Supporting Information For

Investigation of the Relationships Between The Thermodynamic Phase Behavior and Gelation Behavior of a Series of Trisamide Low Molecular-Mass Organic Gelators

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Experimental Methods

<u>Organogelator Synthesis:</u> The synthesis of TREN-EB was as follows: 1 mL (6.68mmol) tris(2-aminoethyl)amine (TREN) 3 mL (21.5mmol) triethylamine, and 40 mL anhydrous dimethylformamide (DMF) were mixed in a 250 mL 3-neck round bottomed flask under nitrogen and placed in an ice bath. 3.2 mL (23.38mmol) 2-ethyl butyryl chloride was added drop-wise with constant stirring. The resulting solution was stirred for 15 min in the ice bath and 2 hours at room temperature. The mixture was poured into 400 mL saturated aqueous sodium bicarbonate solution. The white precipitate that formed was filtered and washed twice with deionized water. The collected product was dried under vacuum at 60°C for 12 hours. For TREN-C5 (valeryl chloride), TREN-C6 (hexanoyl chloride), TREN-C7 (heptanoyl chloride), TREN-C8 (octanoyl chloride), TREN-C9 (nonanoyl chloride) TREN-C10 (decanoyl chloride), and TREN-CH (cyclohexanecarbonyl chloride) 20 mL of ethanol was used in place of the DMF. For each reaction 1 mL of TREN and a molar ratio of acid chloride to TREN of 3.5: 1 was used. The TREN-C5 did not immediately precipitate in water, but was recrystallized at 4 ˚C.

TREN-EB: Yield 38%. ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.88 (t, 6H), 1.5 (m, 4H), 1.96 (m, 1H), 2.58 (t, 2H), 3.3 (q, 2H), 6.43 (t, 1H). ^{13}C-NMR(CDCl$_3$, 300 MHz) δ (ppm) 12.08(-CH$_3$), 25.57(CH$_2$),37.54(NCH$_2$CH$_2$N),50.82(NCH$_2$CH$_2$NC=O),54.72(CH),176.44(C=O). ESI-MS: m/z 441.4 ([M+H]$^+$).

TREN-C5: Yield 15% ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.92 (t, 3H), 1.36 (m, 2H), 1.62 (m, 2H), 2.22 (t, 2H), 2.56 (t, 2H), 3.29 (q, 2H), 6.62 (t, 1H). ^{13}C-NMR (CDCl$_3$, 300 MHz) δ (ppm) 13.77(-CH$_3$), 22.48(CH$_2$CH$_2$CH$_2$CH$_3$), 27.89(CH$_2$CH$_2$CH$_2$CH$_3$), 37.61(CH$_2$CH$_2$CH$_2$CH$_3$), 36.25(NCH$_2$CH$_2$NC=O), 54.51(NCH$_2$CH$_2$NC=O), 173.96(C=O). ESI-MS: m/z 421.3 ([M+Na]$^+$).

TREN-C6: Yield 49.8% ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.89 (t, 3H), 1.30 (m, 4H), 1.62 (m, 2H), 2.19 (t, 2H), 2.53 (t, 2H), 3.26 (q, 2H), 6.53 (t, 1H). ^{13}C-NMR (CDCl$_3$, 300 MHz) δ (ppm) 13.90(-CH$_3$), 22.40(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 25.48(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 31.56(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 36.51(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 37.59(NCH$_2$CH$_2$NC=O), 54.51(NCH$_2$CH$_2$NC=O), 173.92(C=O). ESI-MS: m/z 441.4 ([M+H]$^+$), m/z 463.4 ([M+Na]$^+$).

TREN-C7: Yield 37.5%. ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.88 (t, 3H), 1.30 (m, 6H), 1.63 (m, 2H), 2.21 (t, 2H), 2.53 (t, 2H), 3.29 (q, 2H), 6.55(t, 1H). ^{13}C-NMR(CDCl$_3$, 300 MHz) δ (ppm) 14(-CH$_3$), 22.53(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 25.81(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.13(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 31.60(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 36.59(NCH$_2$CH$_2$NC=O), 37.59(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 54.47(NCH$_2$CH$_2$NC=O), 173.97(C=O). ESI-MS: m/z 483.5 ([M+H]$^+$), 505.5 ([M+Na]$^+$).

