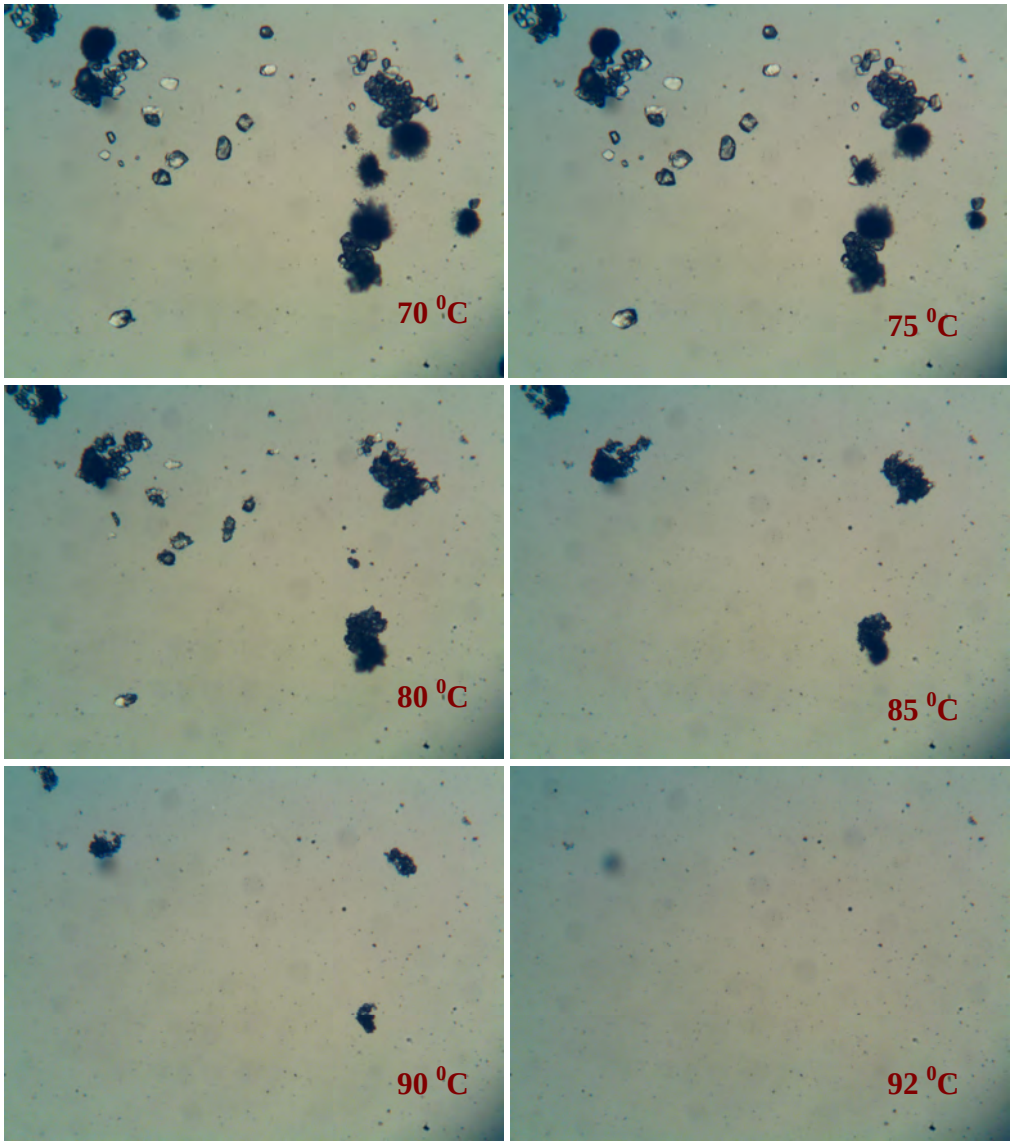

SI fig. 9: Microscopic images of the T-gel at different temperature (70-92 ^{0}C) for 10 mins.