Unique polymeric gel by thiol-alkyne click chemistry

Mutyala Naidu Ganivada, Pawan Kumar and Raja Shunmugam*

Polymer Research Centre, Department of Chemical Sciences,

Indian Institute of Science Education and Research Kolkata.

E-mail: sraja@iiserkol.ac.in

Supporting Information

Content **Page no**

Experimental Procedure

Characterization:

Nuclear Magnetic Resonance (NMR). The ^{1}H NMR and ^{13}C NMR spectroscopy were carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent. ^{1}H NMR and ^{13}C NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00).

Fourier Transform Infra Red (FT-IR). FT-IR spectra were obtained on FT-IR Perkin-Elmer spectrometer at a nominal resolution of 2 cm^{-1}.

Matrix- assisted laser desorption/ionisation (MALDI-TOF). Positive mode electrospray ionization mass spectrometry (ESI-MS) was carried out on a Q-Tof Micro YA263 high resolution (Waters Corporation) mass spectrometer.

Thermogravimetric Analysis (TGA). Thermal studies were carried out using a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min^{-1} with a sample weight of approximately 4−7 mg in nitrogen atmosphere.

FE-SEM Analysis: The interior morphology and porous structures of synthesized chemical gels were characterised by FE-SEM. A small piece of dried gel samples were immersed in DCM and DI-water for 1 hrs to reach its maximum swelling state. The swelled chemical gels were cross sectioned and placed on silicon wafer. These gels were frozen in liquid nitrogen and freeze dried using a lyophilizer (Orleon instrument) under high vacuum at −50 °C for 24 hrs. The dry gel samples were analysed using FE-SEM (Carl ZiessSupra SEM instrument).

Rheology Study: The rheological measurements were carried out on a TA-ARG2 rheometer using a steel parallel plate with 40 mm diameter at 25 °C with 1.0 mm Gap spacing for all gel samples. The dynamic shear moduli (G' and G'') were recorded in the linear viscoelastic regime at a strain of $\gamma = 0.5\%$ as a function of angular frequency (0.1−100 rad/s).

Materials:

Malonic ester was purchased from Alfa Aesar. Sodium hydride and pentaerythritol (3-mercaptopropionate) (PETM) and propargyl bromide were purchased from Sigma Aldrich. Potassium hydroxide (KOH), triethylamine (TEA), diethyl ether, sodium bicarbonate and sodium sulphate anhydrous were purchased from MERCK. Diisopropylazo dicarboxylate (DIAD) and triphenylphosphine (Ph_3P) were purchased from Spectrochem. Poly ethylene glycol (PEG) was purchased from Fisher scientific. Toluene, methanol, dimethyl formamide

(DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), ethyl acetate, hexane, chloroform ($CHCl_3$), acetone, hydrochloric acid (HCl), CDCl3, DMSO-d6, acetonitrile, dichloromethane (DCM), were purchased from Sigma-Aldrich and used as received with further purification over $CaCl_2$. All other solvents were of highest purity and purchased from Sigma-Aldrich.

Synthesis of compound DIACT[1]: Sodium hydride (6 gm, 250 mmol) was dissolved in 100 ml of dry THF at room temperature. Then malonic ester (10 gm, 62.5 mmol) was added drop-wise at 0 °C to the reaction flask. After 30 minutes, propargyl bromide (16.36 gm, 137.5 mmol) was added drop-wise to the reaction mixture. Then the reaction mixture was allowed to stir for 36 hours at room temperature. Finally the reaction mixture was washed with ethyl acetate and water. The organic layer was collected using a separating funnel. After the complete evaporation of the solvent, the compound was dried completely under the vacuum. This produced the final compound which was liquid in nature with yellow in colour. It was kept in freezer to solidify. The solid compound was then dissolved in hexane and the solution was kept in freezer again for the crystallization. The yellow colour was eventually removed by re-precipitation and column chromatography which produced white pure crystals with yield of 90%. ^{1}H - NMR spectroscopy data (δ ppm): 4.20 (q, J = 7.14, 7.14, 7.14 Hz, 4H), 2.96 (d, J = 2.65 Hz, 4H), 2.01 (t, J = 2.57, 2.57 Hz, 2H), 1.24 (t, J = 7.11, 7.11 Hz, 6H). ^{13}C - NMR spectroscopy data (δ ppm): 168, 78, 71, 61, 56, 22, 13. FT-IR: 3919, 3456, 3301, 3272, 2987, 2940, 2873, 2129, 1734, 1466, 1449, 1424, 1390, 1369, 1323, 1243, 1214, 1193, 1092, 1076, 1052, 1004, 956, 853, 835, 799, 760, 702, 674, 636, 540, 460.

Synthesis of compound DIACT-OH[1]: KOH (570 mg, 10.17 mmol) was dissolved in 15 ml of ethyl alcohol in an inert condition. Then compound **DIACT** was dissolved in the above reaction mixture and it was allowed to stir at room temperature for 18 hours. Then the reaction mixture was washed with ethyl acetate, water and saturated solution of sodium bicarbonate for 3 times. Then the aqueous layer was collected, followed by acidification of the solution to pH < 1. Finally, the solution was washed with ethyl acetate and water. The organic layer was collected in a beaker and the solvent was evaporated to get the final product. White pure crystals were formed with yield of 95%. ^{1}H - NMR spectroscopy data (δ ppm): 8.35 (s, 1H), 4.25 (q, J = 7.11, 7.11, 7.10 Hz, 2H), 3.00 (d, J = 2.02 Hz, 4H), 2.05 (t, J = -340, -340 Hz, 2H), 1.28 (t, J = 7.11, 7.11 Hz, 3H). ^{13}C - NMR spectroscopy data (δ ppm):

173, 168, 78, 76, 71, 56, 21, 13. FT-IR: 3933, 3286, 2925, 2854, 1753, 1720, 1433, 1393, 1318, 1294, 1252, 1220, 1194, 1096, 1075, 1055, 957, 910, 854, 812, 797, 752, 663, 618, 536, 477.

