Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

In-situ Formed Methyl-*co*-(bis-R) Silsesquioxane Based Polymer Networks with Solvent Controlled Pore Size Distributions and High Surface Areas

Nai-hsuan Hu,[a] Chamika U. Lenora,[a] Timothy A. May,[a] Nathan C. Hershberger,[b] Joseph C. Furgal[a*]

[a]Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, [b]Bowling Green High School, Bowling Green, OH, USA.

*Email: furgalj@bgsu.edu

Table S2: Surface area, texture, decomposition temperature, and ceramic yield of materials synthesized at room temperature in different solvents (pre-curing).

Solvent	Texture GP = gel particles NG = no gel	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
Acetonitrile	GP	1022	451.6	89.2
Dichloromethane	GP	1076	483.7	89.7
Benzonitrile	GP	844	513.7	87.8
Tetrahydrofuran*	GP	716	286.8	84.5
Acetone	GP	423	209.0	83.1
Ethyl Acetate	GP	287	155.3	75.2
Dioxane	GP	58	147.0	71.3
Ethyl Ether	GP	13	155.7	66.9
Toluene	GP	4	111.0	43.4
Dimethylacetamide*	NG	2	165.0	60.8
Methanol	NG	181	145.9	57.8
2-Propanol	NG	1	94.1	47.4

*****distilled and dried with 3 Å molecular sieves. Other solvents are anhydrous

Table S3: Surface area, decomposition temperature, and ceramic yield of materials synthesized in different solvents (post-curing).

Solvent	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
Acetonitrile	1045	440.6	88.8
Dichloromethane	1080	435.7	88.1
Benzonitrile	877	565.5	89.6
Tetrahydrofuran*	805	489.3	88.4
Acetone	614	471.4	88.6
Ethyl Acetate	492	446.0	88.8
Dioxane	405	473.1	89.0

Ethyl Ether	429	502.6	88.5
Toluene	385	486.5	88.8
Dimethylacetamide*	535	472.9	88.5
Methanol	275	616.0	90.0
2-Propanol	194	332.8	72.6

*distilled and dried with 3 Å molecular sieves. Other solvents are anhydrous

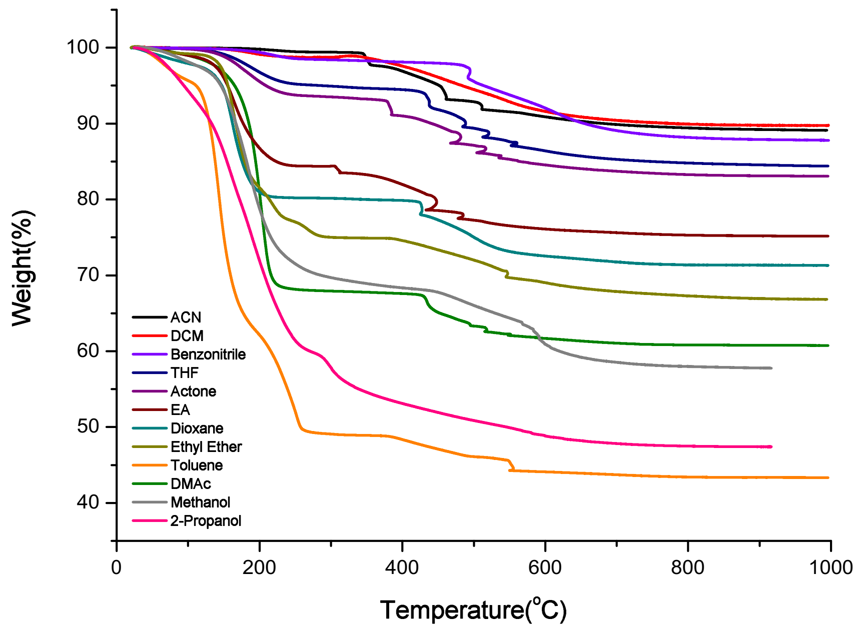
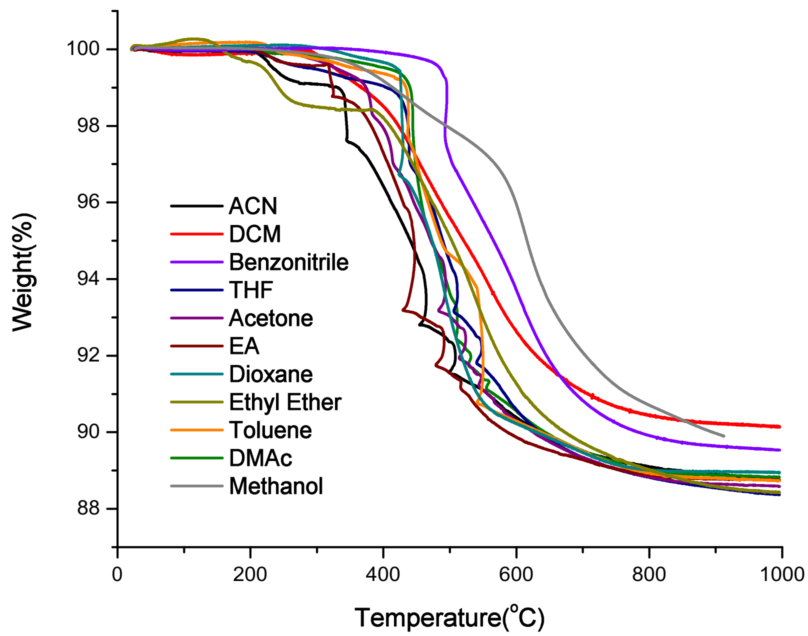


Figure S1. TGA graphs of materials from reactions synthesized in different solvents (pre-curing).



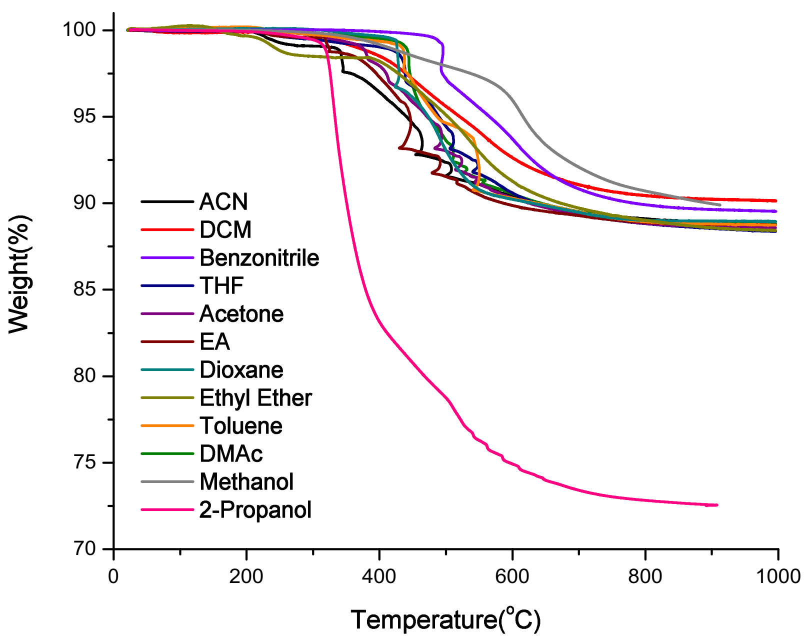
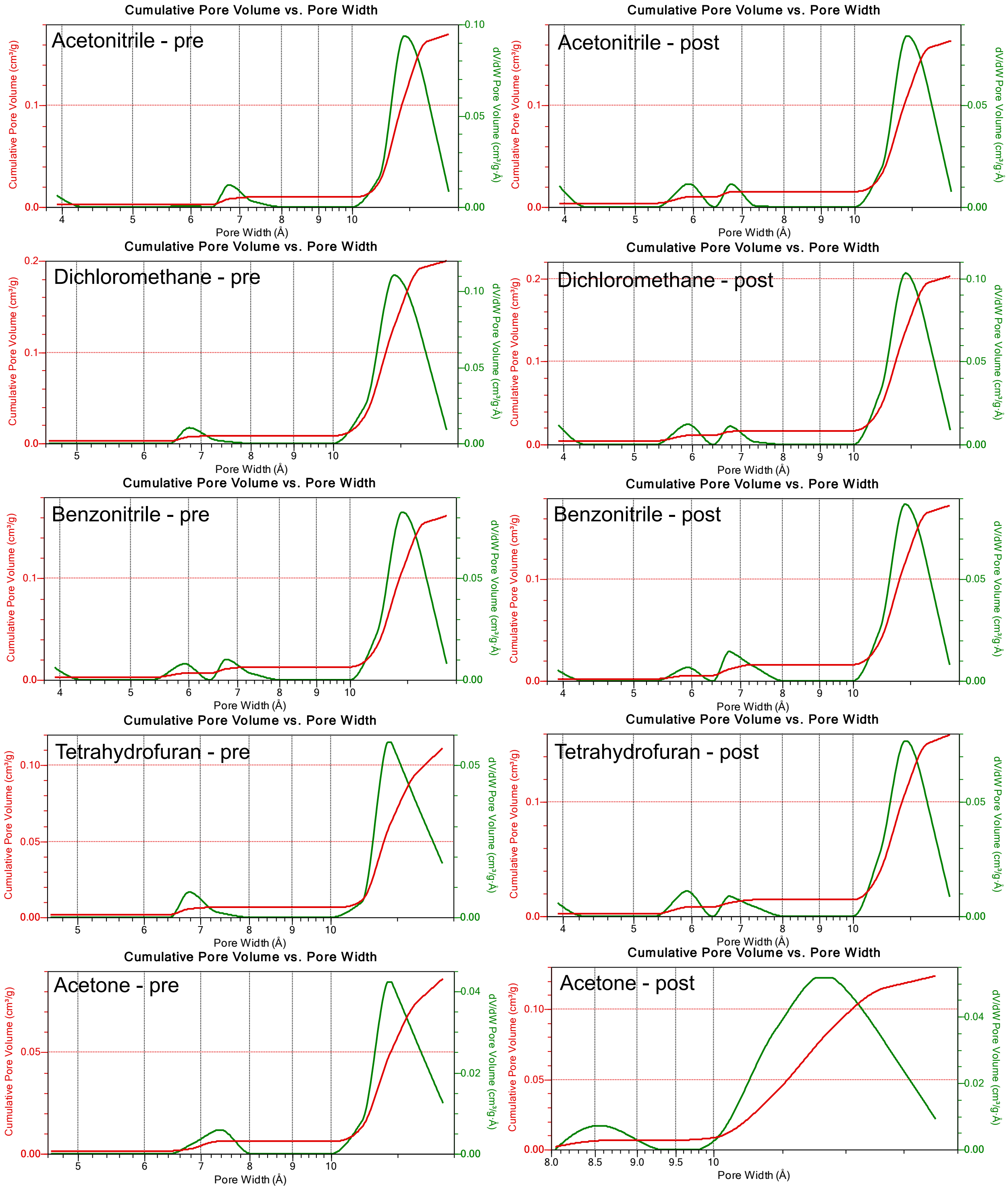


Figure S2. TGA graphs of materials synthesized in different solvents (post-curing).


Cumulative Pore Volume vs. Pore Width
Acetonitrile - pre
Acetonitrile - post
Dichloromethane - pre
Dichloromethane - post
Benzonitrile - pre
Benzonitrile - post
Tetrahydrofuran - pre
Tetrahydrofuran - post
Acetone - pre
Acetone - post
Pore Width (Å)
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)

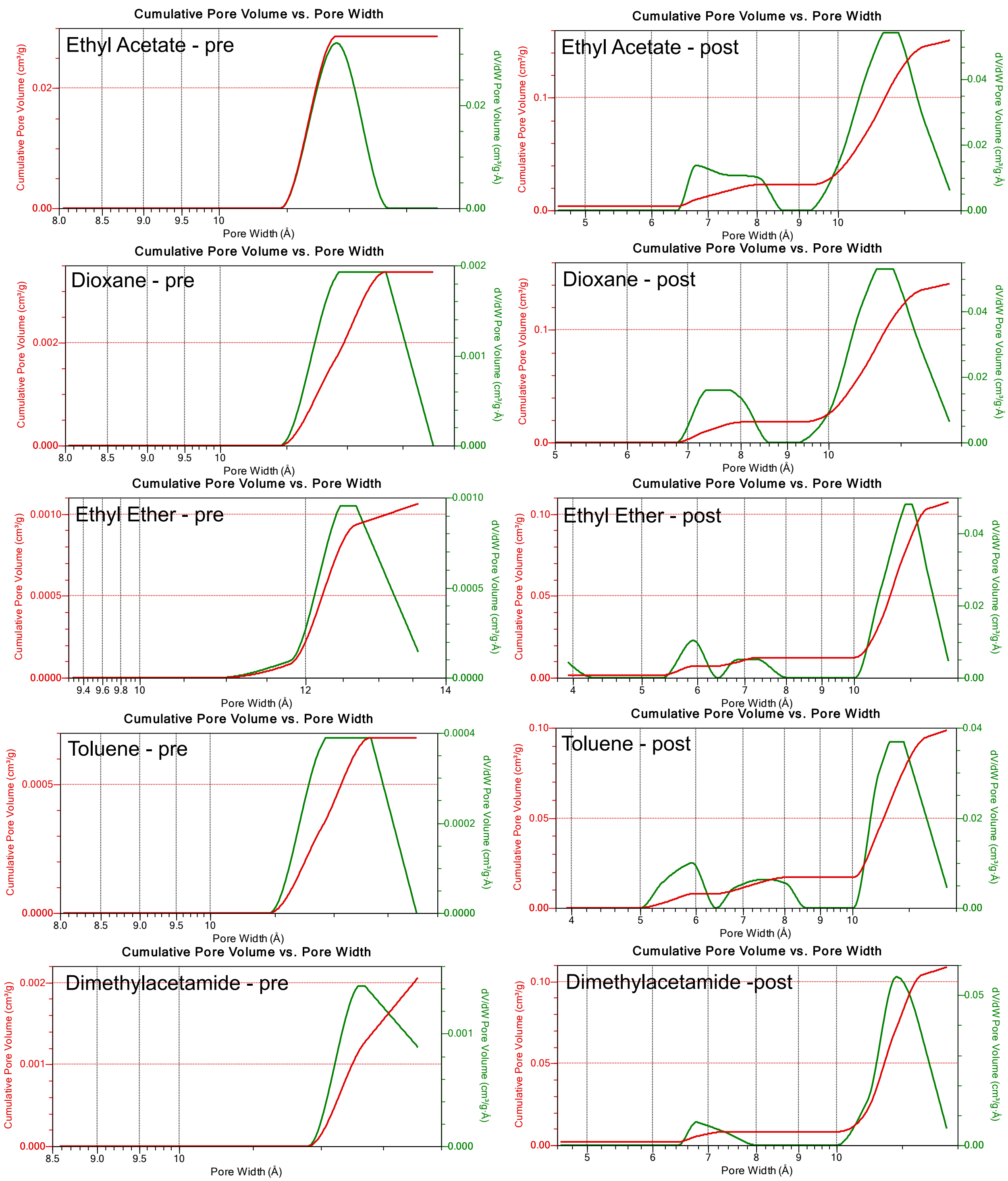
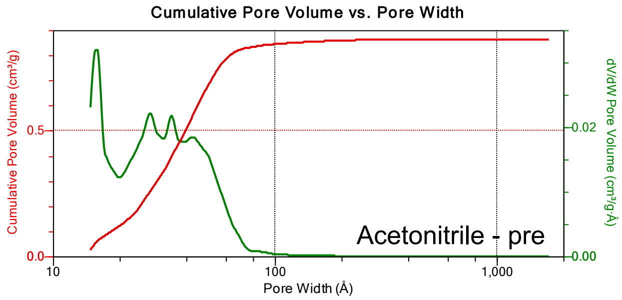
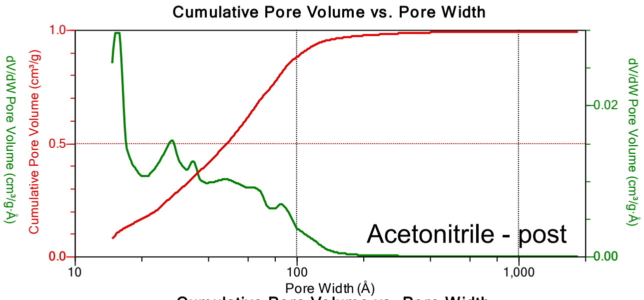
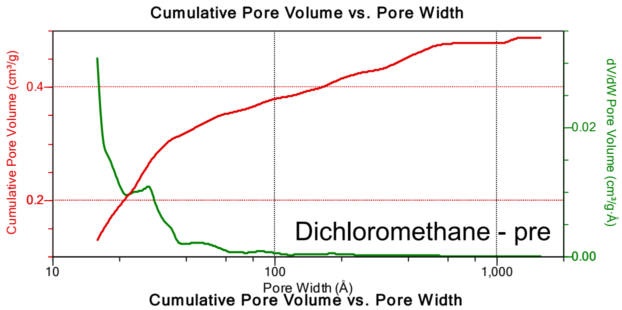
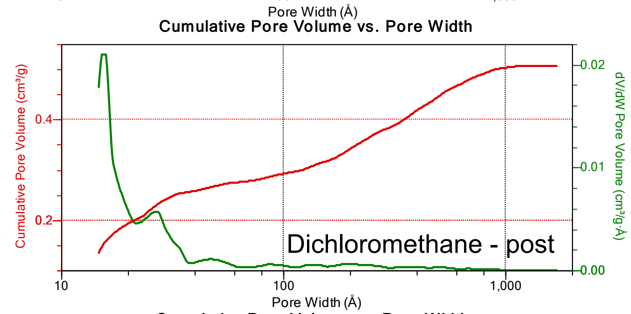


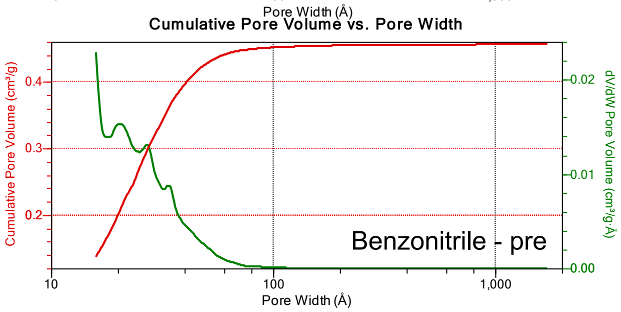
Figure S3. DFT pore size distribution graphs in micropore region of materials synthesized in different solvents (pre-curing and post-curing).