TREN-C8: Yield 56%. ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.87 (t, 3H), 1.28 (m, 8H), 1.62 (m, 2H), 2.19 (t, 2H), 2.53 (t, 2H), 3.28 (q, 2H), 6.49(t, 1H). ^{13}C-NMR(CDCl$_3$, 300 MHz) δ (ppm) 14.02(-CH$_3$), 22.59(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.07(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.42(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 31.73(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 36.58(NCH$_2$CH$_2$NC=O), 25.01(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 36.58(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 54.84(NCH$_2$CH$_2$NC=O), 173.92(C=O). ESI-MS: m/z 525.6 ([M+H]$^+$), 547.6([M+Na]$^+$).

TREN-C9: Yield 10%. ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.88 (t, 3H), 1.27 (m, 10H), 1.6 (m, 2H), 2.21 (t, 2H), 2.54 (t, 2H), 3.27 (q, 2H), 6.56(t, 1H). ^{13}C-NMR (CDCl$_3$, 300 MHz) δ (ppm) 14.07(-CH$_3$), 22.65(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 25.87(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.42(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 31.84(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 36.55(NCH$_2$CH$_2$NC=O), 37.53(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 54.35(NCH$_2$CH$_2$NC=O), 174.02(C=O). ESI-MS: m/z 567.6 ([M+H]$^+$), 589.6 ([M+Na]$^+$).

TREN-C10: Yield 10%. ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.87 (t, 3H), 1.25 (m, 12H), 1.61 (m, 2H), 2.16 (t, 2H), 2.53 (t, 2H), 3.26 (q, 2H), 6.49(t, 1H). ^{13}C-NMR (CDCl$_3$, 300 MHz) δ (ppm) 14.02(-CH$_3$), 22.59(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 25.87(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.07(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.42(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 31.73(-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 36.58(NCH$_2$CH$_2$NC=O), 36.58(-CH2CH2CH2CH2CH2CH2CH2CH2CH3), 54.48(NCH$_2$CH$_2$NC=O), 173.92(C=O). ESI-MS: m/z 609.8 ([M+H]$^+$), 631.8 ([M+Na]$^+$).

TREN-CH: Yield 48%. ^{1}H -NMR (CDCl$_3$, 300 MHz) δ (ppm) 0.88 (t, 6H), 1.5 (m, 4H), 1.96 (m, 1H), 2.58 (t, 2H), 3.3 (q, 2H), 6.43 (t, 1H). ^{13}C-NMR(CDCl$_3$, 300 MHz) δ (ppm) 25.76(-CH$_2$-), 29.74(-CH$_2$-), 37.54(NCH$_2$CH$_2$N), 63.88(NCH$_2$CH$_2$NC=O), 45.23(-CH-),176.81(C=O). ESI-MS: m/z 477.3 ([M+H]$^+$), 499.3([M+Na]$^+$).

<u>Differential Scanning Calorimetry (DSC):</u> Measurements were done using a Q200 differential scanning calorimeter (TA Instruments) under nitrogen atmosphere. Melting points were assigned to the peak of the melting transition. The enthalpy of fusion was determined from the area under the melting peak. Two heating/cooling cycles were carried out for each neat trisamide compound

under the following protocol: samples were heated from room temperature to 250°C at a rate of 10°C/min, held at 250°C for 5 minutes, cooled to 20°C at a rate of 10°C/min, held at 20°C for a 5 minute period, heated to 250°C again at a rate of 10°C/min, held for 5 minutes at 250°C, then cooled to 20°C at a rate of 10°C/min. For the measurements of the melting points of gels, a preformed gel was sealed in a DSC pan. The samples were heated from room temperature at a rate of 5°C/min.