Synthesis of PTETACT: PEG (1.39 gm, 0.96 mmol, MW = 1450 g/mol) was heated for 3 hours at 120 °C. Compound **DIACT-OH** was dissolved in dry THF in a reaction flask. To this, already weighed and heated PEG and Ph_3P (630 mg, 2.40 mmol) were added to the solution. The reaction mixture was allowed to stir at room temperature. Then DIAD (484.8 mg, 2.40 mmol) was added drop-wise fashion to the reaction flask and kept for stirring for 24 hours at room temperature. Then THF from the reaction mixture was allowed to evaporate completely. The resultant solution was precipitated in diethyl ether for 3 times. A viscous liquid was formed as final product with the yield of 90%. FT-IR (cm^{-1}): 3425, 2872, 1801, 1737, 1645, 1455, 1350, 1322, 1295, 1249, 1219, 1191, 1107, 1039, 951, 848, 772, 722, 696, 543. MALDI: 1890.631.

General procedure for gel synthesis: All polymeric gels were synthesised using thiol-alkyene click reaction between **PTETACT** and pentaerythritol (3-mercaptopropionic acid) (**PETM**) in the presence of triethylamine at 80 °C temperature for 4 days. In a typical experiment, **PTETACT** (200 mg, 0.105 mmol), PETM (0.2 ml, 0.525 mmol) and TEA (0.8 ml) were taken in to a glass vial. The vial was sonicated for 15 minutes then heated at 80 °C for 4 days. After that the gel was collected by breaking the vial very carefully and dried in air for 1 day followed by drying under high vacuum at 40 °C for 3 days. Same procedure was followed to prepare all other gels.

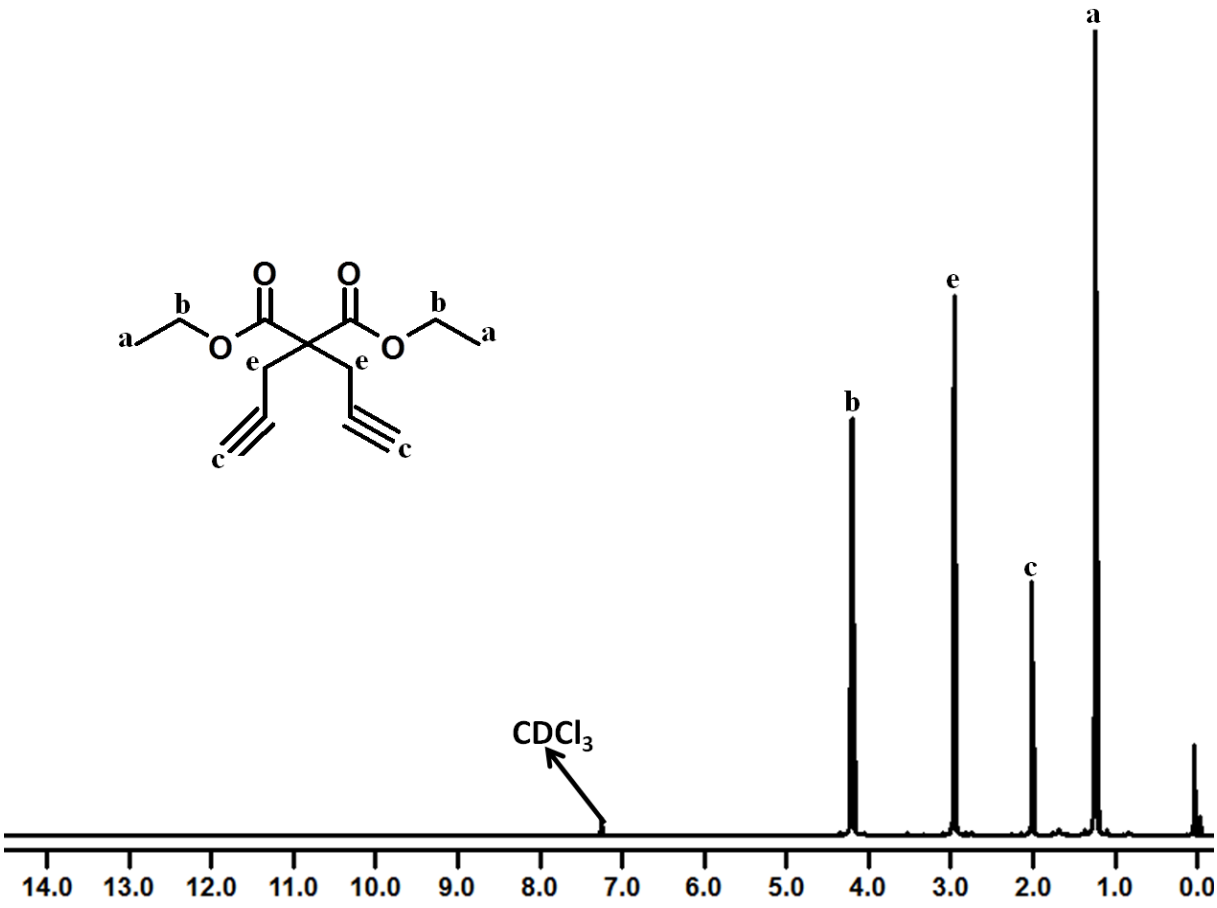

Figure S1. ^{1}H NMR spectrum of compound **DIACT** in $CDCl_3$.