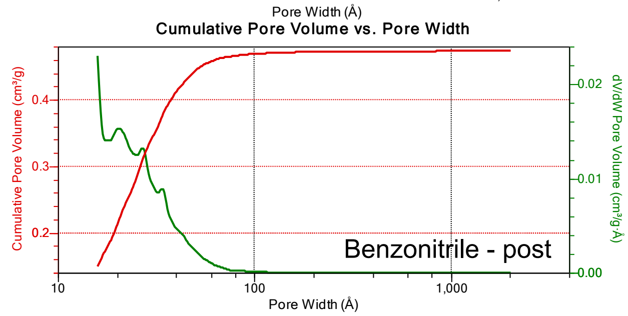

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Acetonitrile - pre

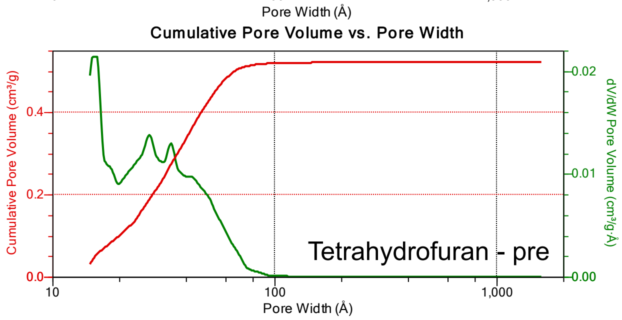

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Acetonitrile - post

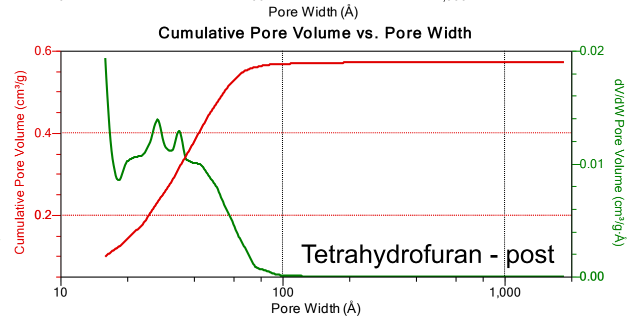

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Dichloromethane - pre

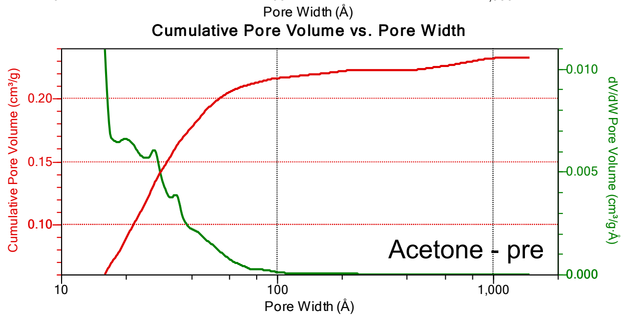

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Dichloromethane - post

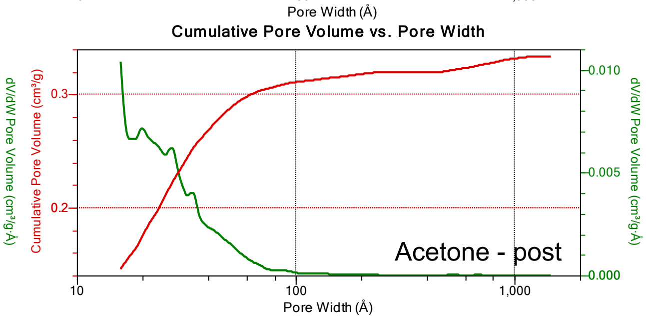

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Benzonitrile - pre

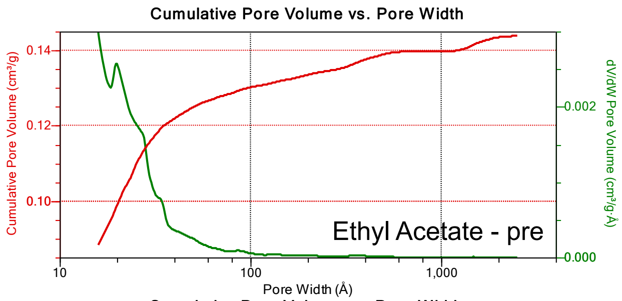

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Benzonitrile - post

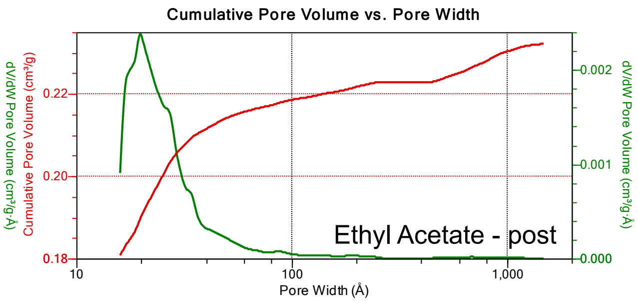

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Tetrahydrofuran - pre

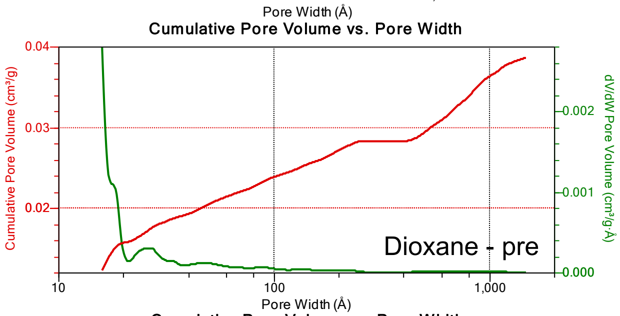

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Tetrahydrofuran - post

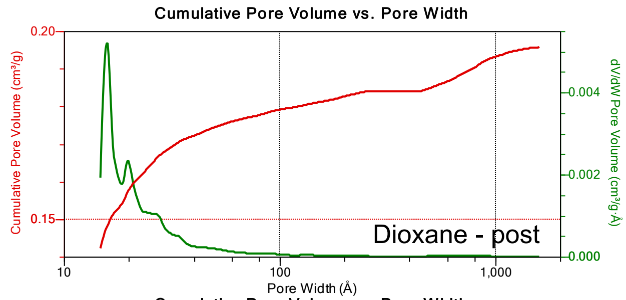

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Acetone - pre

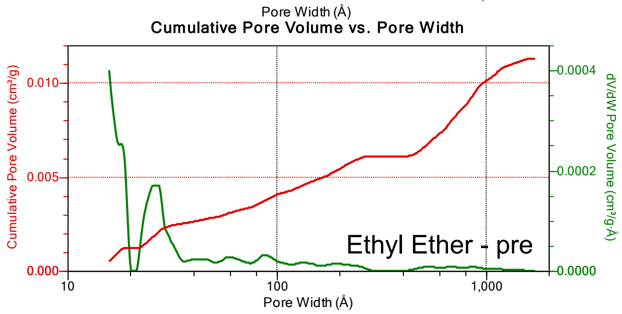

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
Acetone - post

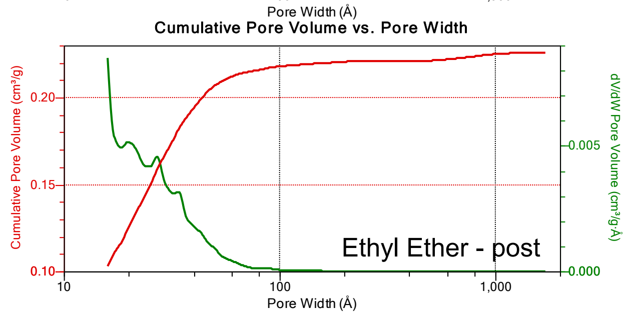

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.14
0.12
0.10
0.002
0.000
10
100
1,000
Ethyl Acetate - pre

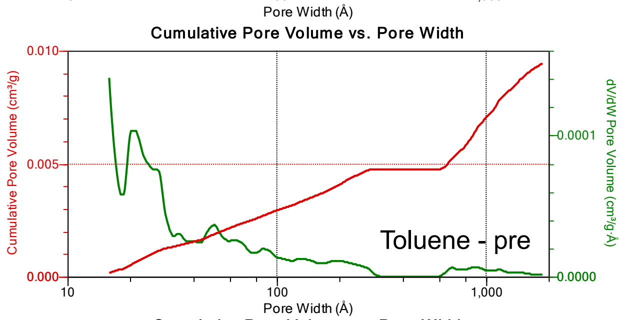

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.22
0.20
0.18
0.002
0.001
0.000
10
100
1,000
Ethyl Acetate - post

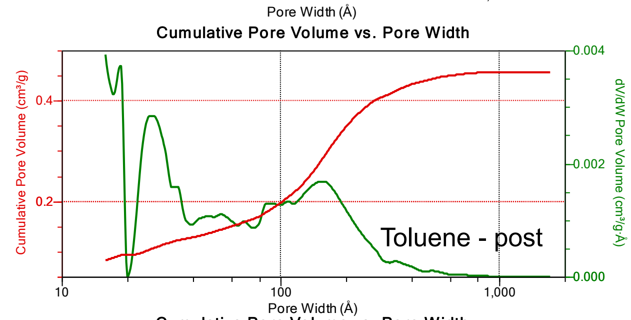

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.04
0.03
0.02
0.002
0.001
0.000
10
100
1,000
Dioxane - pre

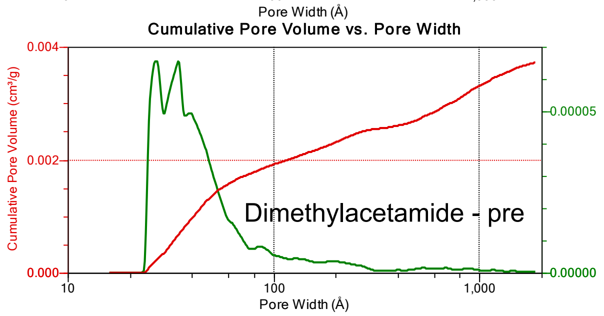

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.20
0.15
0.004
0.002
0.000
10
100
1,000
Dioxane - post

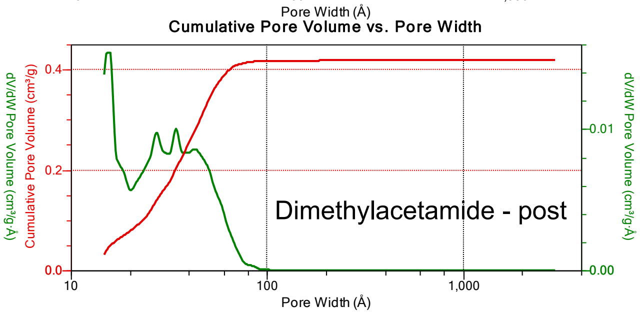

Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.010
0.005
0.000
0.0004
0.0002
0.0000
10
100
1,000
Ethyl Ether - pre


Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.20
0.15
0.10
0.005
0.000
10
100
1,000
Ethyl Ether - post


Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.010
0.005
0.000
0.0001
0.0000
10
100
1,000
Toluene - pre


Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.4
0.2
0.004
0.002
0.000
10
100
1,000
Toluene - post


Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.004
0.002
0.000
0.00005
0.00000
10
100
1,000
Dimethylacetamide - pre


Cumulative Pore Volume vs. Pore Width
Cumulative Pore Volume (cm³/g)
dV/dW Pore Volume (cm³/g·Å)
Pore Width (Å)
0.4
0.2
0.0
0.01
0.00
10
100
1,000
Dimethylacetamide - post

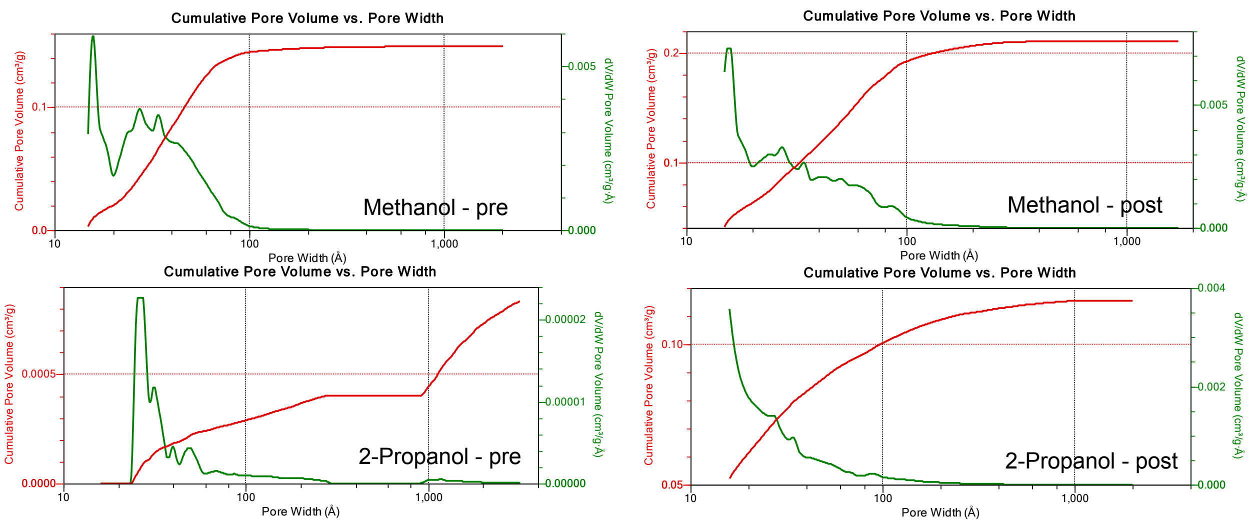


Figure S4. DFT pore size distribution graphs in mesopore and macropore region of materials synthesized in different solvents (pre-curing and post-curing).

Table S4. Cumulative volume of mesopore, micropores of materials synthesized in different solvents (pre-curing and post curing).

Solvent	Cumulative mesopore volume (0-100nm, cm^3/g)	Cumulative micropore volume (0-1.37nm, cm^3/g)	Micropore content (%)
Acetonitrile			
Pre-curing	0.86	0.17	19.8
Post curing	0.99	0.17	16.8
Dichloromethane			
Pre-curing	0.48	0.2	41.7
Post curing	0.42	0.2	48.7
Benzonitrile			
Pre-curing	0.46	0.16	35.4
Post curing	0.47	0.17	36.7
Tetrahydrofuran			
Pre-curing	0.52	0.11	21.3
Post curing	0.58	0.16	27.8
Acetone			
Pre-curing	0.23	0.09	36.5
Post curing	0.33	0.12	37.1
Ethyl Acetate			
Pre-curing	0.14	0.03	20.4
Post curing	0.23	0.15	65.2
Dioxane			
Pre-curing	0.00*	0.00*	9.3
Post curing	0.19	0.14	73.1
Ethyl Ether			
Pre-curing	0.01	0.00*	10.6
Post curing	0.23	0.11	47.3
Toluene			
Pre-curing	0.01	0.00*	9.7
Post curing	0.46	0.10	21.4

Dimethylacetamide			
Pre-curing	0.00*	0.00*	66.7
Post curing	0.42	0.11	25.9
Methanol			
Post curing	0.21	0.09	42.8
2-Propanol			
Post curing	0.12	0.08	66.7

*Values for micropore percent calculated from original long form data.

Table S5. Average and median pore width comparison of the materials synthesized in different solvents (pre-curing and post curing).

Solvent	Avg. width (Å) Pre-curing	Avg. width(Å) Post curing	Med. width (Å) Pre-curing	Med. width (Å) Post curing
Acetonitrile	39.3	40.1	29.4	29.4
Dichloromethane	33.5	35.9	21.6	17.1
Benzonitrile	26.4	23.4	38.4	34.3
Tetrahydrofuran	30.5	32.5	27.3	29.4
Acetone	29.6	30.8	23.4	23.4
Ethyl Acetate	32.3	34.5	21.6	23.4
Dioxane	46.2	32.1	18.5	20.0
Ethyl Ether	70.4	28.0	25.1	23.4
Toluene	91.3	85.6	27.3	46.6
Dimethylacetamide	71.6	31.8	36.9	29.4
Methanol	33.6	33.6	31.8	31.8
2-Propanol	93.3	35.5	31.8	23.4

*See supporting information 2 for equations.

Table S6. Surface area, decomposition temperature, and ceramic yield of materials synthesized in mixed solvents.

Solvent	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
Dichloromethane + acetonitrile (1:1)	524	210.4	82.5
Dichloromethane + tetrahydrofuran (1:1)	516	216.5	83.3
Dichloromethane + acetone(1:1)	685	239.3	84.8
Dichloromethane + methanol(3:1)	16	166.3	68.6
Dichloromethane + ethanol(3:1)	4	164.1	68.5
Dichloromethane + isoporpanol(3:1)	498	332.0	82.0
Dichloromethane + pyridine(3:1)	403	172.2	81.6

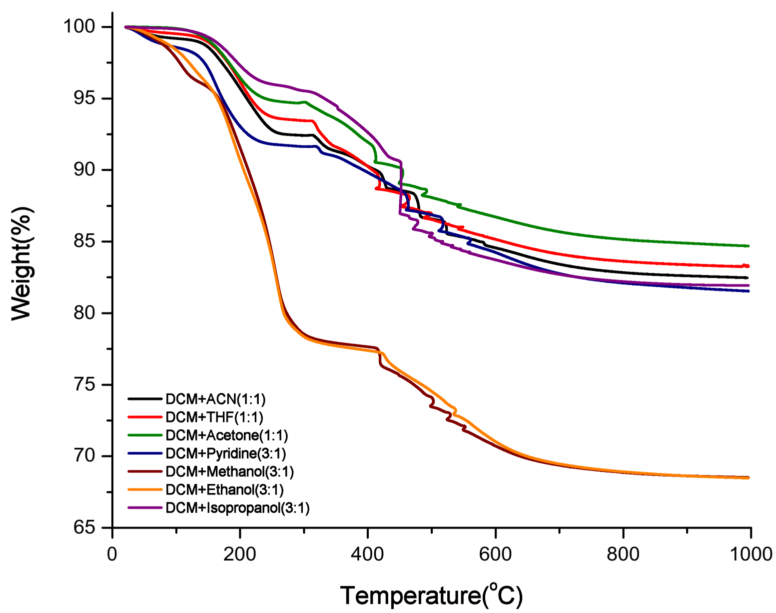


Figure S5. TGA graphs of materials synthesized in mixed solvents.

