Electronic Supplementary Material (ESI) for Soft Matter

Supporting information

Table S1. Gelation behavior of PM in methanol-water mixtures with different water content.

Water content	Gelation behavior	Gelation after cooled at 20 ^{o}C
0%	S	-
10%	S	-
20%	S	-
25%	G	27min
30%	G	13min
40%	G	5min
50%	G	3min
60%	G	3min
70%	P	-
100%	P	-

Concentrations: 4% w/v. G: gel; S: solution; P: precipitation.

Table S2. Summary of group additivity values of PM.

Fedors Method								
Groups	$-CH_3$	$-CH_2$	$-CH<$	$-NH_2$	$-PO_3^{-a}$	$-C=N-$	$=N^+H-^b$	conjugated double bond
Occurrences, N_i	4	10	2	3	1	3	1	3
E_i(J/mol)	4710	4940	3430	12560	14230	18840	11720	1670
V_i(cm^3/mol)	33.5	16.1	-1	19.2	22.7	23.1	5	-2.2
Sum	$E_{coh}=\sum E_iN_i=196920$ $V=\sum V_i N_i=441$							
$\delta(J^{1/2}/cm^{3/2})$	$\delta=(E_{coh}/V)^{1/2}=21.1$							

[a] the value of $-PO_3$for $-PO_3^-$; [b]the value of $=N-$for $=N^+H-$

These data are taken fromVan Krevelen, D. W. H. P. J. Properties of Polymers. Elsevier Scientific Publishing: New York, 1976.

Table S3. Calculated Hansen solubility parameters of mixed-solvents

Solvents	δ_d/MPa$^{1/2}$	δ_p/MPa$^{1/2}$	δ_h/MPa$^{1/2}$	Gelation behavior
MeOH:H_2O(v/v)				
90:10	15.14	12.7	24.3	S
75:25	15.20	13.2	27.3	G
70:30	15.22	13.4	28.3	G
60:40	15.26	13.8	30.3	G
50:50	15.30	14.2	32.3	G
40:60	15.34	14.5	34.3	G
30:70	15.38	14.9	36.3	P
10:90	15.46	15.6	40.3	P
EtOH:H_2O(v/v)				
90:10	15.8	9.5	21.7	S
70:30	15.7	11.0	26.3	S
50:50	15.7	12.4	30.9	G
30:70	15.6	13.8	36.4	G
10:90	15.5	15.3	40.0	P
n-propanol:H_2O(v/v)				
90:10	16.0	7.7	19.9	S
70:30	15.9	9.6	24.9	S
50:50	15.8	11.4	29.9	G
30:70	15.7	13.2	34.8	G
10:90	15.6	15.1	39.8	G-P
EG[b]:H_2O(v/v)				
90:10	16.9	11.5	27.6	G
70:30	16.6	12.5	30.9	G
50:50	16.3	13.5	34.2	G
30:70	16.0	14.5	37.4	G-P
10:90	15.7	15.5	40.7	P
GL[c]:H_2O(v/v)				
90:10	17.2	12.5	30.6	G
70:30	16.8	13.3	33.2	G
50:50	16.5	14.1	35.8	P
30:70	16.1	14.8	38.4	P
10:90	15.7	15.6	41.0	P
DMF:H_2O(v/v)				
90:10	17.2	13.9	14.4	S
70:30	16.8	14.4	20.6	G
50:50	16.5	14.9	26.8	G
30:70	16.1	15.3	33.0	G

10:90	15.7	15.8	39.2	G
DMSO:H_2O(v/v)				
90:10	18.1	16.4	13.4	S
70:30	17.5	16.3	19.8	G
50:50	17.0	16.2	26.3	G
30:70	16.4	16.1	32. 7	G
10:90	15.8	16.0	39.1	G

[a] Concentration: 4% (w/v). S: solution; G: gel; P: precipitation; G-P: gel-then-precipitation.
[b] ethylene glycol; [c] glycerol

The solubility parameter values of the mixed solvents calculated according to $\delta=\Sigma\varphi_i\delta_i$ (Equ. 68 of Chemical Reviews, 1975, 75, 731-753.)