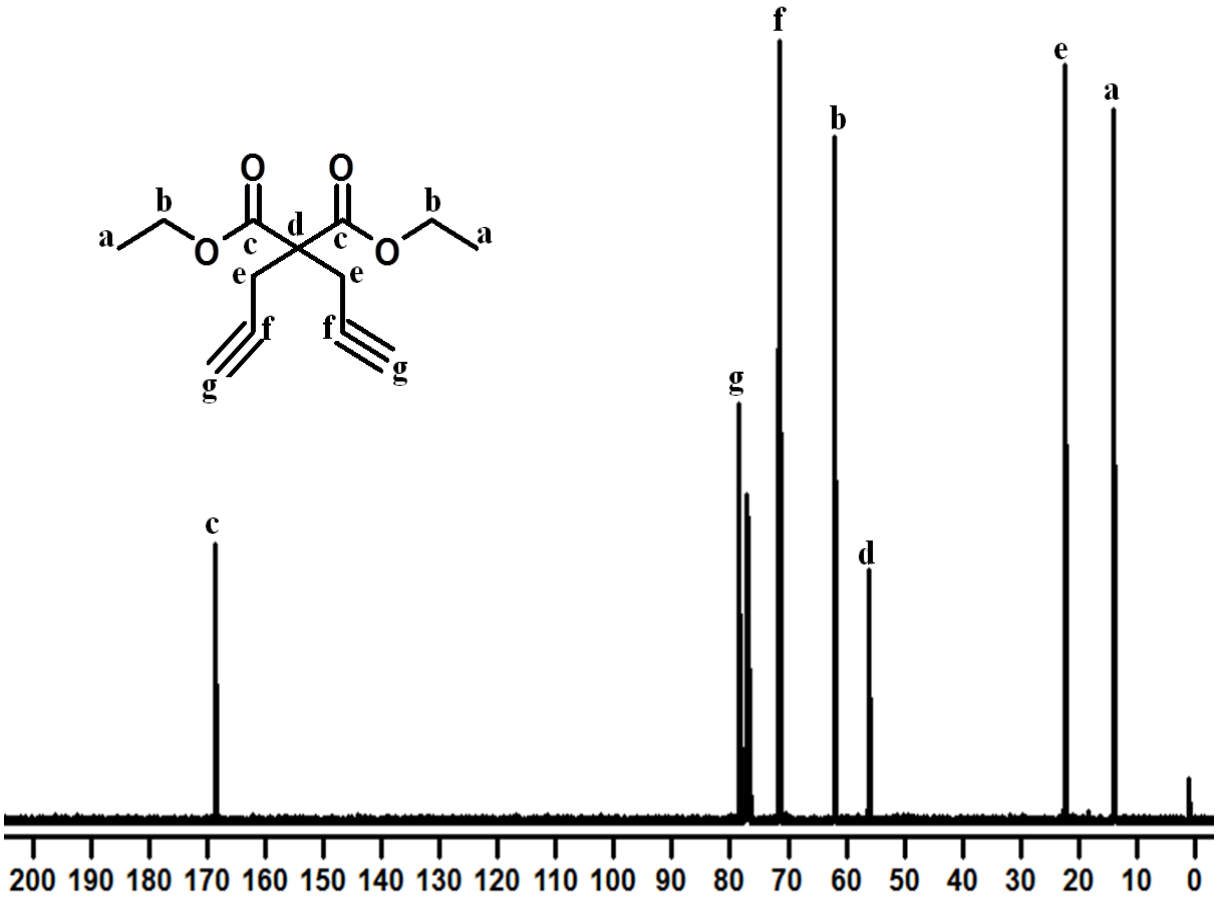

Figure S2. ^{13}C NMR spectrum of compound **DIACT** in $CDCl_3$.