Figure S6. DFT pore size distribution graphs in mesopore and macropore region of materials synthesized in mixed solvents.

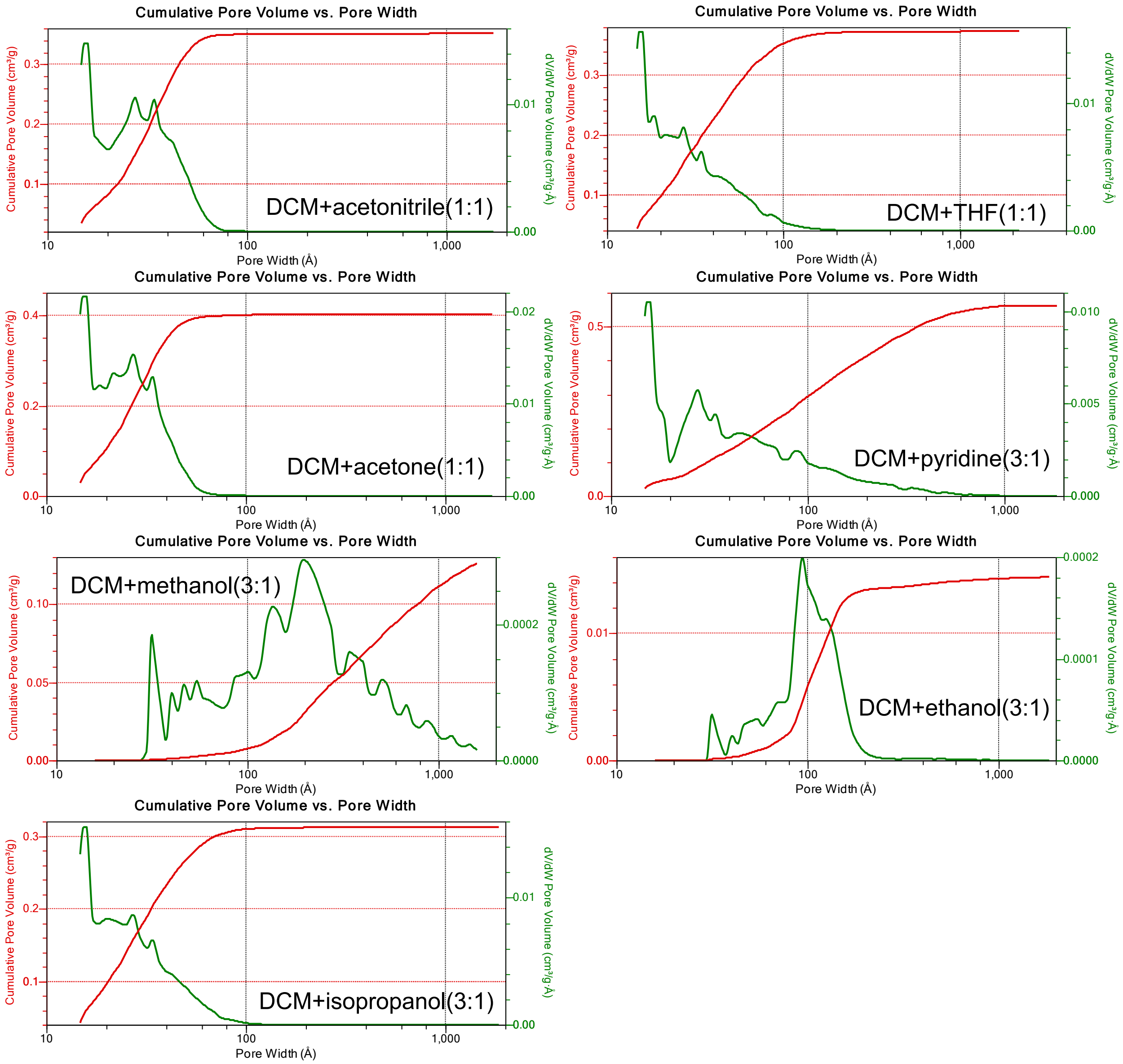


Table S7. Surface area, decomposition temperature, and ceramic yield of materials synthesized in different amounts of acetonitrile.

Amount of acetonitrile (mL)	Concentration of ethoxy group (M)	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
50 mL	0.90	608	153.2	76.7
100 mL	0.45	897	186.3	82.7
200 mL	0.23	866	214.9	85.0
300 mL	0.15	892	199.7	84.1
400 mL	0.11	426	170.5	76.8

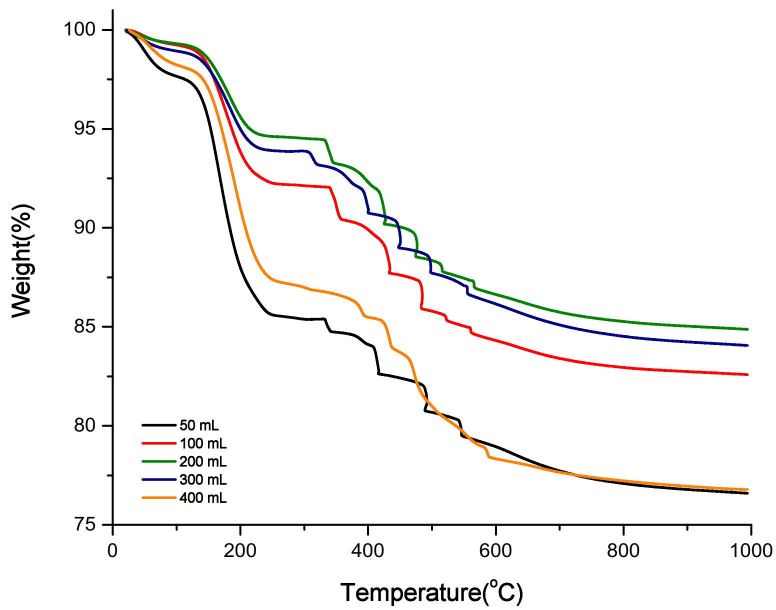


Figure S7. TGA graphs of samples from material synthesized in different amounts of acetonitrile.

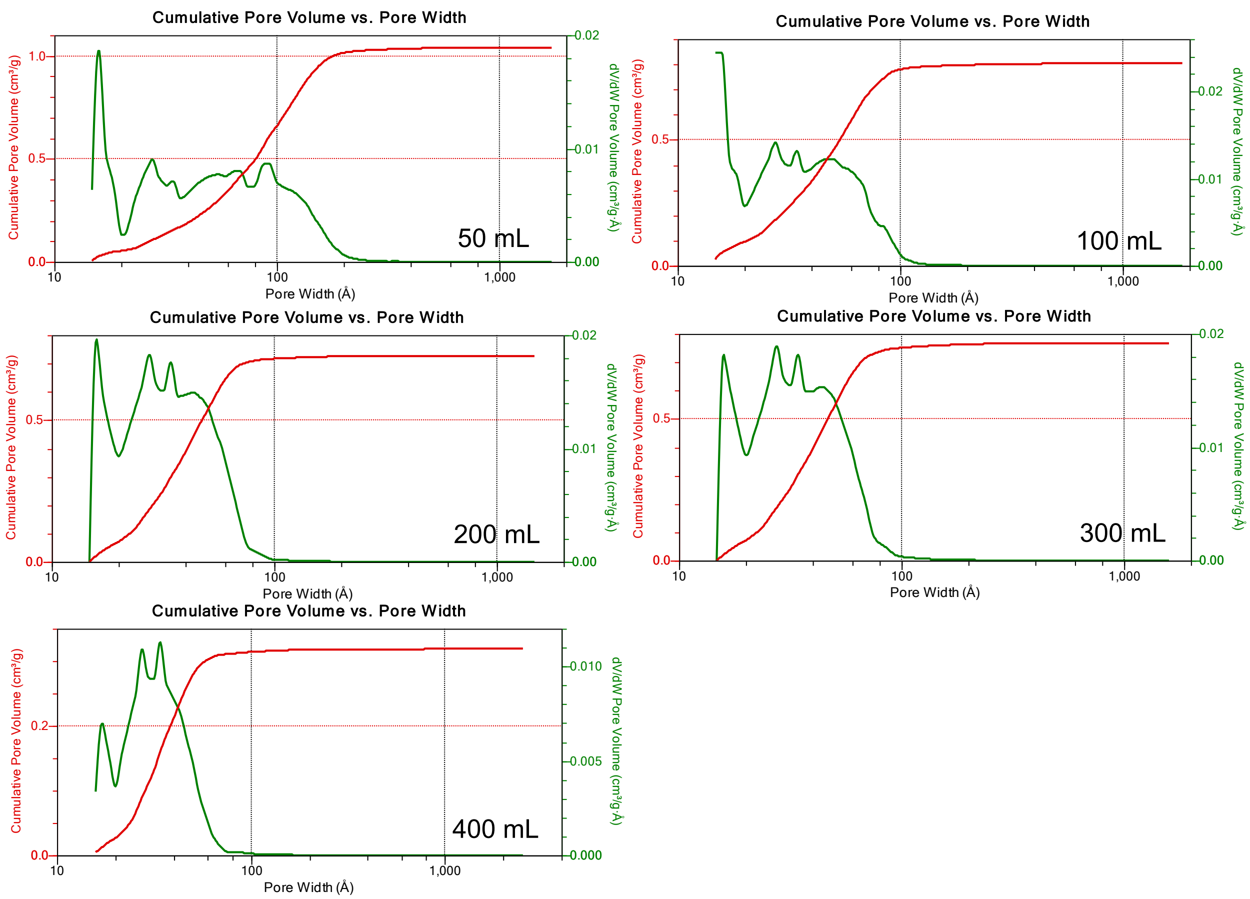


Figure S8. DFT pore size distribution graphs of material synthesized in different amounts of acetonitrile.

Table S8. Surface area, decomposition temperature, and ceramic yield of materials synthesized in dichloromethane with different amounts of water.

Amount of water (mL)	Ratio (ethoxy: H_2O)	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
0.188mL	1:0.2	947	411.7	87.7
0.375 mL	1:0.5	803	338.9	85.4
0.75 mL	1:1	1076	483.7	89.7
1.5 mL	1:1.8	629	374.5	84.5
2.25 mL	1:2.8	339	195.1	82.5
3 mL	1:3.7	84	227.3	81.1

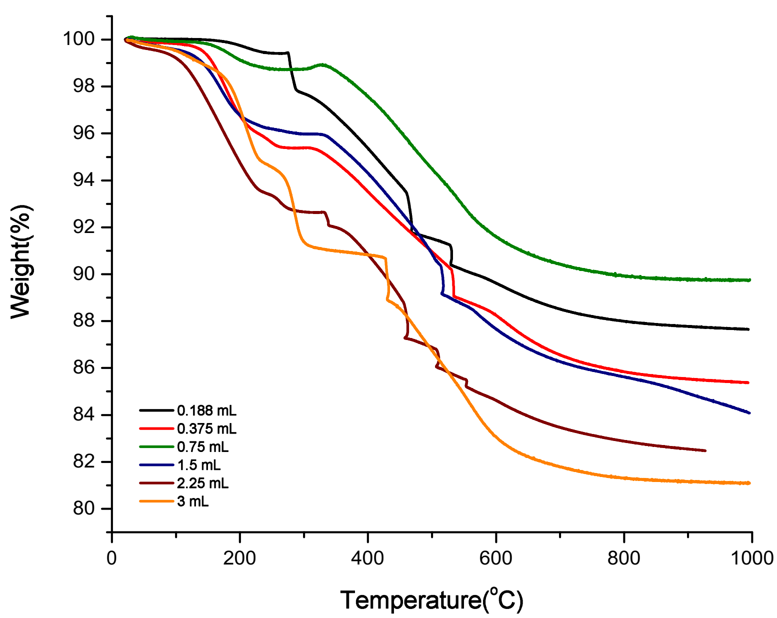


Figure S9. TGA graphs of materials synthesized in dichloromethane with different amounts of water.

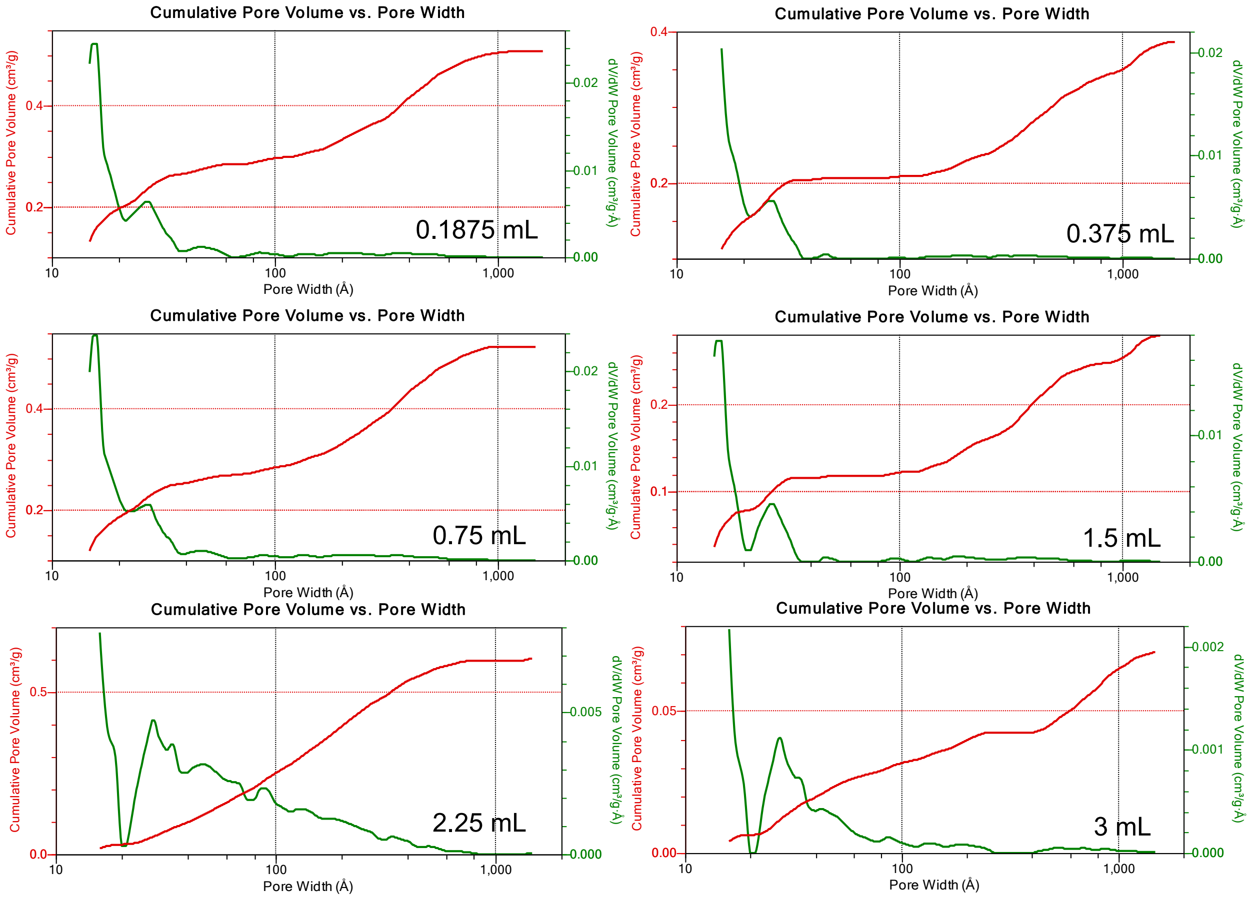


Figure S10. DFT pore size distribution graphs of material synthesized in dichloromethane with different amounts of water.

Table S9. Surface area, decomposition temperature, and ceramic yield of materials synthesized in acetonitrile with different amounts of water.

Amount of water (mL)	Ratio (ethoxy: H_2O)	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
0.75 mL	1 : 1	686	210	83.7
1.5 mL	1 : 2	642	239.3	83.4
3 mL	1 : 4	812	379.7	86.9
6 mL	1 : 7	825	392.7	87.4
12 mL	1 : 15	886	424	88.1
25 mL	1 : 31	925	385.2	87.2
50 mL	1 : 61	753	426.3	87.8

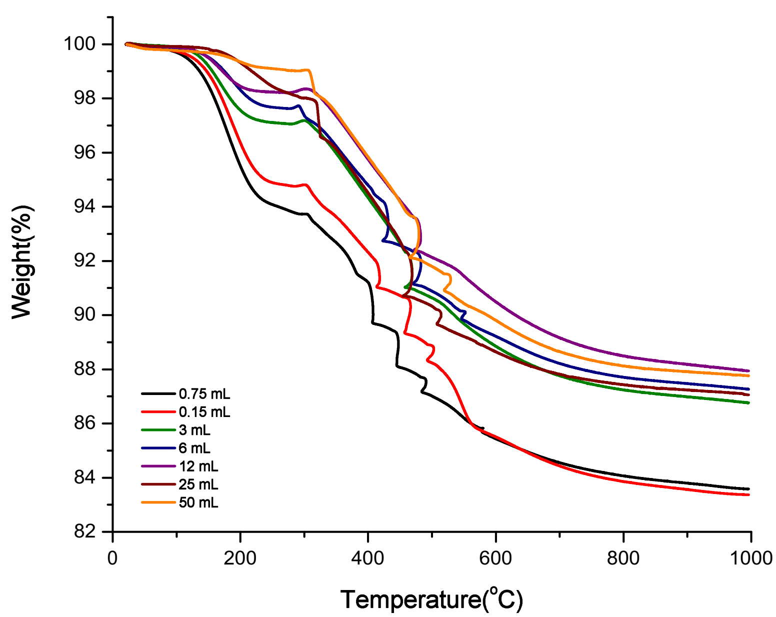


Figure S11. TGA graphs of materials synthesized in acetonitrile with different amounts of water.