Table S4. Calculated solubility parameters and Flory-Huggins parameter for PM and mixed-solvents

Solvents	Hildebrand solubility parameter(δ) ($J^{1/2}/cm^{3/2}$)	Molar volume(V)(cm^3 /mol)	Flory-Huggins parameter (χ)	gelation behavior[a]
PM	21.1			
MeOH:H_2O(v/v)				
90:10	31.5	36.2	1.58	S
75:25	34.3	31.0	2.16	G
70:30	35.2	29.5	2.36	G
60:40	37.0	27.1	2.75	G
50:50	38.8	25.0	3.16	G
40:60	40.6	23.2	3.56	G
30:70	42.4	21.6	3.97	P
10:90	46.1	19.1	4.80	P
EtOH:H_2O(v/v)				
90:10	28.2	47.8	0.97	S
70:30	32.6	34.9	1.85	S
50:50	37.0	27.5	2.79	G
30:70	41.3	22.7	3.75	G
10:90	45.7	19.3	4.73	P
n-propanol:H_2O(v/v)				
90:10	26.7	56.7	0.71	S
70:30	31.4	38.1	1.63	S
50:50	36.1	28.8	2.61	G
30:70	40.8	23.2	3.64	G
10:90	45.5	19.4	4.68	G-P
EG[b]:H_2O(v/v)				
90:10	31.7	46.1	2.09	G
70:30	35.3	34.2	2.79	G
50:50	38.9	27.2	3.48	G
30:70	42.5	22.6	4.17	G-P
10:90	46.1	19.3	4.87	P
GL[c]:H_2O(v/v)				
90:10	35.2	56.1	4.51	G
70:30	38.0	38.2	4.42	G
50:50	40.9	29.0	4.56	P
30:70	43.7	23.3	4.79	P

10:90	46.5	19.5	5.07	P
DMF:H_2O(v/v)				
90:10	27.1	57.9	0.84	S
70:30	31.7	38.8	1.77	G
50:50	36.4	29.1	2.73	G
30:70	41.0	23.3	3.72	G
10:90	45.6	19.5	4.71	G
DMSO:H_2O(v/v)				
90:10	26.8	55.0	0.73	S
70:30	31.5	37.8	1.65	G
50:50	36.2	28.7	2.64	G
30:70	40.9	23.2	3.66	G
10:90	45.6	19.5	4.70	G
acetone-water (1:1 v/v)	34.1	29.0	1.98	G
acetonitrile-water (1:1 v/v)	36.1	26.8	2.44	G
[a] Concentration: 4% (w/v). S: solution; G: gel; P: precipitation; G-P: gel-then-precipitation. [b] ethylene glycol; [c] glycerol				

The solubility parameter values of the mixed solvents calculated according to $\delta=\Sigma\phi_i\delta_i$ (Equ. 68 of Chemical Reviews, 1975, 75, 731-753.)