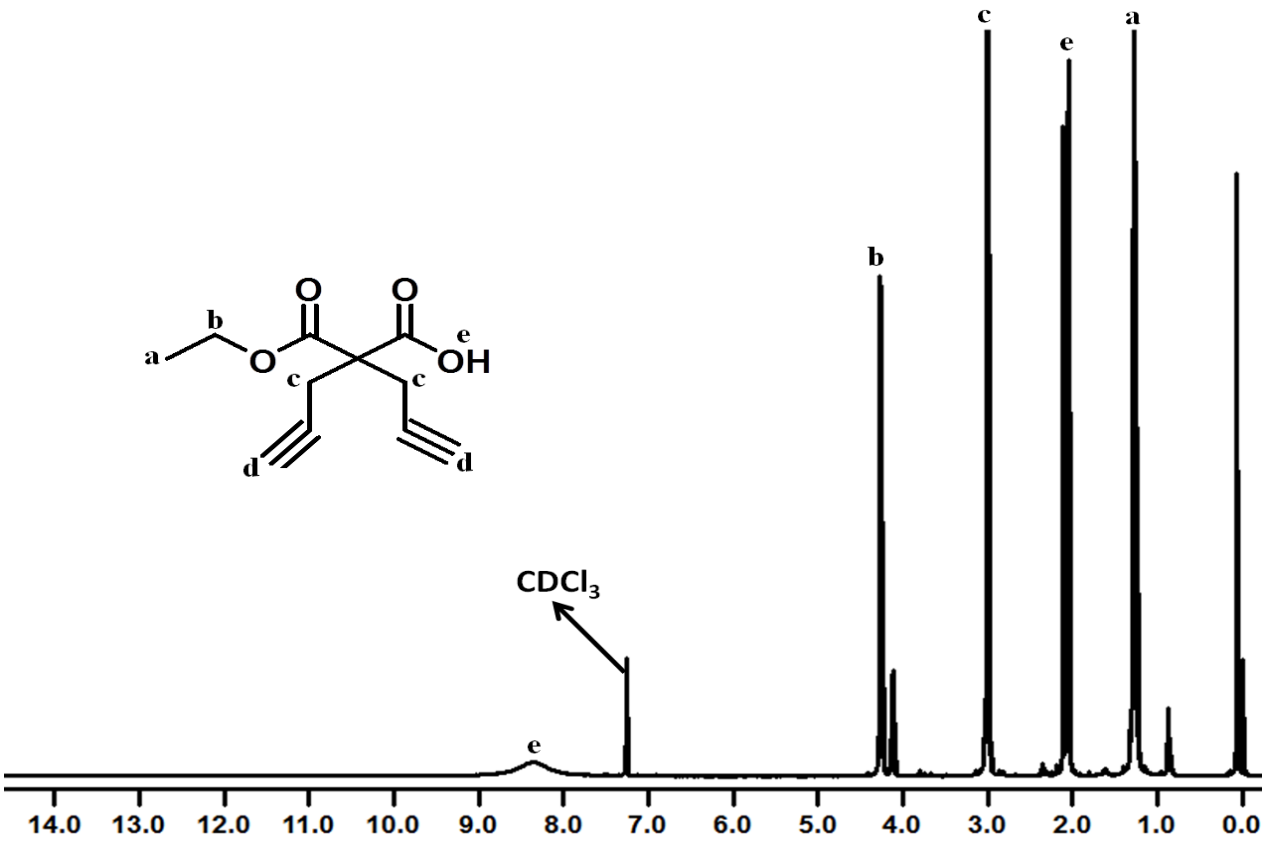

Figure S3. ^{1}H NMR spectrum of compound **DIACT-OH** in $CDCl_3$.

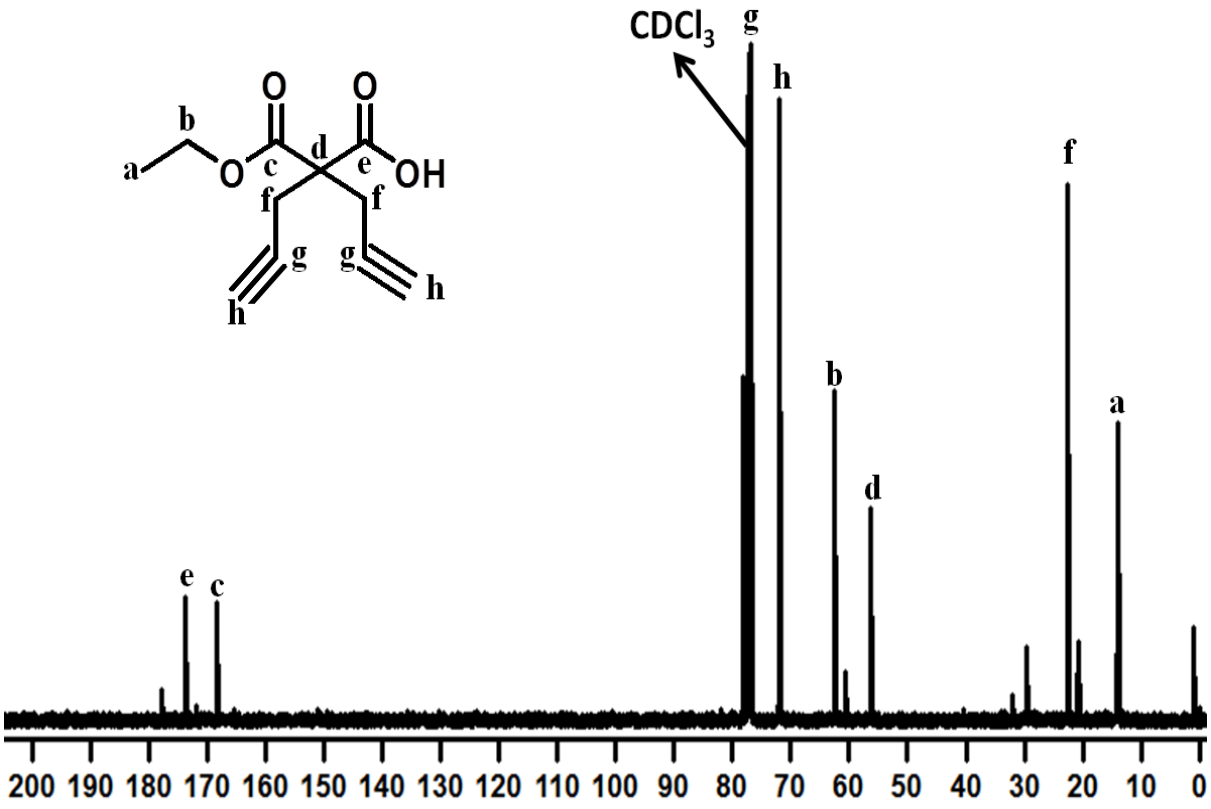

Figure S4. ^{13}C NMR Spectrum of compound **DIACT-OH** in $CDCl_3$.