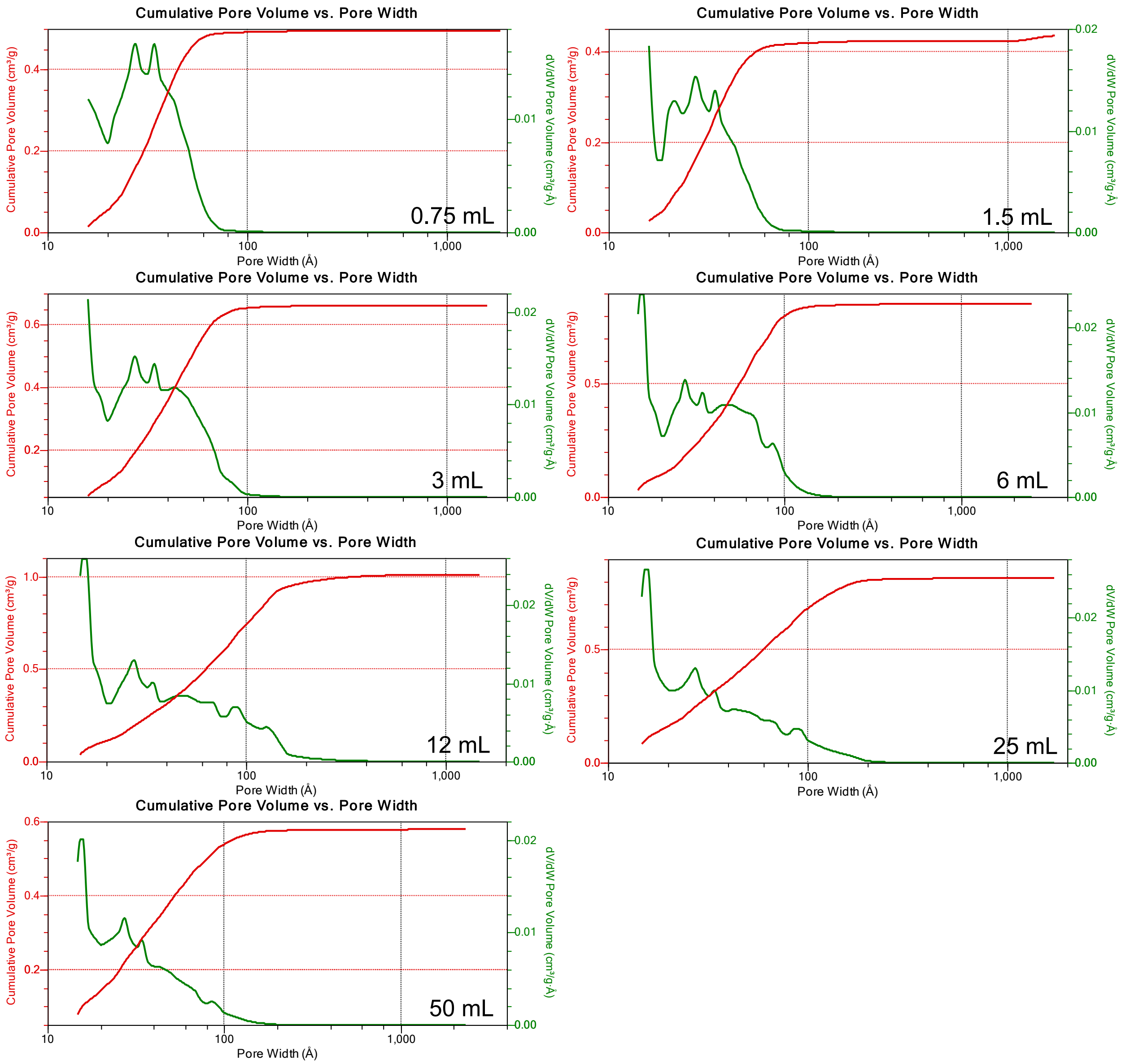


Figure S12. DFT pore size distribution graphs of material synthesized in acetonitrile with different amounts of water.

Table S10. Surface area, decomposition temperature, and ceramic yield of materials synthesized in dichloromethane at different temperatures.

Temperature (°C)	Texture GP = gel particle NG = no gel	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
0	NG	(No precipitation)	-	-
5	GP	214	167.5	78.2
12.5	GP	537	186.5	83.7
RT	GP	1076	483.7	89.7
30	GP	808	381.7	86.5
39	GP	892	339.6	85.6

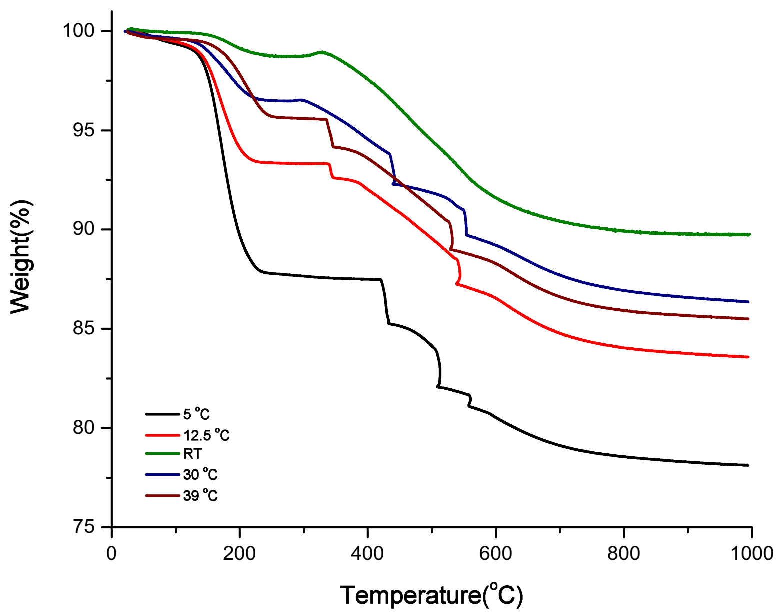


Figure S13. TGA graphs of materials synthesized in dichloromethane at different temperatures.

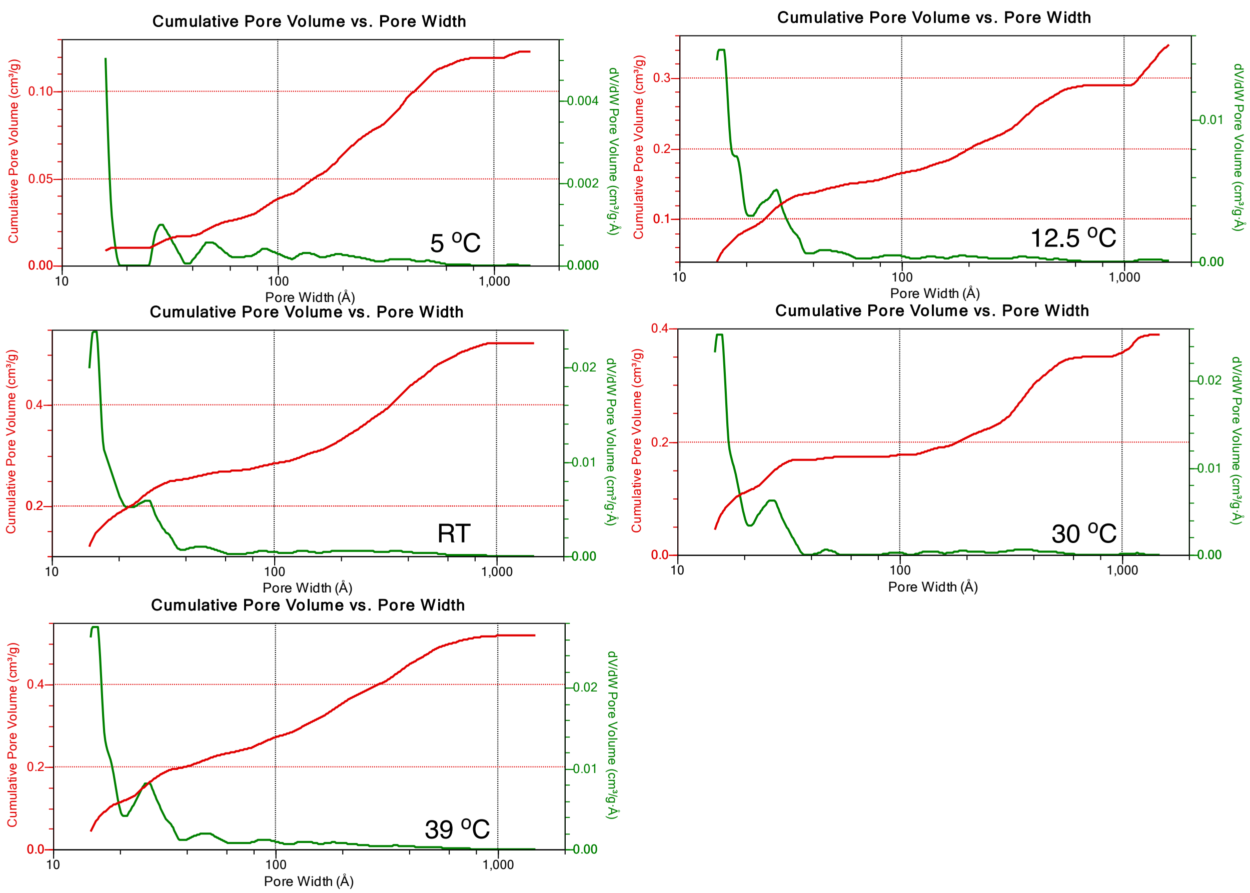


Figure S14. DFT pore size distribution graphs of materials synthesized in dichloromethane at different temperatures.

Table S11. Surface area, decomposition temperature, and ceramic yield of materials synthesized in acetonitrile at different temperatures (25 mL H_2O).

Temperature (°C)	Drying method	Surface area (m^2g^{-1})	Decomposition 5% (°C)	Ceramic yield (%)
RT	Air dry	102	151.3	70.3
35	Air dry	283	182.8	78.3
45	Air dry	336	167.4	76.8
55	Air dry	279	171.1	76.4
65	Air dry	156	143.1	69.9
70	Air dry	239	134.0	66.9
35	Air dry	998	398.3	87.4
35	Freeze dry (rinsed)	830	344.4	85.6
55	Air dry (rinsed)	780	358.1	85.9
55	Freeze dry (rinsed)	790	374.1	86.8
70	Air dry (rinsed)	785	467.8	89.8
70	Freeze dry (rinsed)	633	418.4	87.0

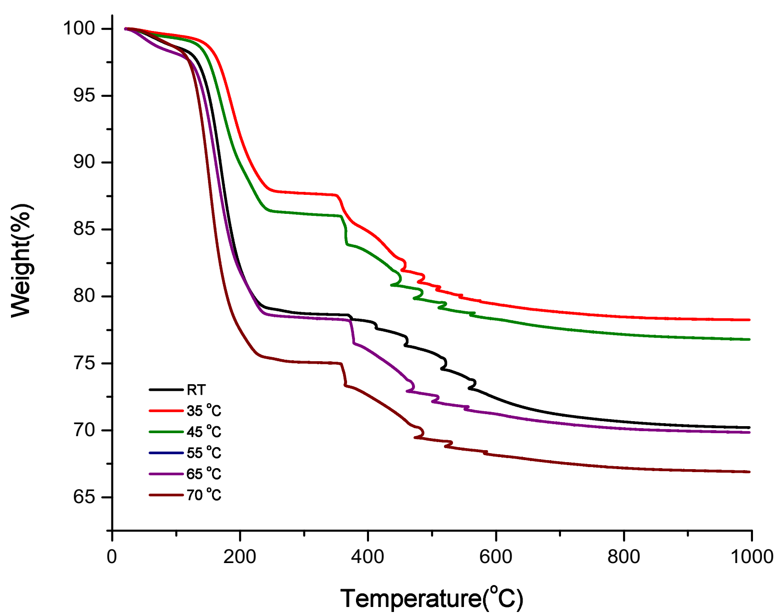


Figure S15. TGA graphs of samples from materials synthesized in acetonitrile at different temperatures.

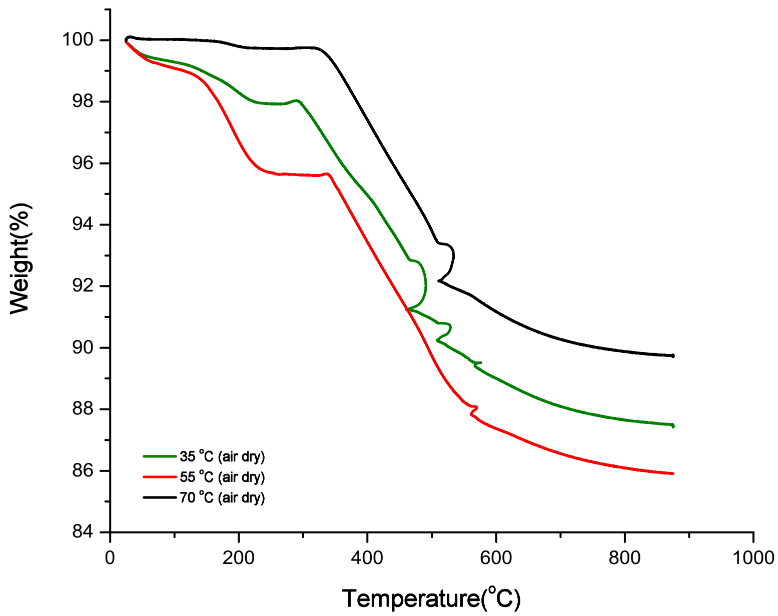


Figure S16. TGA graphs from materials synthesized in acetonitrile at different temperatures (gel washed by solvent).

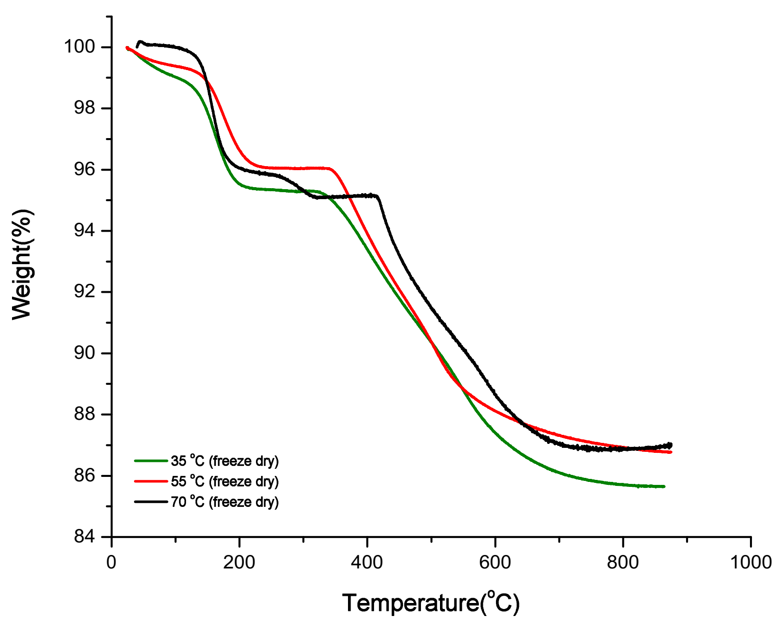


Figure S17. TGA graphs from materials synthesized in acetonitrile at different temperatures (gel washed by solvent and freeze dried).

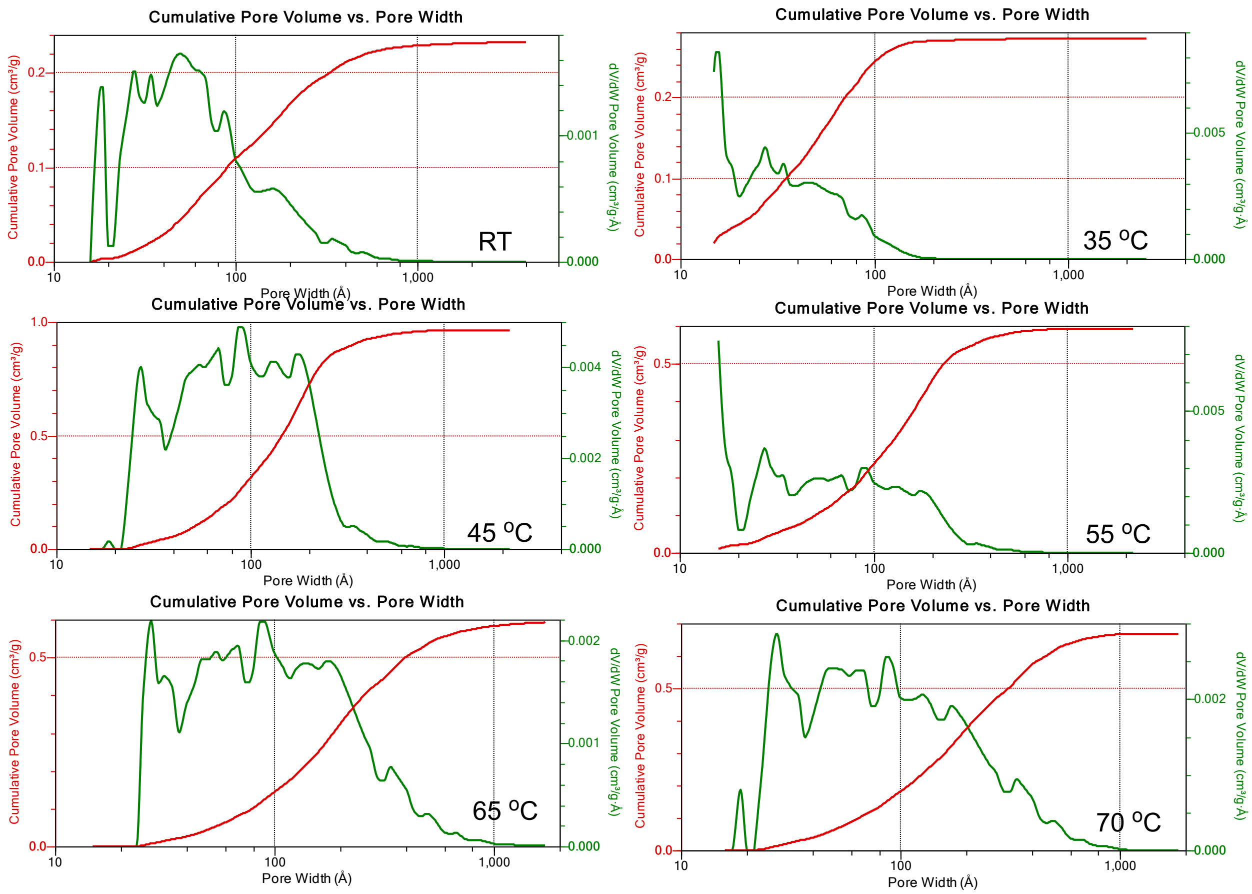


Figure S18. DFT pore size distribution graphs of materials synthesized in acetonitrile at different temperatures.