Minimum Gelation Concentration: Gelation of organic solvents by the trisamide compounds was tested by dissolving 20 mg of the compound in 1 mL of solvent in a 20 mL scintillation vial at elevated temperature to form a homogeneous, clear solution followed by quenching the solution to room temperature for five minutes using a 25°C water bath. Gels were identified as solutions that exhibited no flow when inverted. If a gel was formed the minimum gelation concentration for a particular trisamide/solvent pair was determined by adding solvent in 0.5 mL increments and repeating the heating-quenching experiment until a portion of the solution flowed upon inversion of the cooled sample.

Calibration of Heating Block: Thermal measurements of trisamide solutions were conducted using a 48 well, anodized aluminum thermostated heating block (Chemglass) regulated with a magnetic stir plate with a temperature probe (IKA RCT basic). The temperature controller was calibrated by measuring the temperature of a stirred solution of *n*-dioctylphthalate from 25 to 200 °C with a digital thermometer. This thermometer was independently verified by simultaneously measuring the temperature of a heated oil bath using an immersion thermometer and the digital thermometer and controlling the temperature with the stir plate temperature probe. These two thermometers were within ± 1°C of the setpoint of the stir plate from 25 to 140 °C. Using the aluminum heating block the solution temperature was found to systematically lower than the set-point temperature especially at higher temperature. A calibration curve was constructed by fitting a third order polynomial to a plot of the measured solution temperature ($T_{measure}$) vs. the set point temperature of the stir plate (T_{set}),

$$T_{measure} = -103.4 + 1.914T_{set} - 0.0026T_{set}^2 + 2.33\text{x}10^{-6}T_{set}^3$$
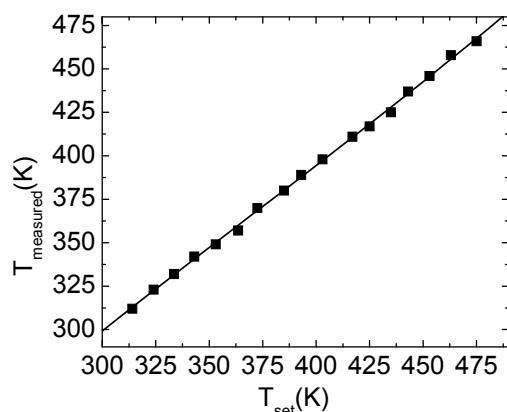
Figure S1. Calibration curve of the aluminum heating block.

Gel Transition Temperature: A known amount of TREN-EB was mixed with 1 mL of organic solvent in a 4 mL vial and heated to completely dissolve the gelator, then cooled to in a water bath to form gels. Then the vial was annealed in a thermostated heating block. Starting at 30°C the temperature was increased in increments of 2°C and left to equilibrate for 15 minutes at each new setting. The gel transition temperature was defined as the temperature at which a gel visibly flowed upon tilting the sample 90°.

Solubility Measurements: The melting temperature (T_m) of TREN-EB as a function of composition in aromatic solvents was determined as follows. A known amount of TREN-EB was mixed with 1 mL of organic solvent in a 4 mL vial with a stir-bar. The solution was annealed in a thermostated heating block. Starting at 30°C the temperature was increased in increments of 2°C and left to equilibrate for 10 minutes at each new setting. T_m was defined as the temperature at which the mixture formed a clear homogeneous solution. This could be determined visually as insoluble TREN-EB caused a noticeable clouding of the solution.

Freeze Drying of Gels: Gels of TREN-EB and solvent were formed by mixing a known amount of TREN-EB and 1 mL of solvent in a 4 mL vial, heating the solution at elevated temperature and then quenching the vials in a water bath. These gels were freeze-dried to obtain xerogels by attaching the vial to a Schlenk line, freezing the gel in a liquid nitrogen bath, and then pulling vacuum on the vial for 2 hours.

Scanning Electron Microscopy: The morphologies of the xerogels were examined by scanning electron microscopy. Carbon double-sided tape was used as a conductive mounting adhesive. Sample pieces were mounted onto aluminum SEM stubs (diameter 12 mm). The samples were

coated with silver with a thickness of ca. 10nm using EMITECH K575X Turbo Sputter Coater. Samples were then examined in a JEOL JSM5310 scanning electron microscope.