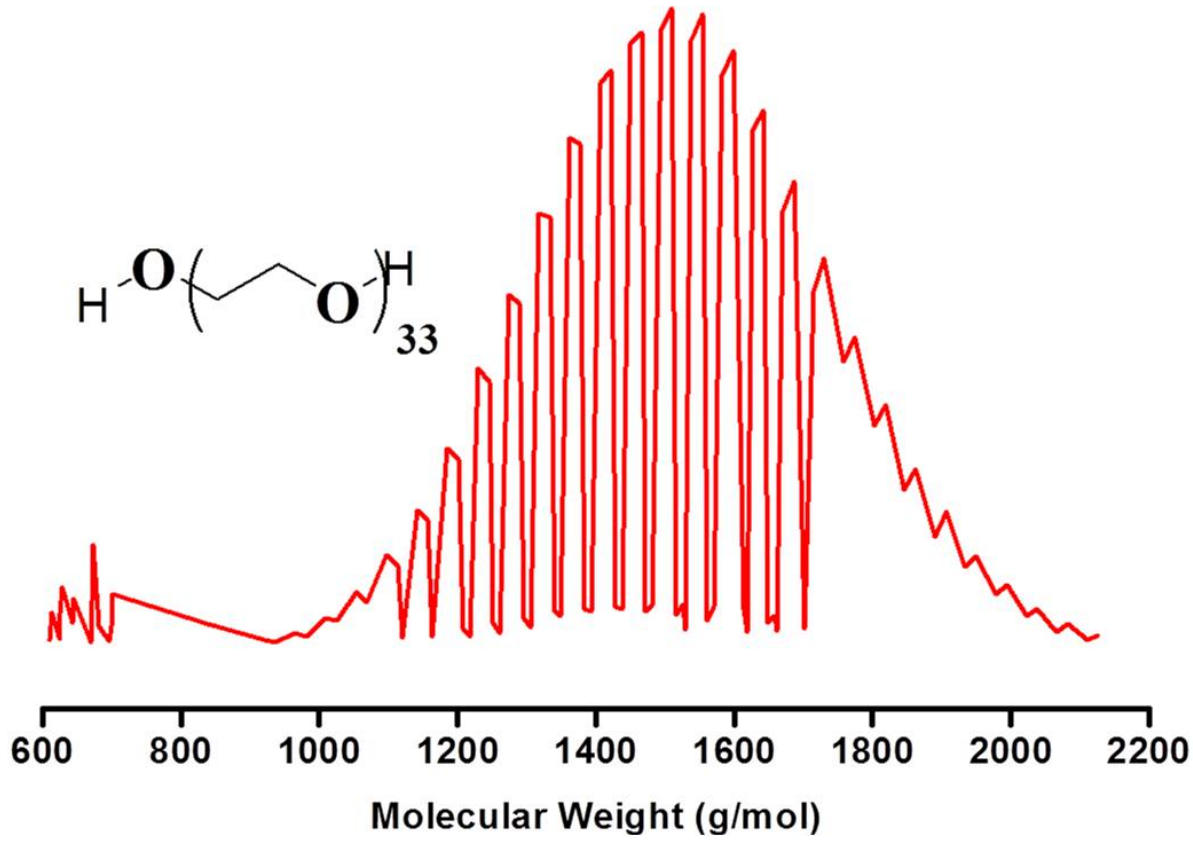

Figure S5. MALDI-TOF spectrum of polyethylene glycol (MW =~ 1450 g/mol).

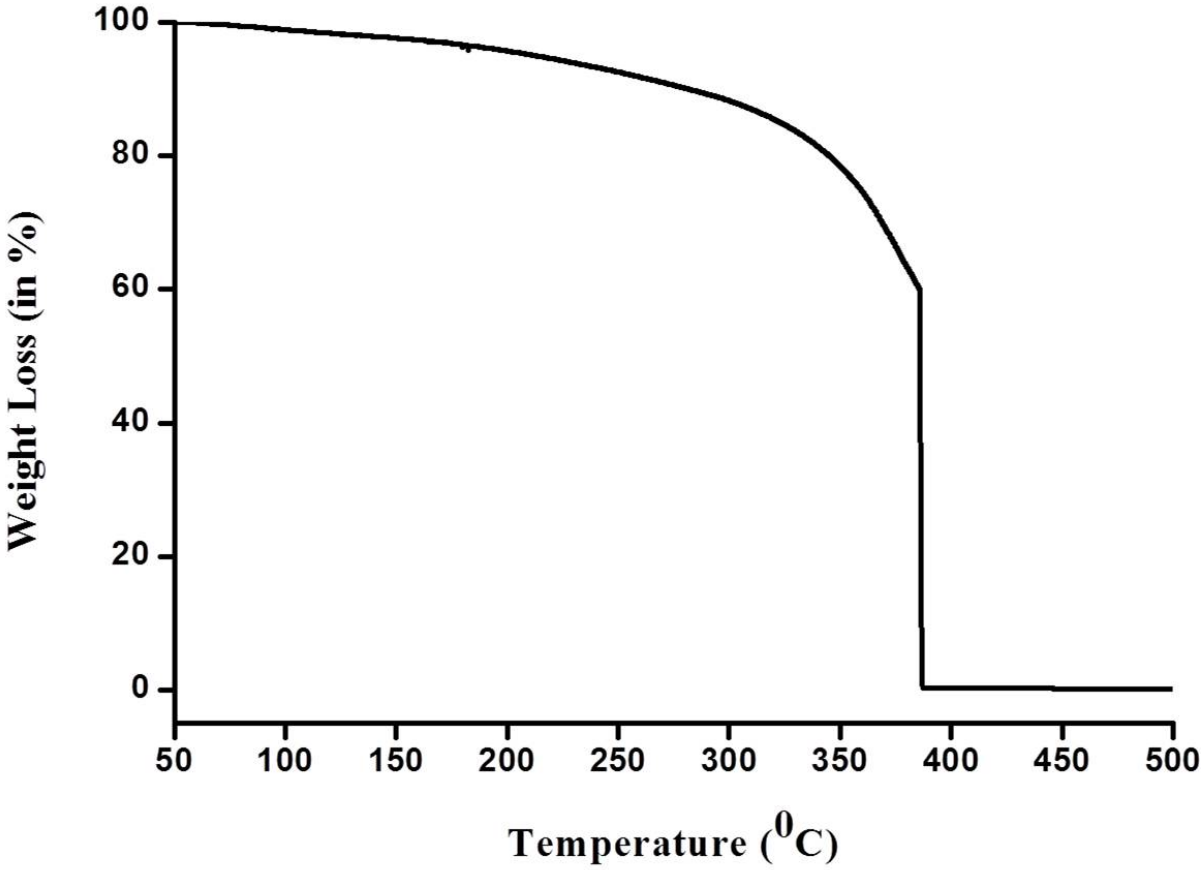

Figure S6. Thermogravimetric thermogram of dry Gel ([PTETACT]:[PETM] : [1:3]).