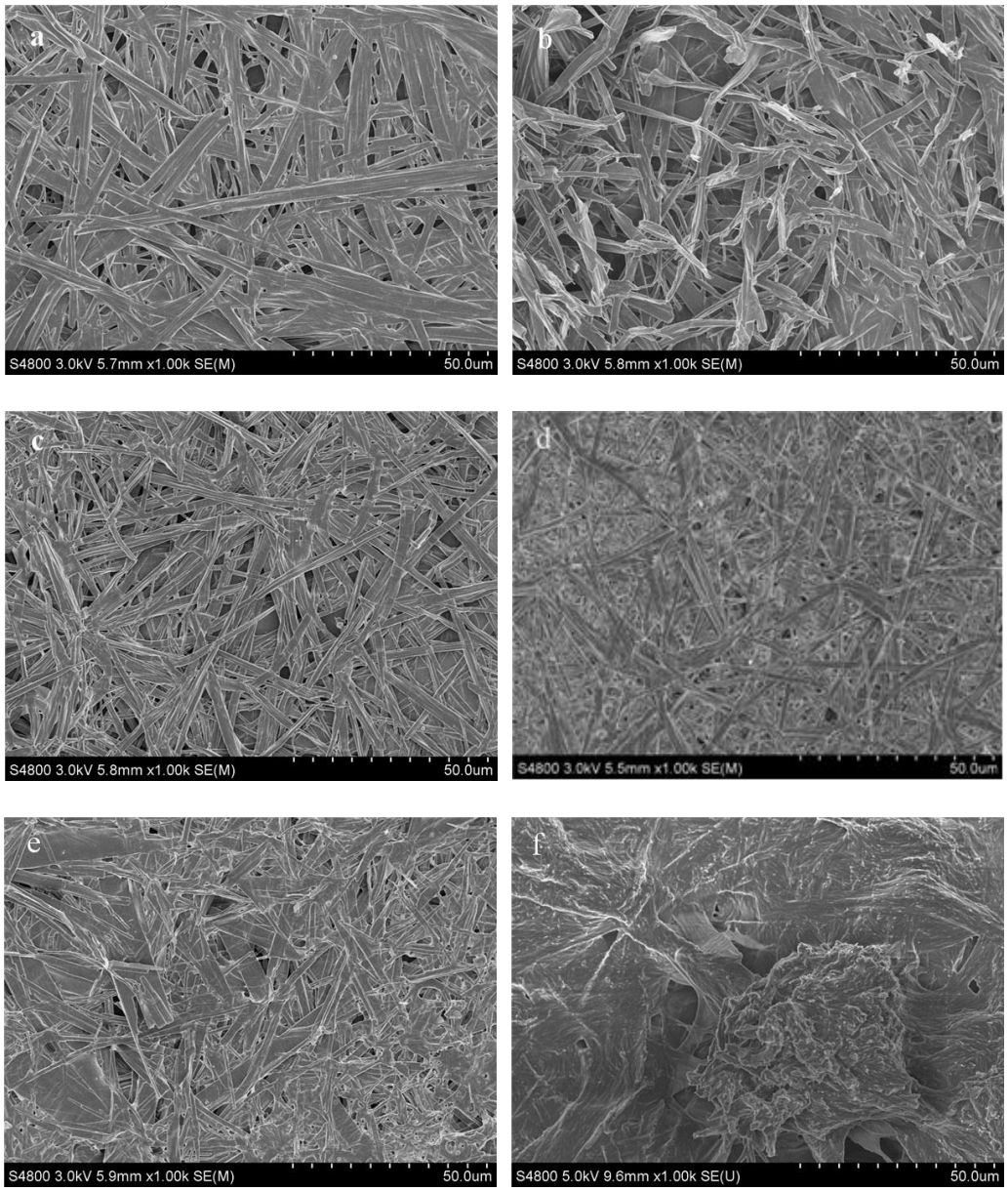

Fig. S1 SEM images of xerogels (4% w/v) at different water content: (a) 25%; (b) 30%; (c) 40%; (d) 50%; (e) 60%; (f) 70%.

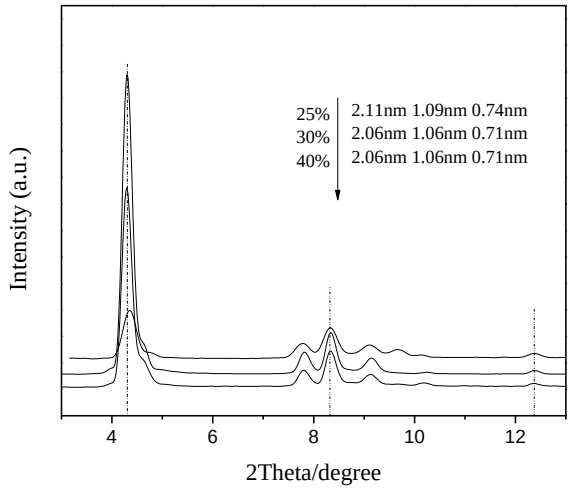

Fig. S2 XRD patterns of xerogels (4% w/v) at different water content: 25%, 30% and 40%.