Wide Angle X-ray Scattering: Samples were analyzed by wide-angle X-ray diffraction scanning (WXDS) using a 40 mA–40 kW Bruker AX8 diffractometer with Cu K-alpha radiation. The scan speed was 1°/min and scan time was 10 minutes.
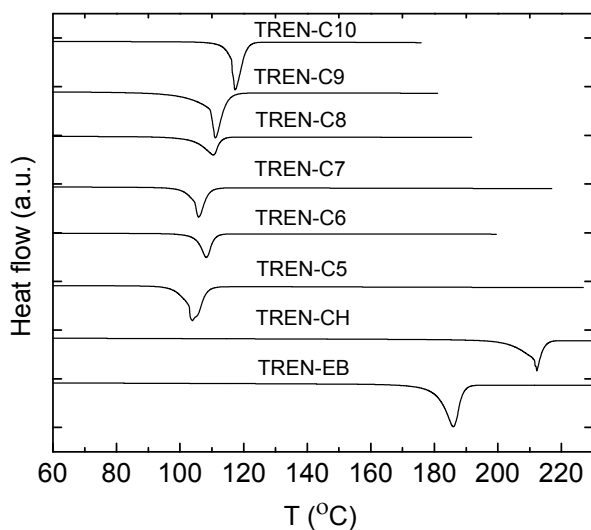
Additional Figures

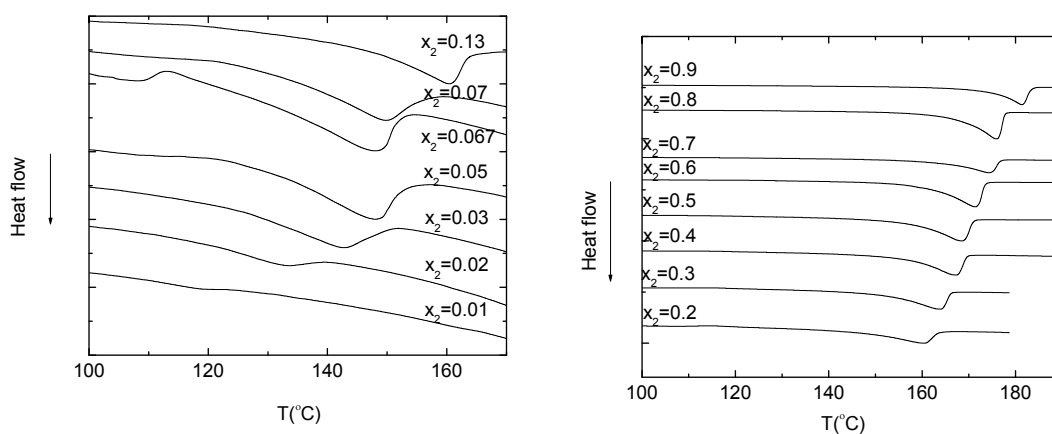**Figure S2.** DSC heating traces of TREN-CX compounds (10 °C/min heating rate).