Table S1. Gel formation details.

S. No.	PTETACT (in mg)	PETM (in ml)	TEA (in ml)	Gel	Strength	Molar Ratio (PTETACT:PETM)
1.	100	0.3	0.3	No	-	1:14
2.	200	0.3	0.3	Yes	Weak	1:7
3.	300	0.3	0.3	Yes	Strong	1:5
4.	400	0.3	0.3	Yes	Very Strong	1:3
5.	200	0.2	0.3	Yes	Strong	1:5
6.	200	0.4	0.3	Yes	Weak	1:10
7.	200	0.6	0.3	Yes	Very Weak	1:15
8.	200	0.8	0.3	No	-	1:20

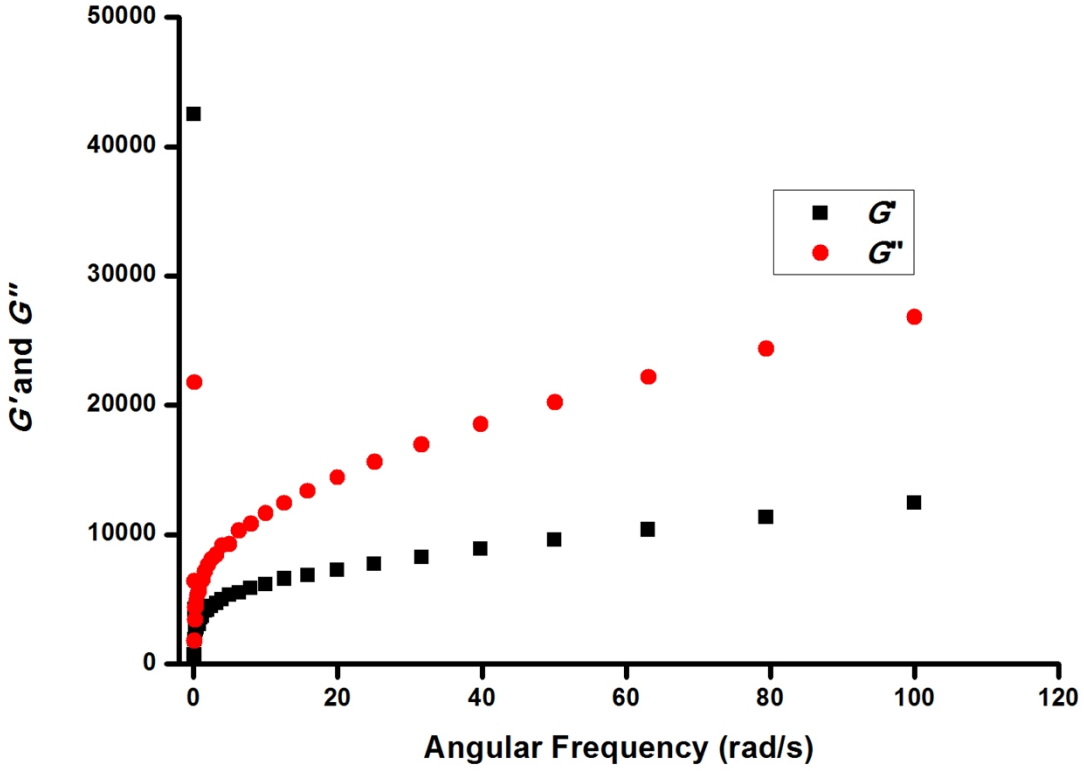

Figure S7. Variation of storage modulus (G') and loss modulus (G'') of weak gel ([PTETACT]:[PETM] : [1:7]).