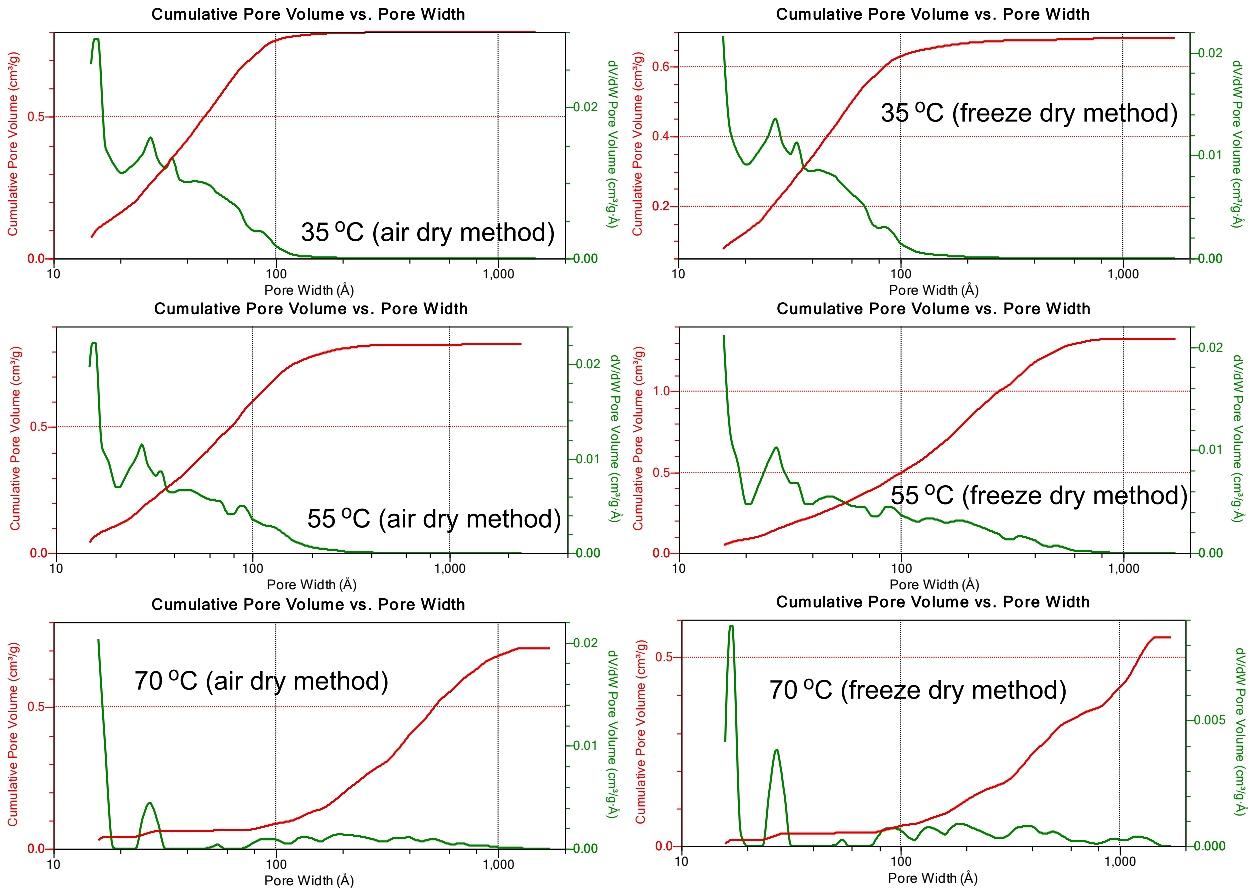


Figure S19. DFT pore size distribution graphs of materials synthesized in acetonitrile at different temperatures (gel washed by solvent (left), washed by solvent then freeze dried(right)).

SEM images

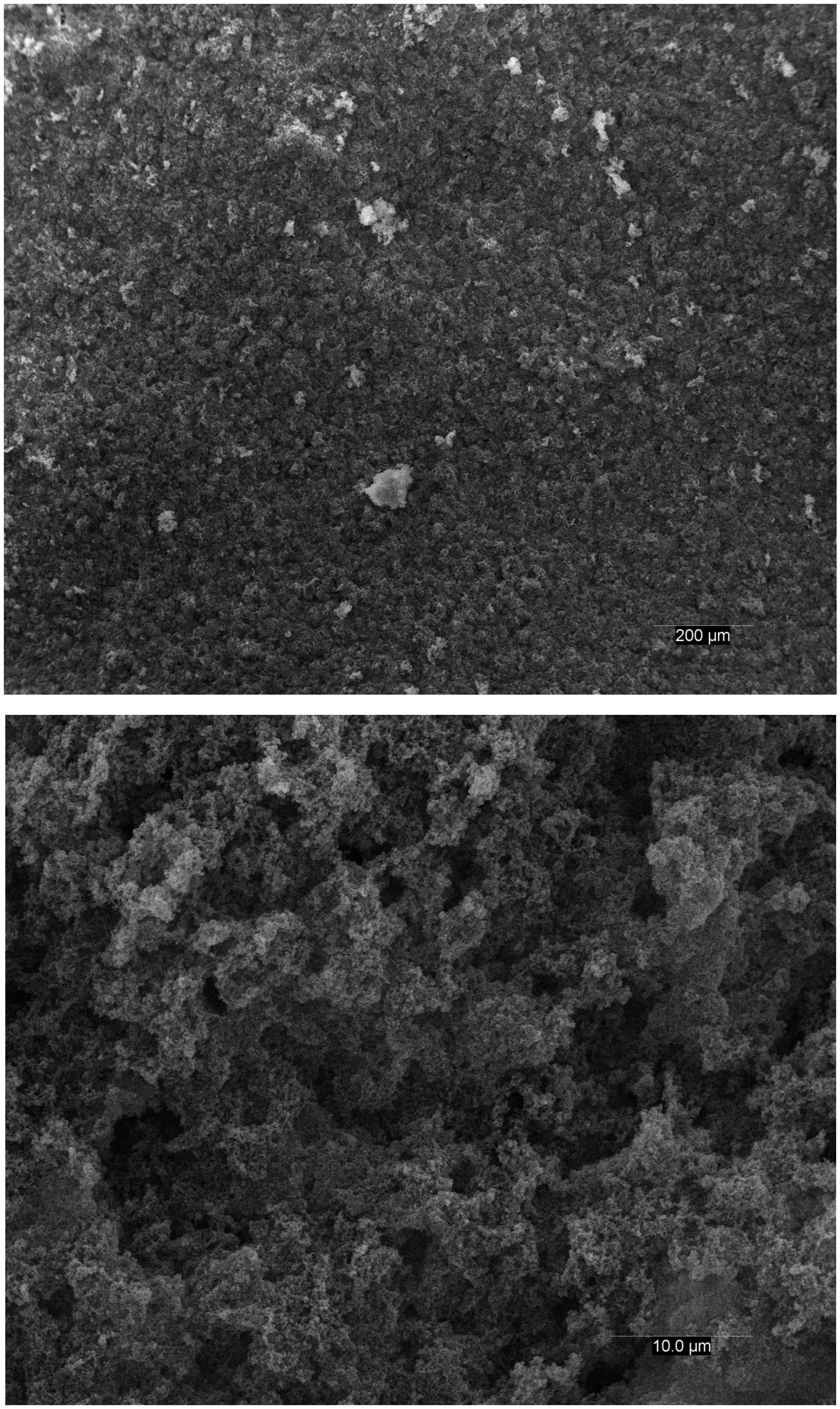


Figure S20. SEM images of particle gels synthesized in dichloromethane at room temperature (air dry method).

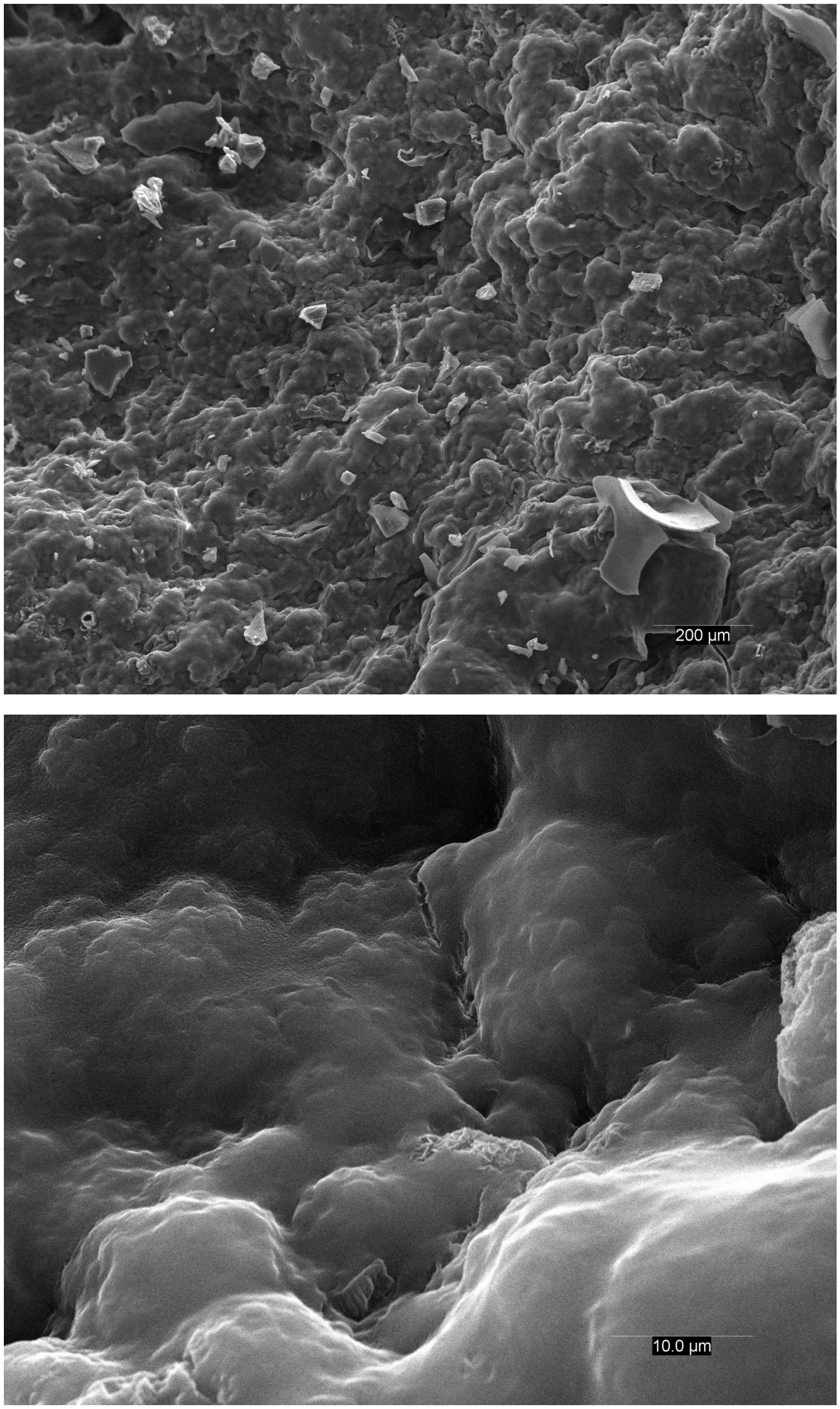


Figure S21. SEM images of particle gels synthesized in acetonitrile at room temperature (air dry method).

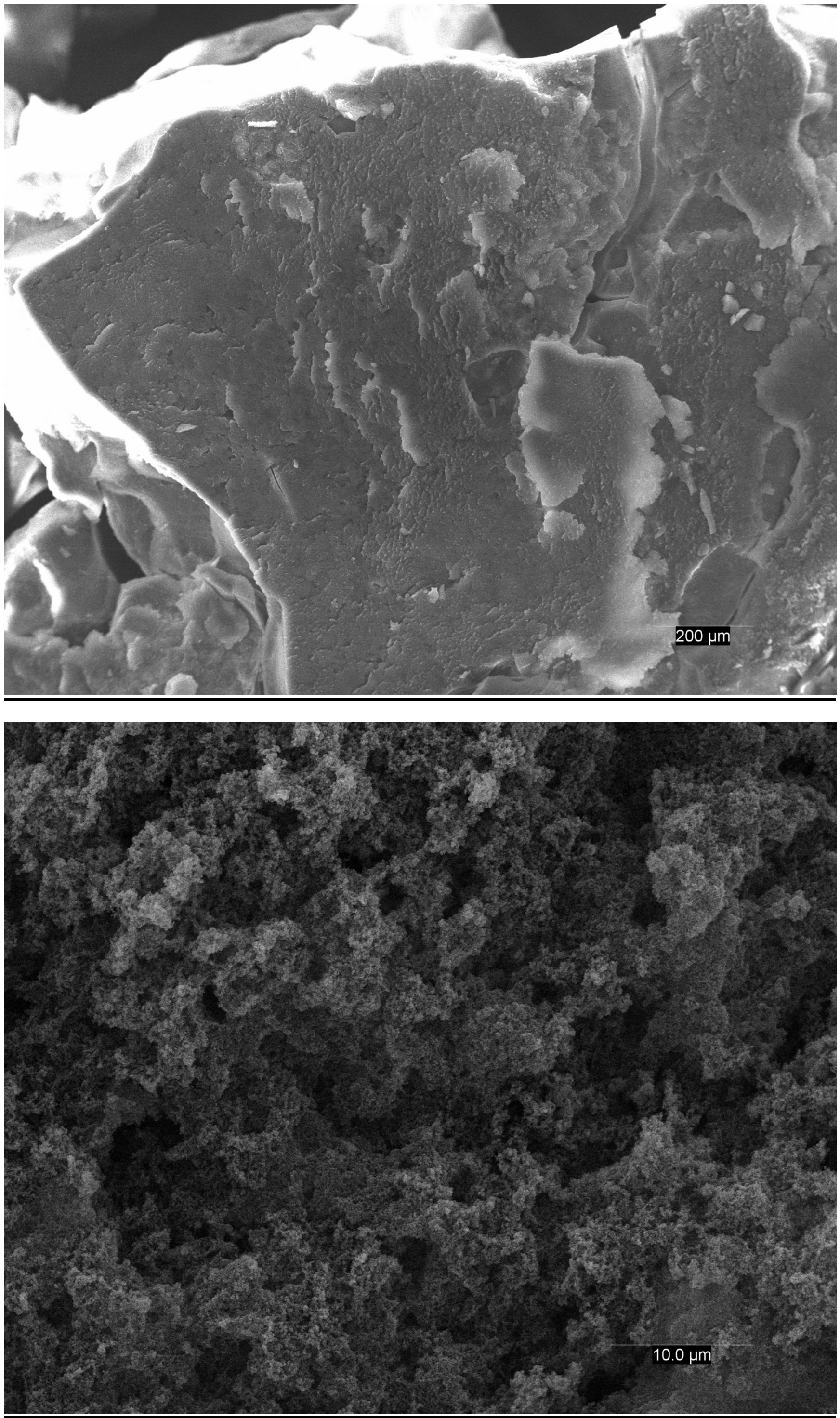


Figure S22. SEM images of light gel synthesized in acetonitrile at 70 °C with 25 mL of water (air dry method).

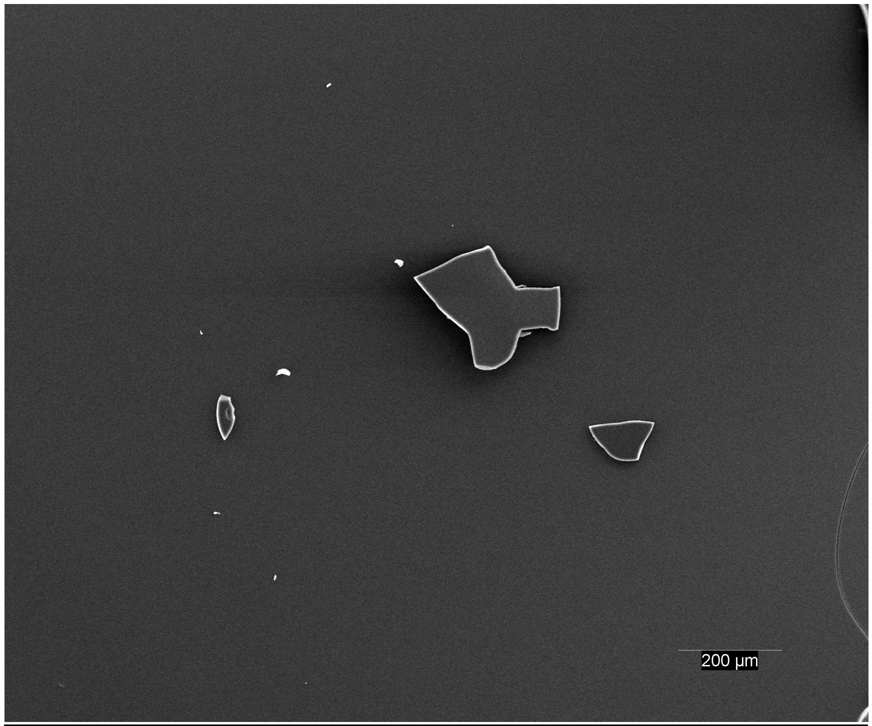


Figure S23. SEM images of condensed gel synthesized in acetonitrile at 70 °C with 0.75 mL of water (air dry method).