Figure S3. DSC traces of TREN-EB/DOP organogels at (a) low concentration and (b) high concentration.
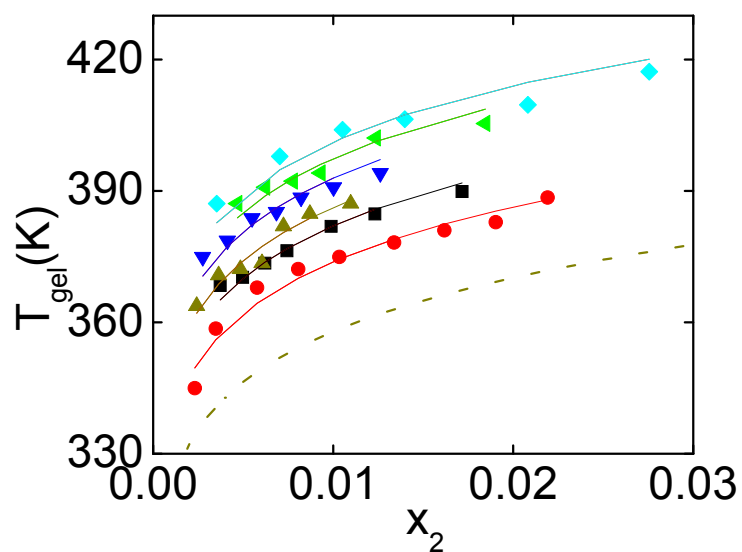
Figure S4. T_{gel} vs. x_2 for TREN-EB in different aromatic solvents: chlorobenzene (red circles), chlorobenzene + *o*-xylene (black squares), toluene (olive upward triangles), *o*-xylene (blue downward triangles), *o*-xylene + *sec*-butyl benzene (green left triangles), *sec*-butyl benzene (light blue diamonds). The dotted line is the predicted line for an ideal solution ($\chi = 0$).
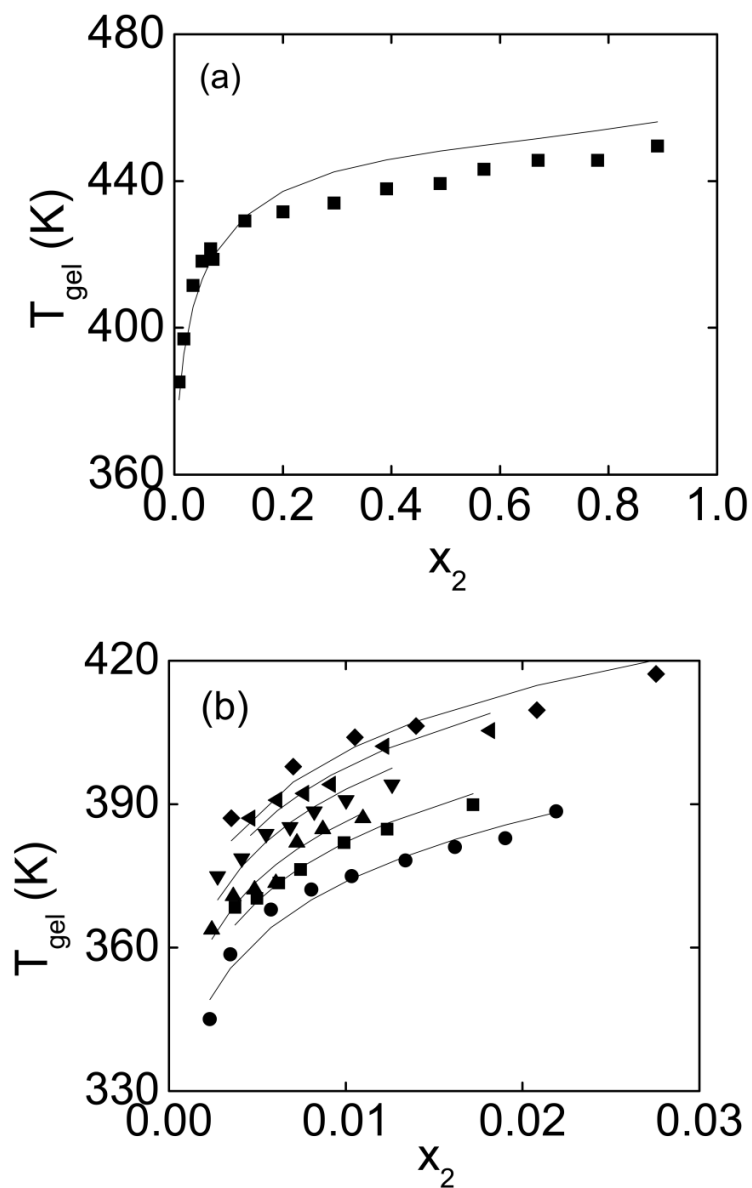
Figure S5. T_{gel} vs. x_2 fit with Equation 9 for (a) TREN-EB in DOP and (b) TREN-EB in different aromatic solvents: chlorobenzene (circles), chlorobenzene + *o*-xylene (squares), toluene (upward triangles), *o*-xylene (downward triangles), *o*-xylene + *sec*-butyl benzene (left triangles), *sec*-butyl benzene (diamonds).