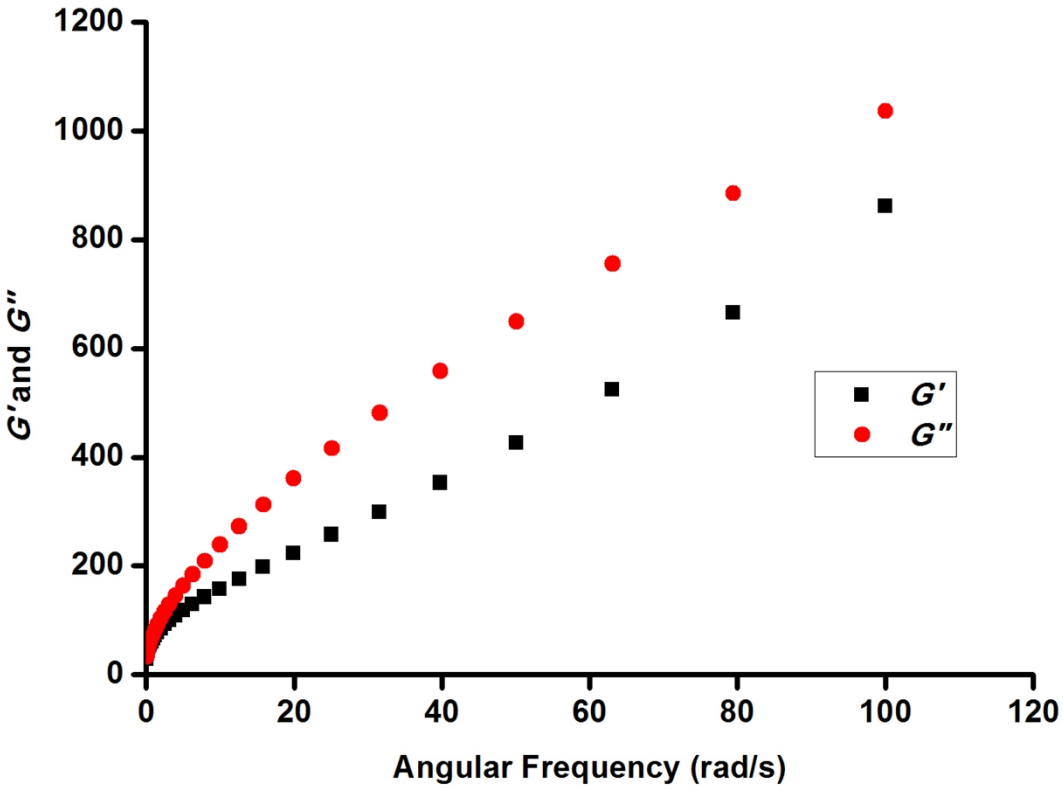

Figure S8. Variation of storage modulus (G') and loss modulus (G'') of very weak gel ([PTETACT]:[PETM] : [1:15]).

Swelling Ratio Data, Weight taken in (mg)						
Time/Solvent	**DMSO**	**DMF**	**DCM**	**Chloroform**	**Toluene**	**Water**
0 min	6.75	5.82	5.13	8.39	8.73	9.55
10 min	20.61	24.11	23.62	36.24	9.16	16.12
20 min	24.90	29.61	30.24	48.39	9.16	16.12
30 min	30.59	32.44	37.19	57.93	9.16	16.96
40 min	38.77	35.72	42.38	65.72	9.16	18.91
50 min	45.63	42.32	44.44	68.82	11.79	19.93
1 hour	46.32	44.56	45.12	69.16	12.13	22.03
1 hr 30 min	46.52	44.85	45.36	69.65	13.78	24.37
2 hour	46.78	44.97	45.46	69.97	14.11	24.63
2 hr 30 min	46.82	44.99	45.51	70.01	14.21	24.84
3 hour	46.84	45.02	45.55	70.07	14.28	24.90
4 hour	46.84	45.04	45.58	70.12	14.35	24.94
5 hour	46.86	45.07	45.63	70.19	14.44	24.97
6 hour	46.89	45.11	45.69	70.24	14.68	25.03
9 hour	46.91	45.17	45.77	70.33	14.96	25.09
12 hour	46.93	45.18	45.79	70.37	14.12	25.11
24 hour	46.97	45.26	45.85	70.47	15.32	25.19

Table S2. Swelling of Gel ([PTETACT]:[PETM] : [1:3]) in different solvent (in mg).

Swelling Ratio Data (in %)						
Time/Solvent	**DMSO**	**DMF**	**DCM**	**Chloroform**	**Toluene**	**Water**
0 min	0	0	0	0	0	0
10 min	205	314	360	331	5	68
20 min	268	408	489	476	5	68
30 min	353	457	624	590	5	77
40 min	474	513	726	683	5	98
50 min	576	627	766	720	35	108
1 hour	586	665	779	724	38	130
1 hr 30 min	589	670	784	730	57	155
2 hour	593	672	786	733	61	157
2 hr 30 min	593	672	787	734	62	160
3 hour	593	673	787	735	63	160
4 hour	593	673	788	735	64	161
5 hour	593	673	789	736	65	161
6 hour	593	675	790	737	68	162
9 hour	593	676	792	738	71	162
12 hour	593	676	792	738	61	162
24 hour	593	677	793	739	75	163

Table S3. Swelling of Gel ([PTETACT]:[PETM] : [1:3]) in different solvent (in %).

Weight Gain (%) = $\frac{Wet\ Weight - Original\ Weight}{Original\ Weight}$ **X 100%**

Equation 1[2]