XRD spectra

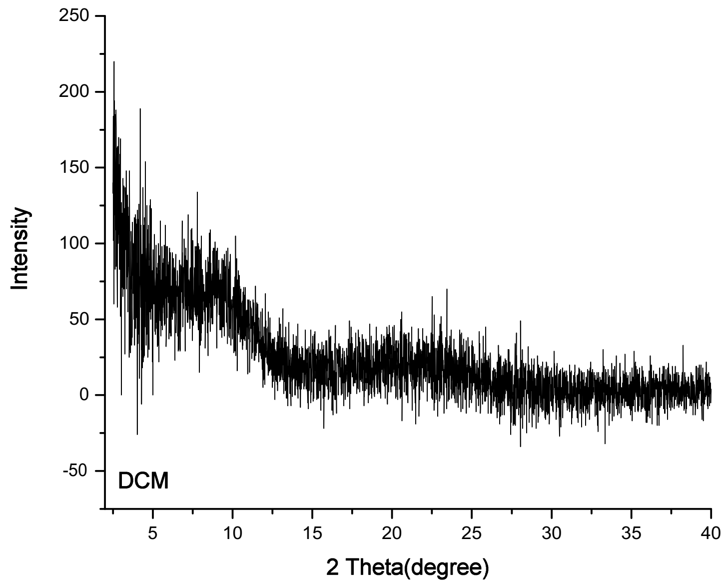


Figure S24. XRD spectra of material synthesized in dichloromethane at room temperature (air dry method).

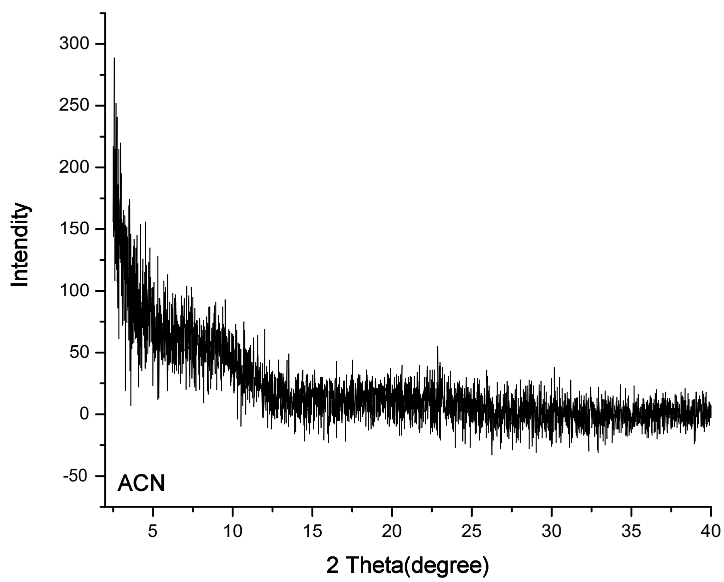


Figure S25. XRD spectra of material synthesized in acetonitrile. at room temperature (air dry method).

Solvent Uptake

Table S12. Drying and reabsorption behavior of materials synthesized in acetonitrile at 70°C (% base on original weight).

Drying time	Original weight	Dried to Weight	Weight After Reabsorption
1hr	4.426g	2.919g (66%)	3.794g (85.7%)
2hr	4.383g	1.191g (27%)	1.989g (45.4%)
3hr	4.532g	0.601g (13.3%)	1.279g (28.2%)
4hr	4.682g	0.177g (3.8%)	1.26 (26.9%)

Table S13. Drying and reabsorption recycle test of materials synthesized in acetonitrile at 70°C (% base on original weight).

Recycle times	Original weight	Dried to Weight	Weight After Reabsorption
0	4.426g	2.919g (66.0%)	3.794g (85.7%)
1	3.794g (85.7%)	1.793g (40.5%)	3.154g (71.3%)
2	3.154g (71.3%)	1.189g (26.9%)	2.811g (63.5%)

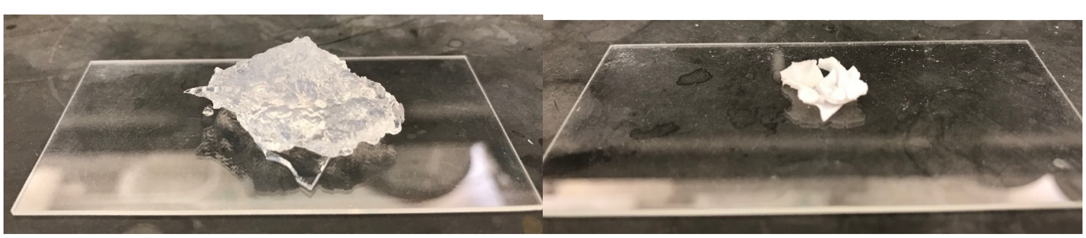


Figure S26. Before (left) and after (right) drying of material synthesized in acetonitrile at 70°C.

^{29}Si MAS-NMR

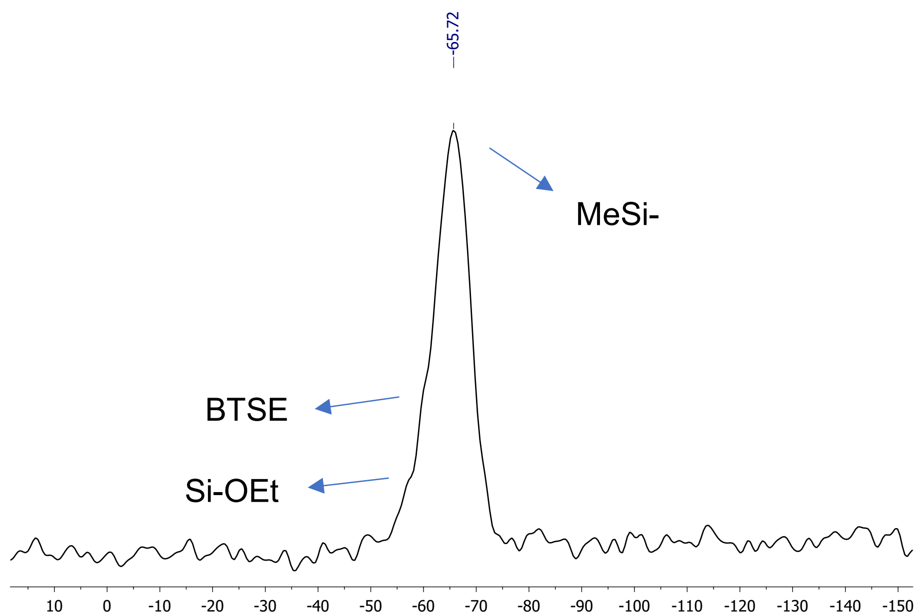


Figure S27. Si SSNMR spectra of material synthesized in acetonitrile.

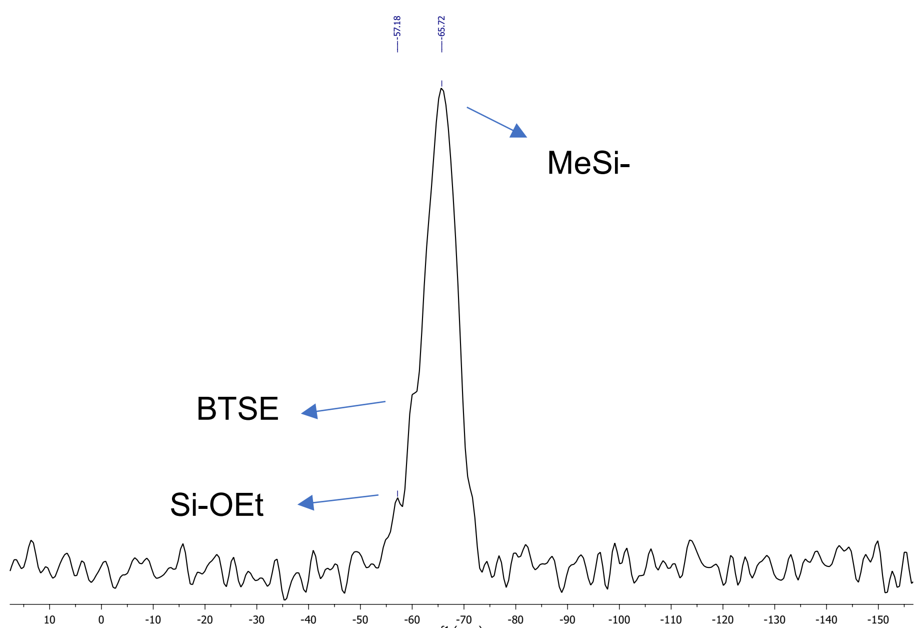


Figure S28. Si SSNMR spectra of material synthesized in dichloromethane.

Adsorption/Desorption Isotherm

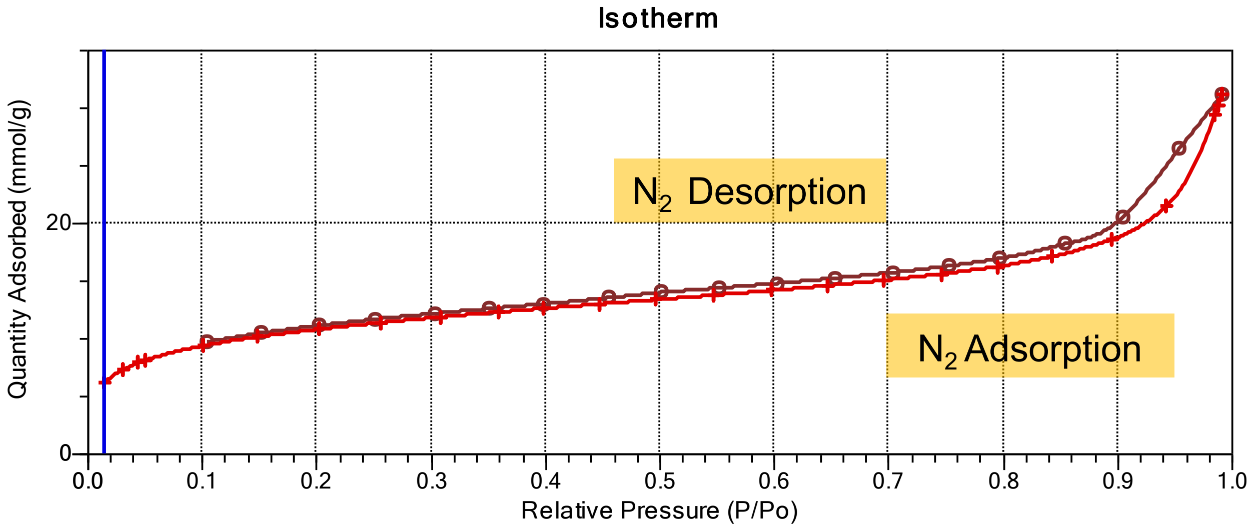
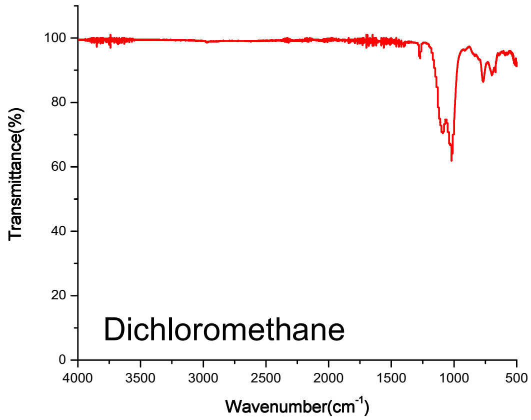
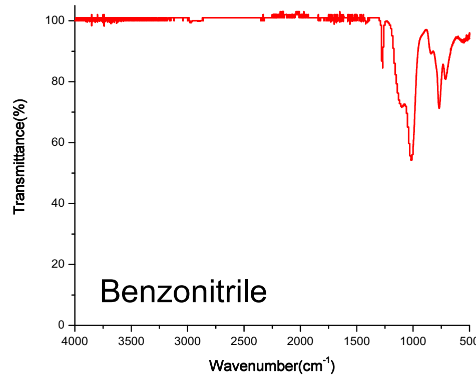
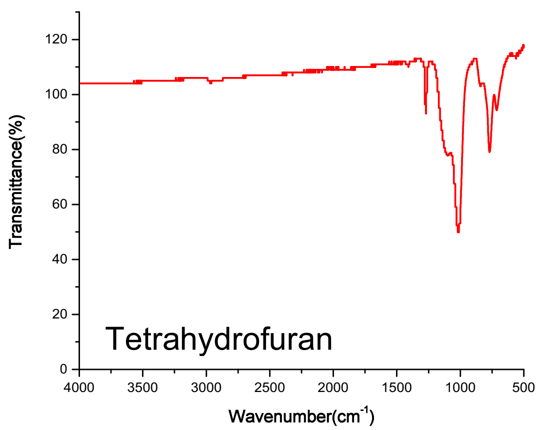
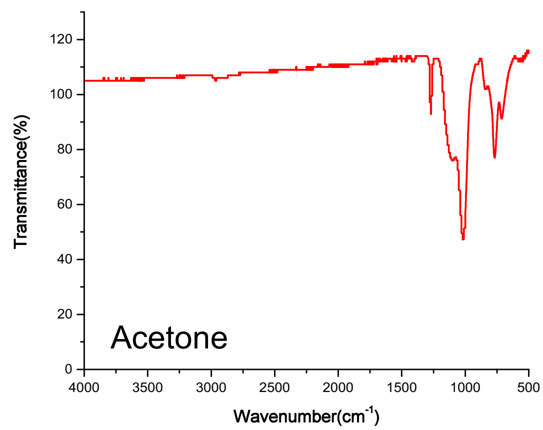


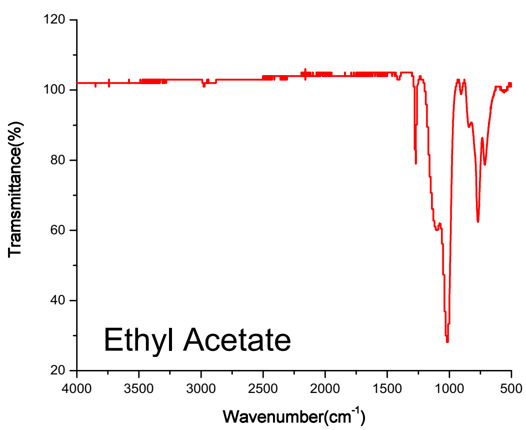
Figure S29. Representative example of nitrogen adsorption and desorption isotherm for the BET surface area analysis of material synthesized in dichloromethane under standard conditions.