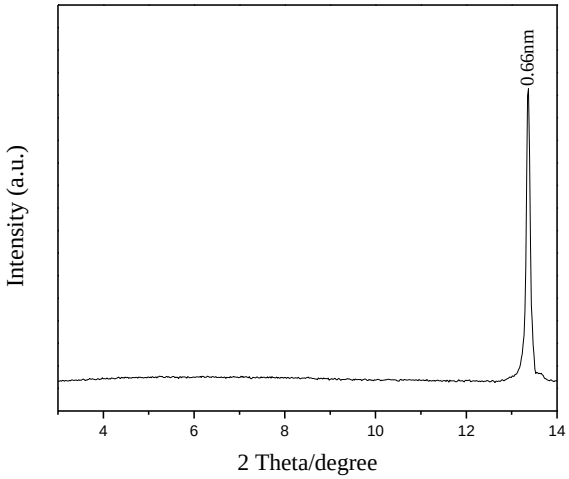

Fig. S3 XRD patterns of melamine.

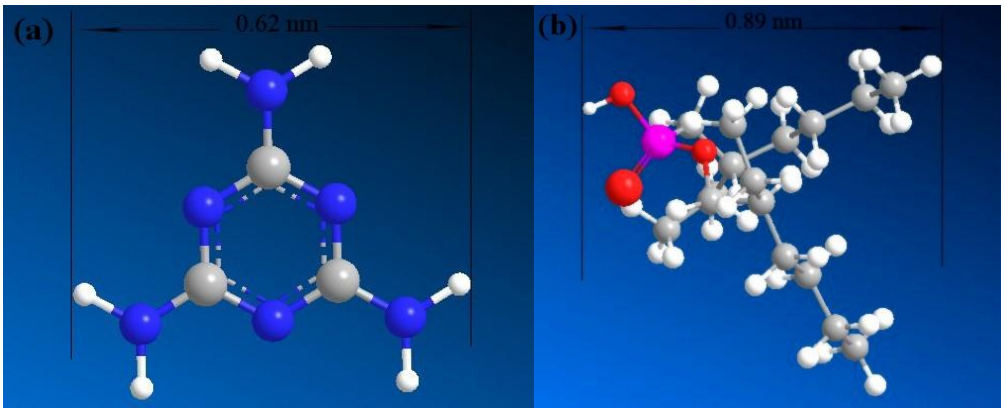

Fig. S4 Energy minimized molecular models calculated by MM2 method: (a) melamine and (b) 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester.

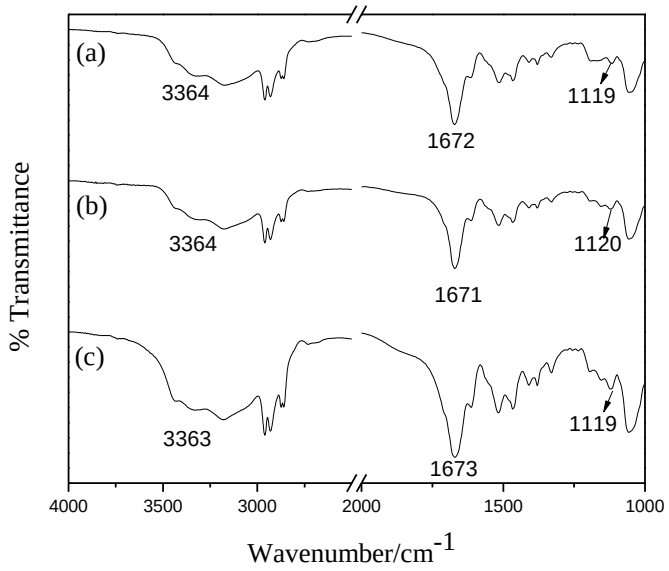

Fig. S5 FTIR spectra of PM (4% w/v) at different water content: (a) 25%, (b) 30%, (c) 40%.