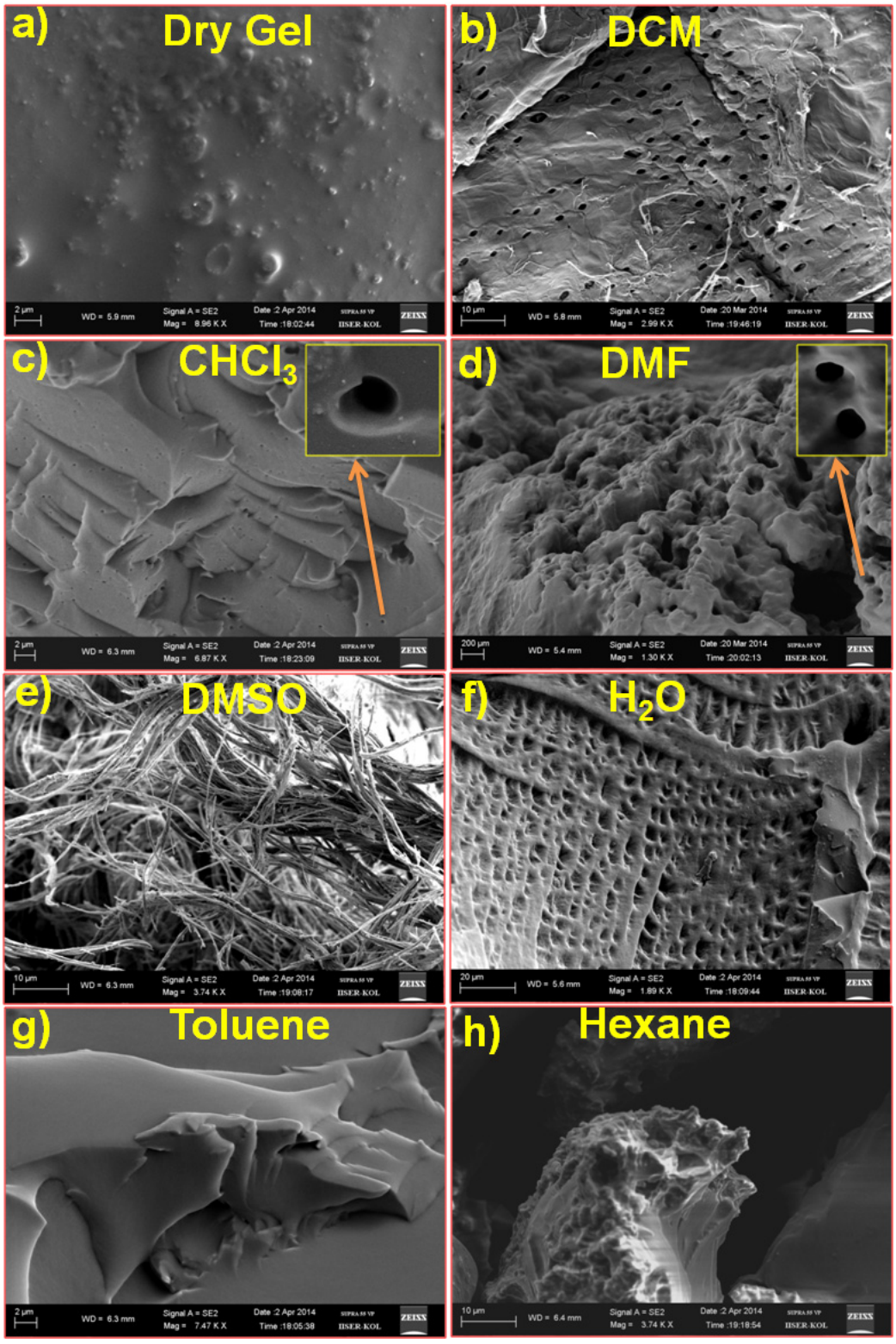

Figure S9. SEM images of a) dry gel; b) to h) swollen gel in different solvents.

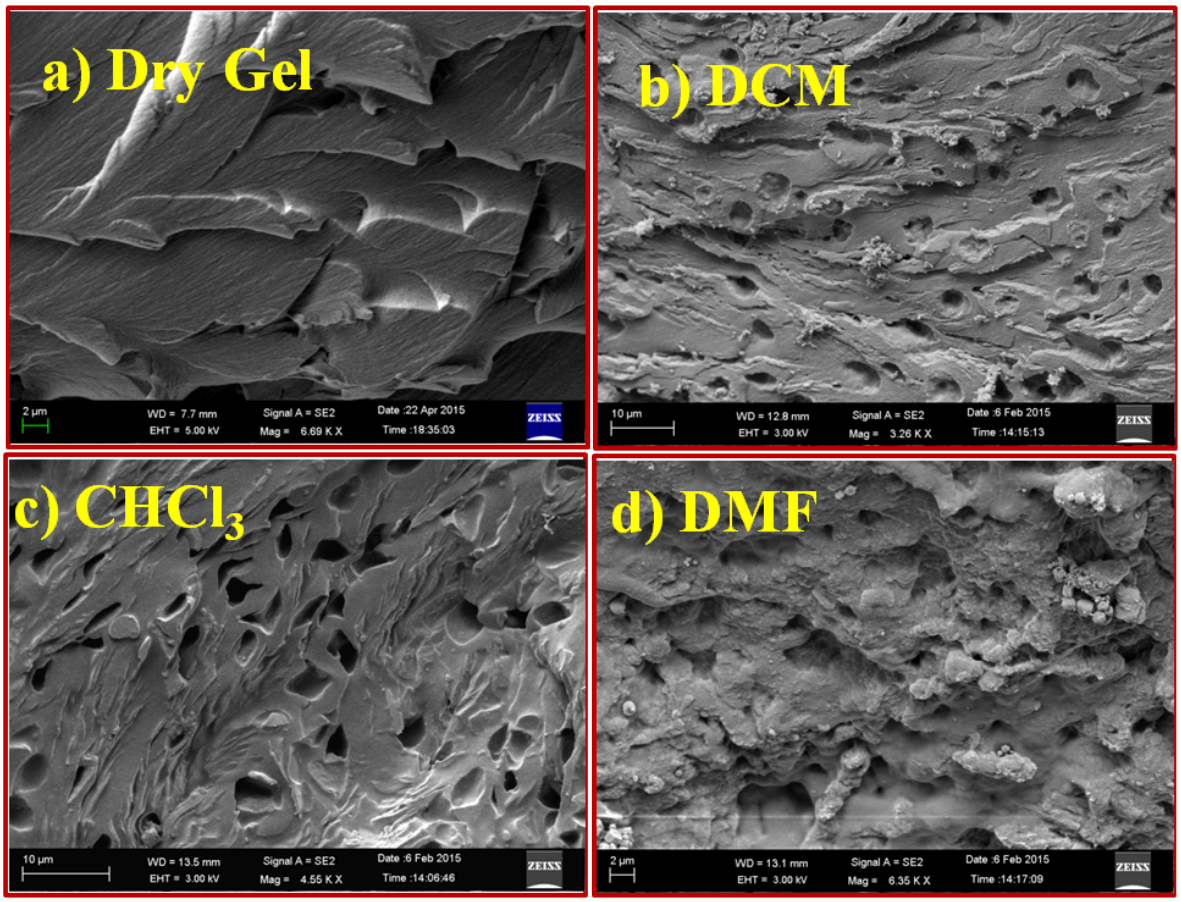

Figure S10. CRYO-SEM images of some of swollen gel in different solvents.

References:

1) Aleman, J.; Solar,V. D.; Ranninger, C. N. *Chem. Commun.* **2010**, *46*, 454-456.
2) Roy, S. G.; Haldar, U.; De, P. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4233−424.