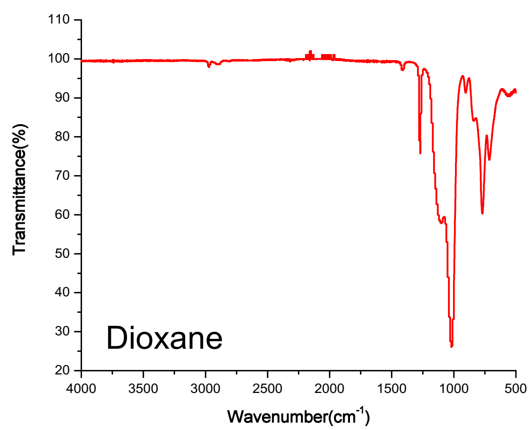

Dichloromethane
Transmittance(%)
Wavenumber(cm-1)


Benzonitrile
Transmittance(%)
Wavenumber(cm-1)


Tetrahydrofuran
Transmittance(%)
Wavenumber(cm-1)


Acetone
Transmittance(%)
Wavenumber(cm-1)


Ethyl Acetate
Transmittance(%)
Wavenumber(cm-1)


Dioxane
Transmittance(%)
Wavenumber(cm-1)

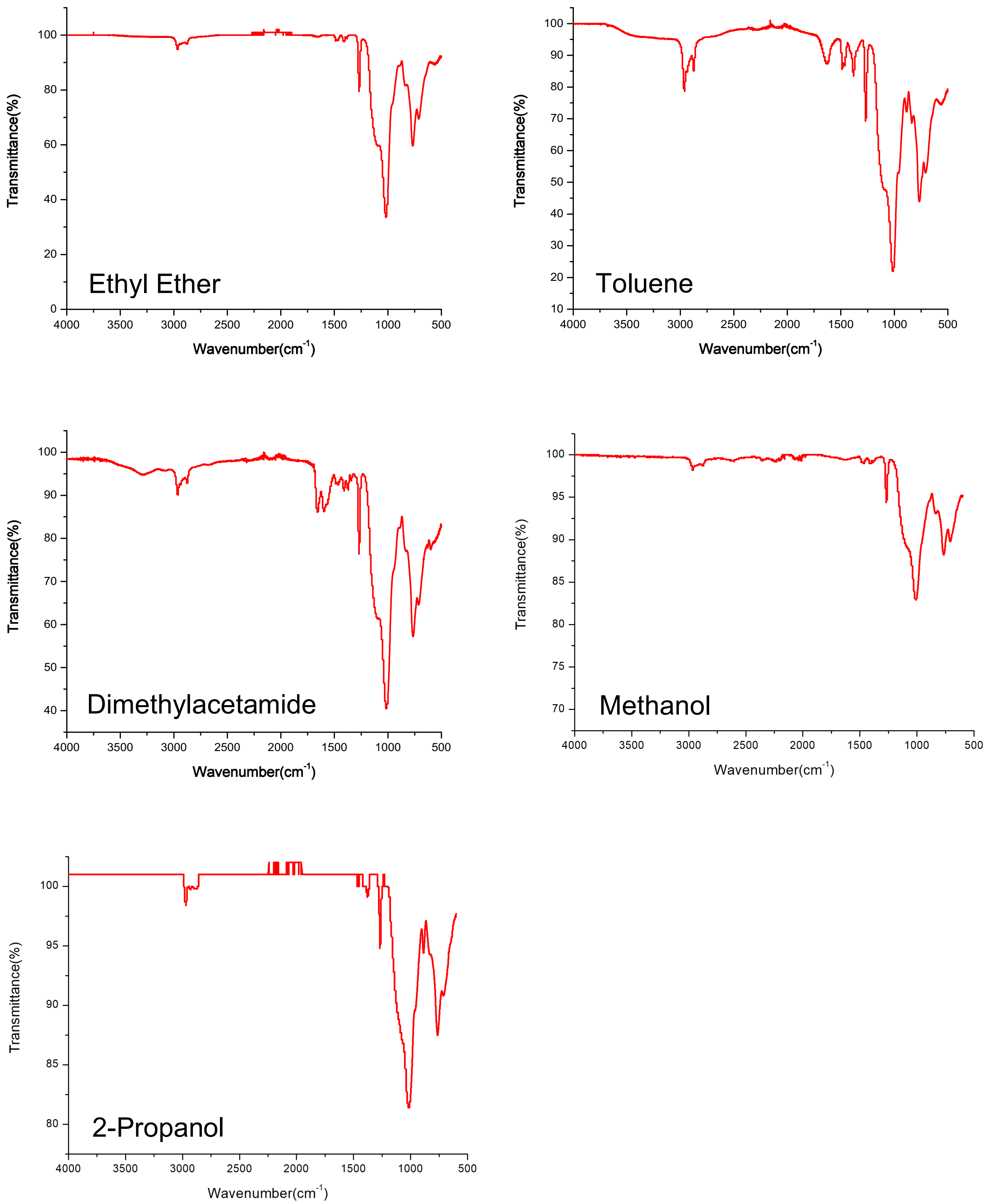
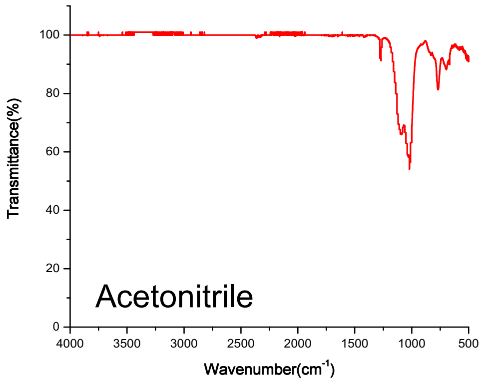
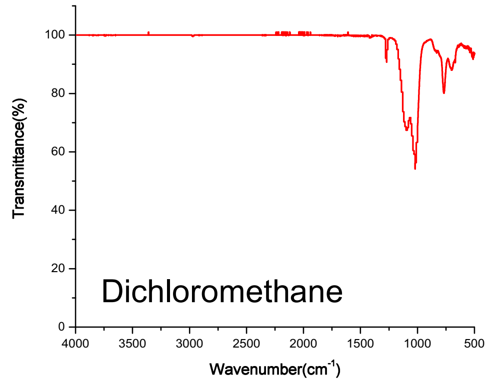
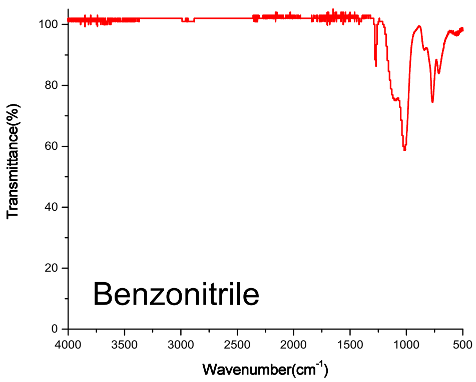
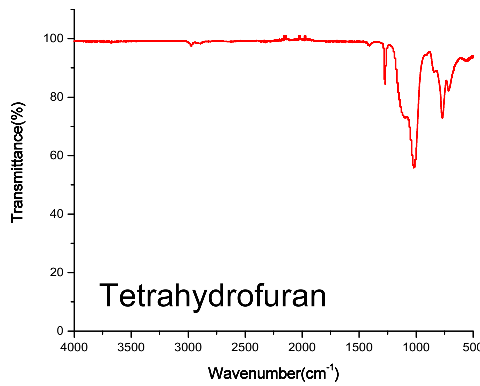


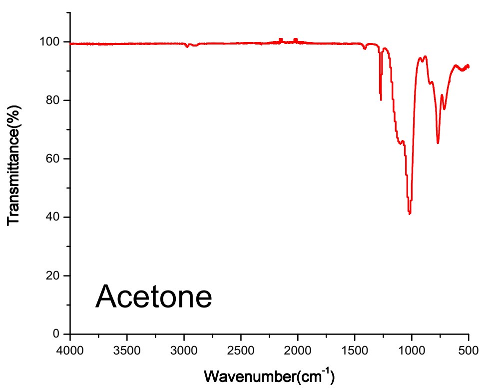
Figure S30. FTIR spectra of materials synthesized in different solvents (pre-curing).

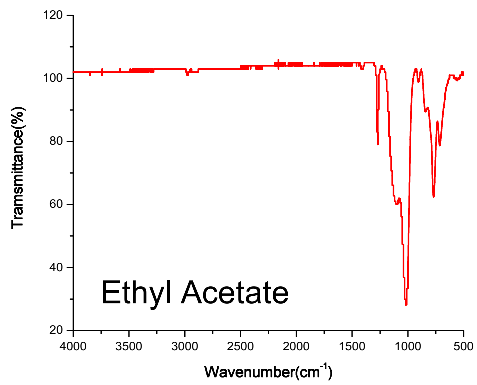

Acetonitrile
Transmittance(%)
0
20
40
60
80
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


Dichloromethane
Transmittance(%)
0
20
40
60
80
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


Benzonitrile
Transmittance(%)
0
20
40
60
80
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


Tetrahydrofuran
Transmittance(%)
0
20
40
60
80
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


Acetone
Transmittance(%)
0
20
40
60
80
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)


Ethyl Acetate
Tramsmittance(%)
20
40
60
80
100
120
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

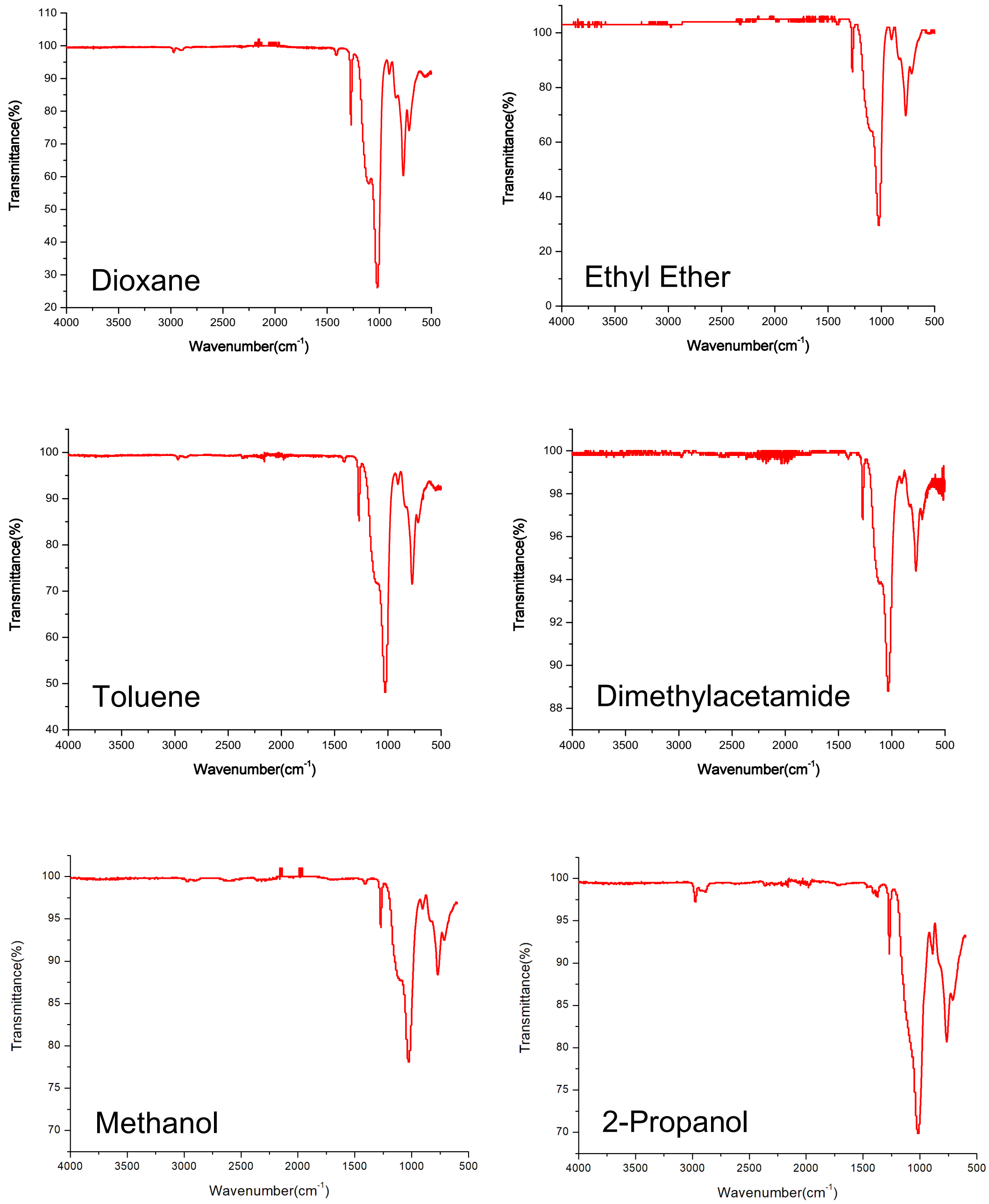
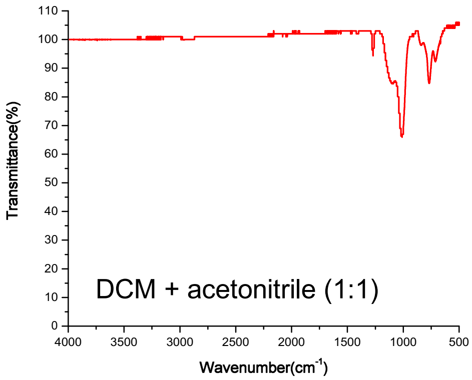
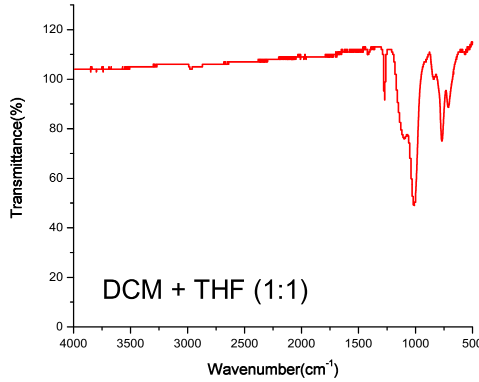
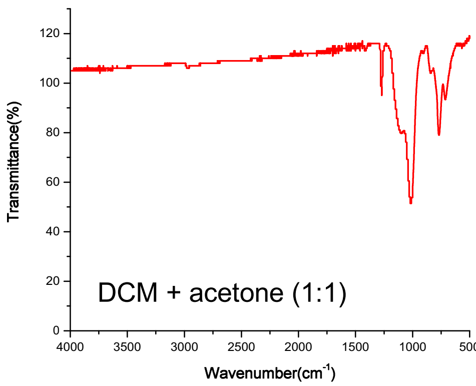
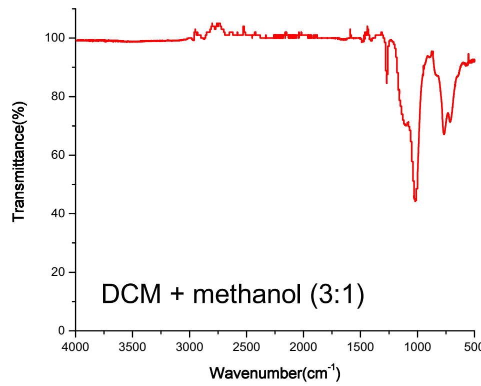


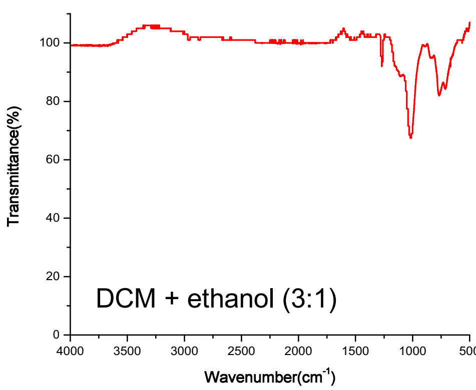
Figure S31. FTIR spectra of materials synthesized in different solvent (post-curing)

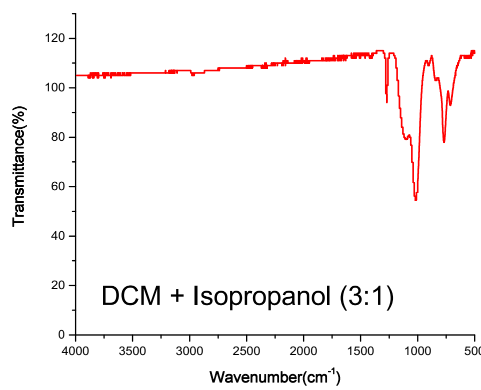

Transmittance(%)
Wavenumber(cm^{-1})
DCM + acetonitrile (1:1)


Transmittance(%)
Wavenumber(cm^{-1})
DCM + THF (1:1)


Transmittance(%)
Wavenumber(cm^{-1})
DCM + acetone (1:1)


Transmittance(%)
Wavenumber(cm^{-1})
DCM + methanol (3:1)


Transmittance(%)
Wavenumber(cm^{-1})
DCM + ethanol (3:1)


Transmittance(%)
Wavenumber(cm^{-1})
DCM + Isopropanol (3:1)

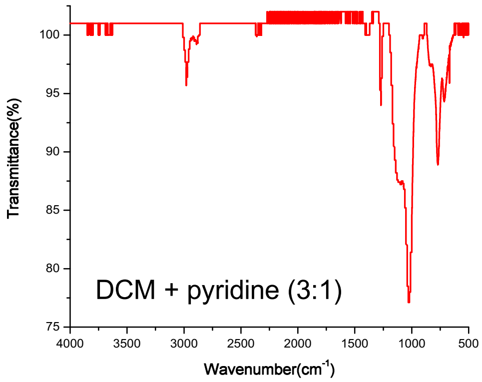
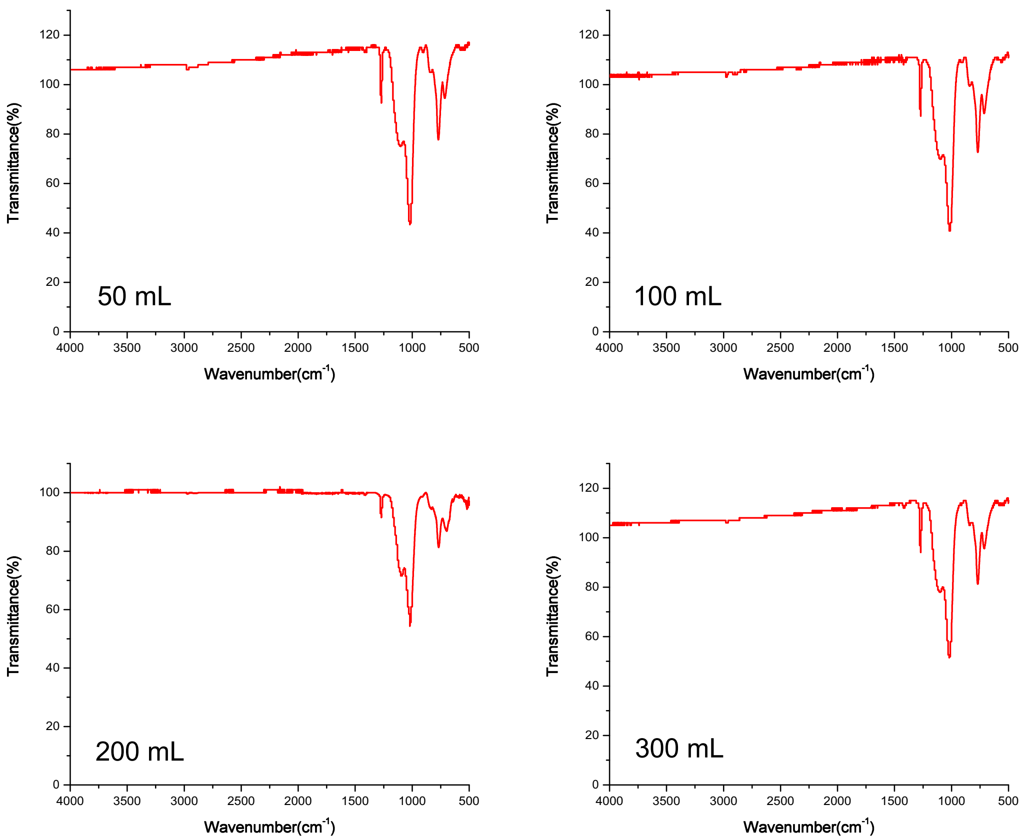


Figure S32. FTIR spectra of materials synthesized in in mixed solvents.