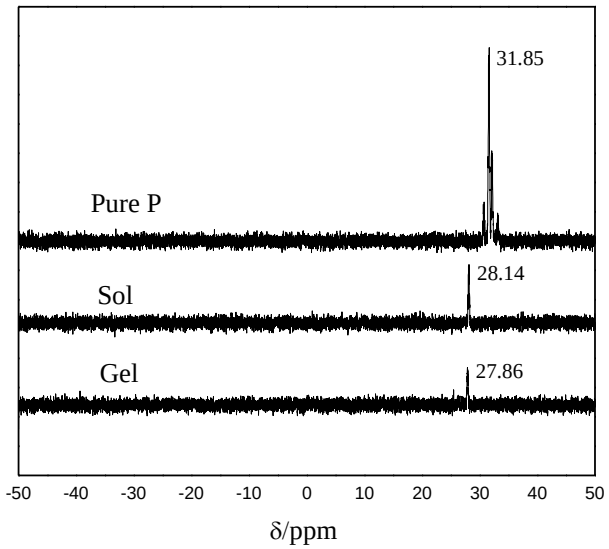

Fig. S6 ^{31}P-NMR spectra of pure P, the mixed-solvent gel system of their sol and gel states in MeOH-D_2O (v/v=1:1).

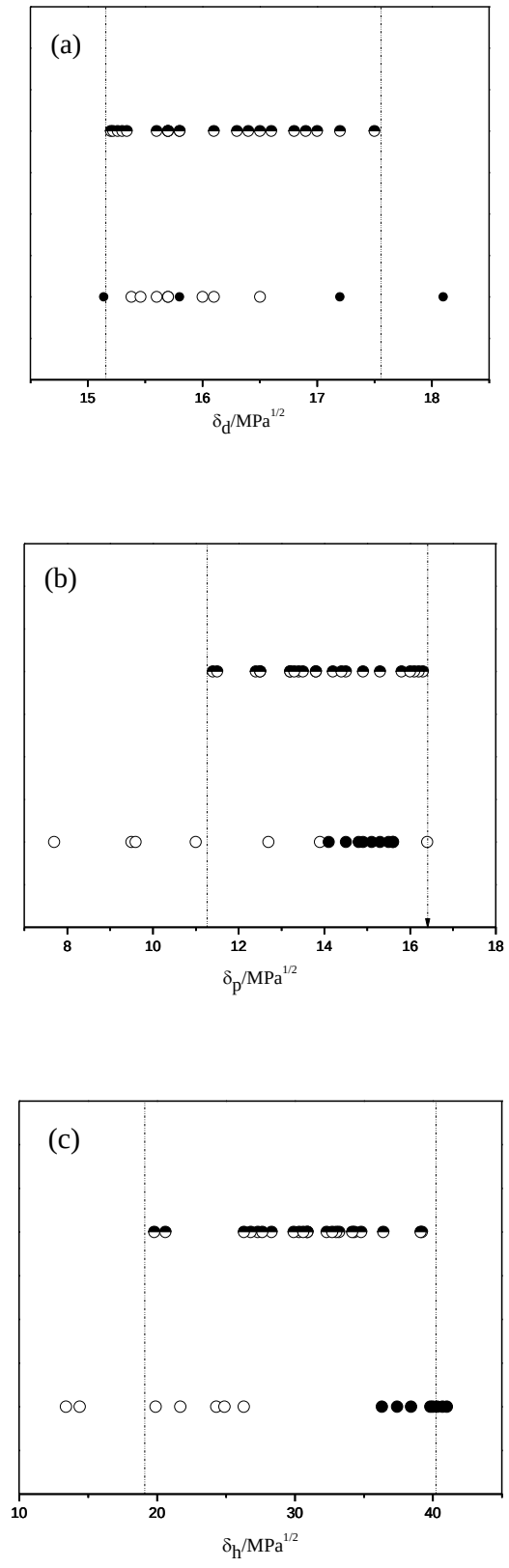

Fig. S7 Hansen-parameter-depending behaviors of PM in the studied solvents: (a) δ_d, (b) δ_p, (c) δ_h. S: solution, open circles; G: gelation, half closed cycles; P: precipitation, closed cycles.