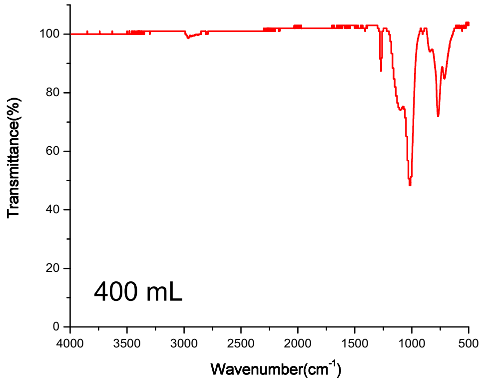
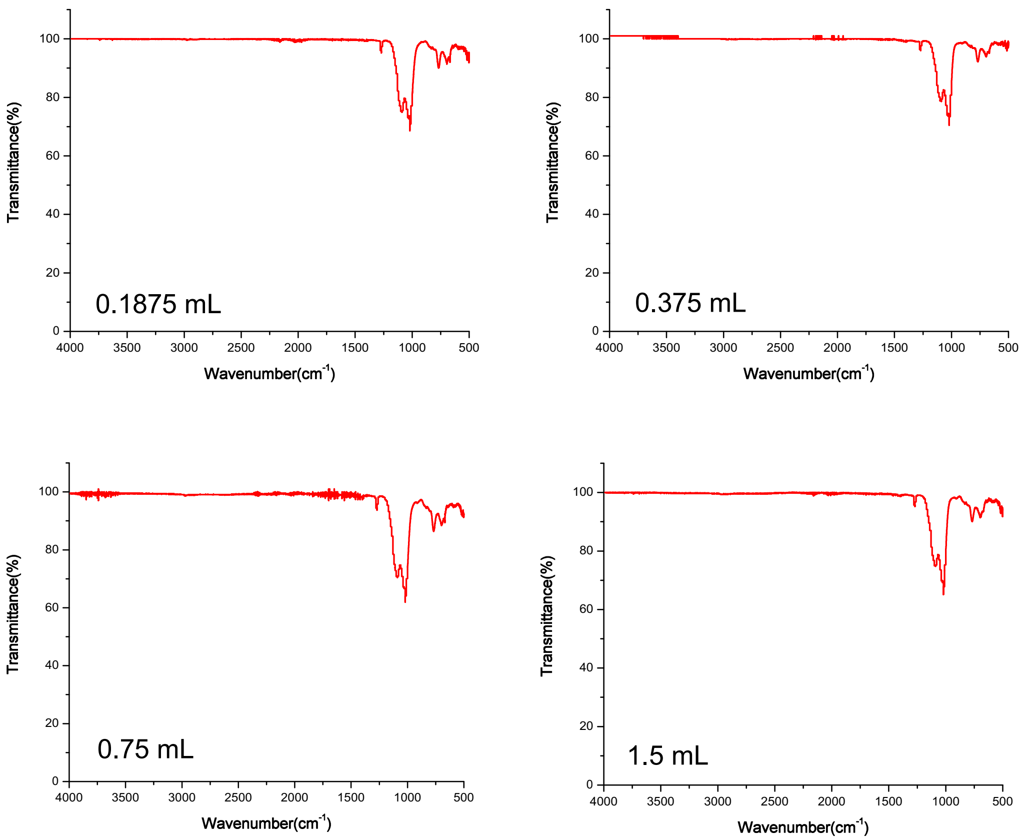


Figure S33. FTIR spectra of materials synthesized in different amounts of acetonitrile.



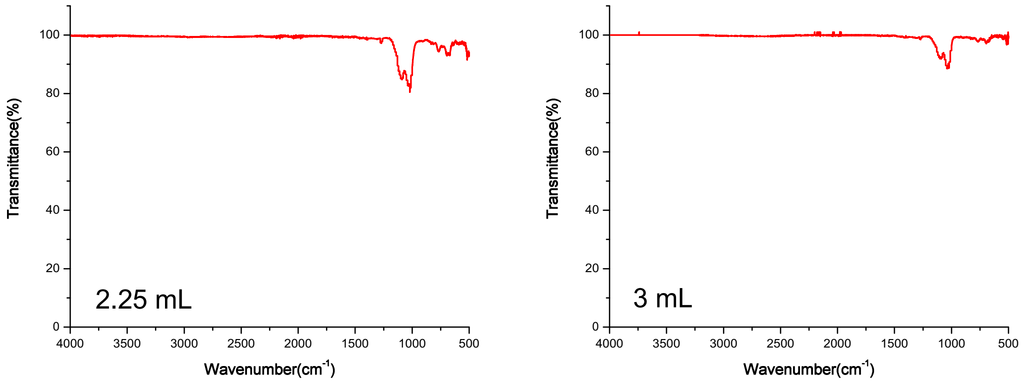
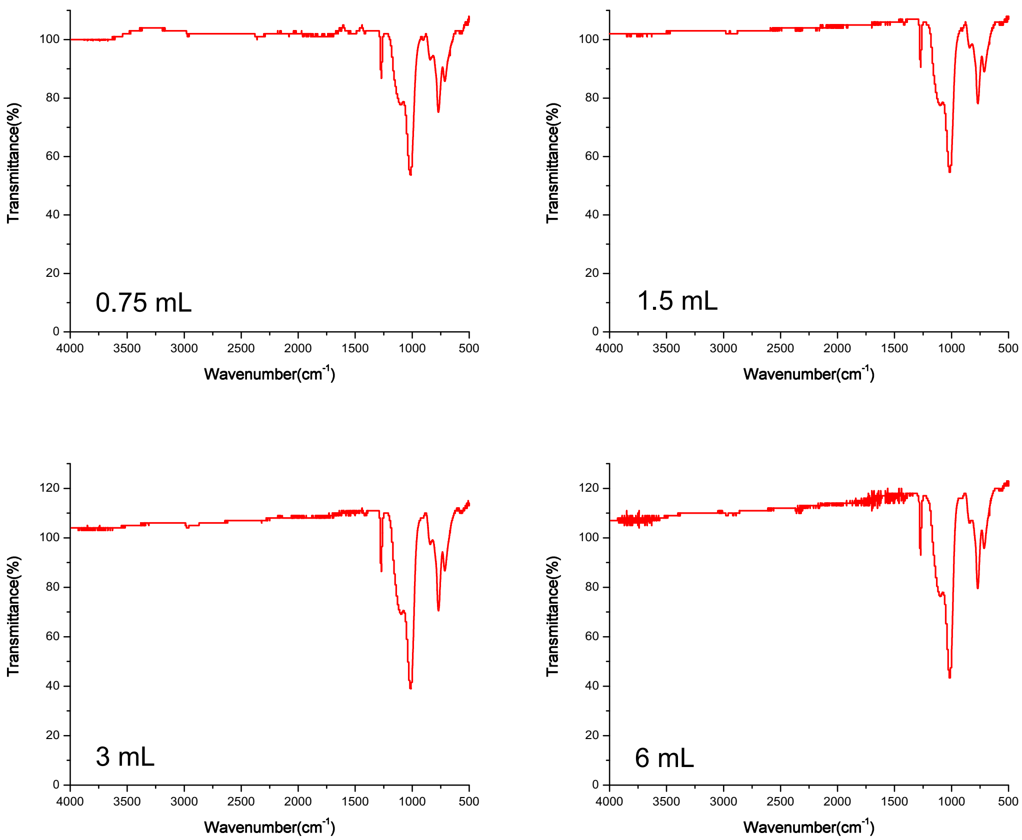


Figure S34. FTIR spectra of materials synthesized in dichloromethane with different amounts of water.



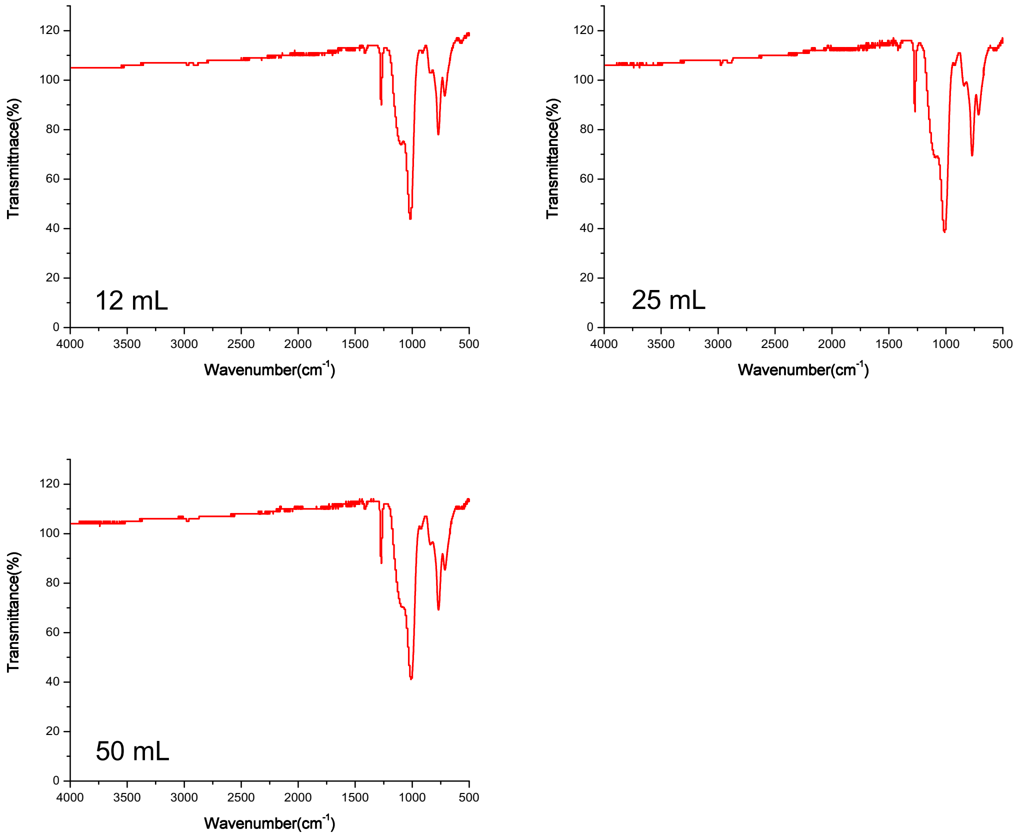


Figure S35. FTIR spectra of materials synthesized acetonitrile with different amounts of water.

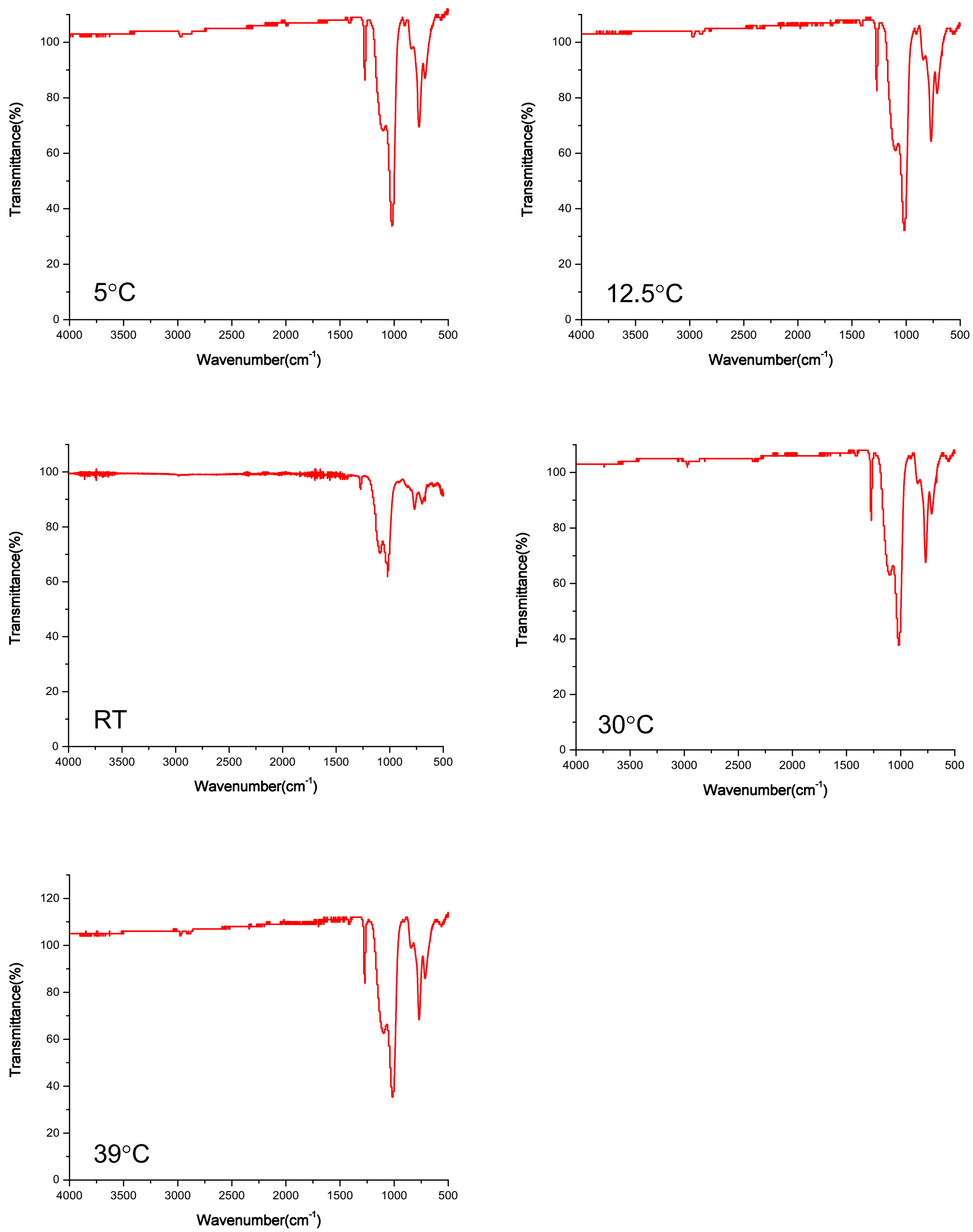


Figure S36. FTIR spectra of materials synthesized in dichloromethane at different temperatures.

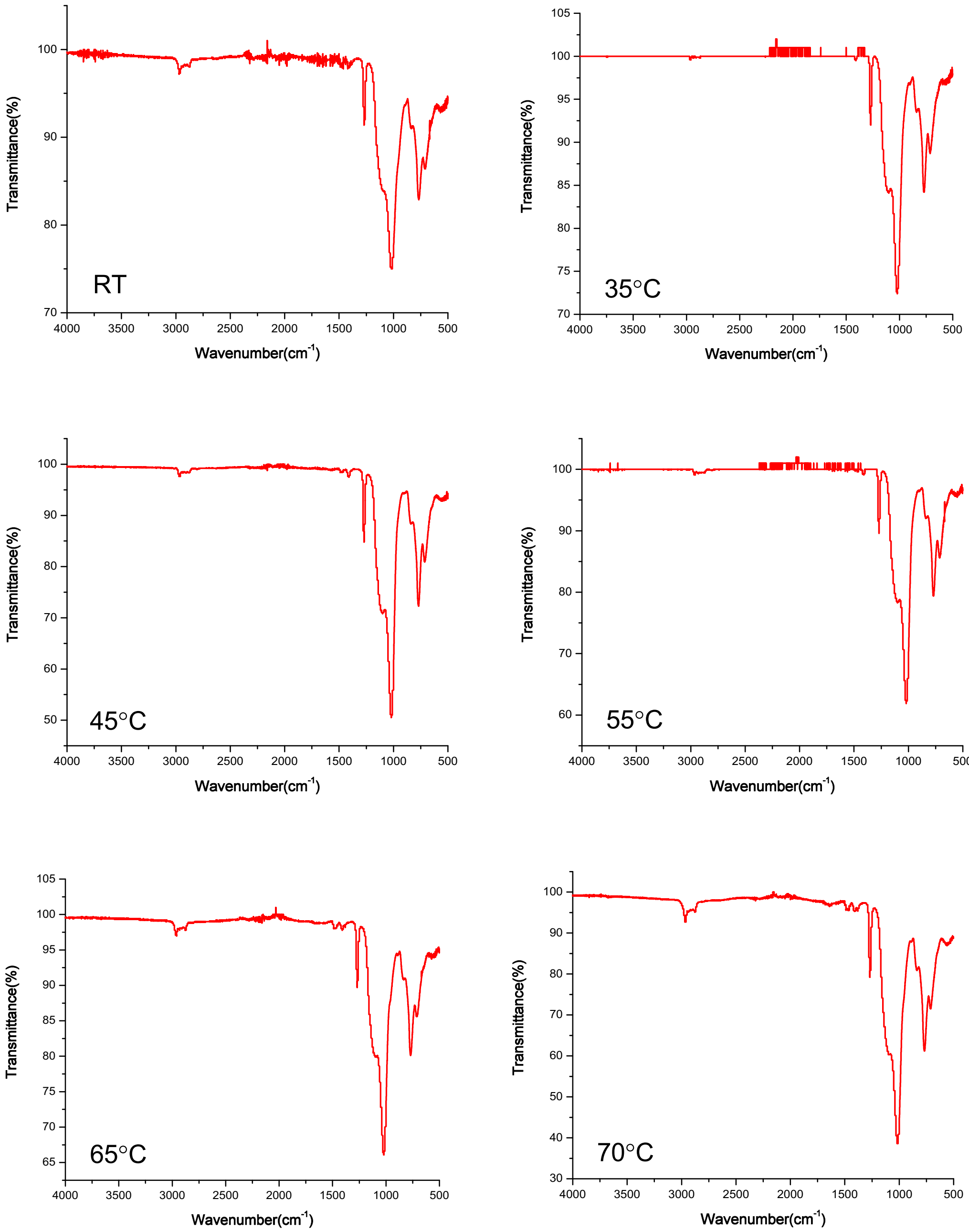


Figure S37. FTIR spectra of materials synthesized in acetonitrile at different temperatures.