

Electronic Supporting Information for:

Replacement of Hazardous Chemicals Used in Engineering Plastics with Safe and Renewable Hydrogen-Bond Donor and Acceptor Solvent-Pair Mixtures

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Table S1. Experimental results of preparing poly(amic acid) (PAA) solutions with solvent and solvent-pairs along with solubility parameter (δ) and Kamlet-Taft solvatochromic (K-T) parameters.

Monomer and polymer		PAA ^a	δ (MPa ^{0.5})	K-T Parameters			Ref.	
				α	β	π^*		
Poly(amic acid) (PAA)		n/a	22.1 ^c	n/a	n/a	n/a	-	
4,4'-oxidianiline (ODA)		n/a	21.0 ^c	n/a	n/a	n/a	-	
Pyromellitic dianhydride (PMDA)		n/a	24.5 ^c	n/a	n/a	n/a	-	
No.	Pure Solvent	Conc. (wt%)	PAA ^a	δ (MPa ^{0.5}) ^e	K-T Parameters			
<u>HBA solvent</u> (PAA-soluble)				α	β	π^*	Ref.	
1	<i>N</i> -cyclohexyl-2-pyrolidone (CHP)	5	○ ²⁰	20.8	n/a	n/a	n/a	-
2	Diethyl acetamide (DEA)	5	○ ²⁰	21.3	0	0.78	0.80	1
3	Pyridine (Pyr)	5	○	21.8	0	0.64	0.87	1
4	Diethyl formamide (DEF)	5	○ ²⁰	21.9	0	0.79	0.88	1
5	Hexamethyl phosphoramide (HMPA)	5	○ ²⁰	21.9	0	1.00	0.87	1
6	Dimethylacetamide (DMA)	5	○	22.8	0	0.76	0.85	1
7	<i>N</i> -methyl-2-pyrrolidone (NMP)	5	○	22.9	0	0.72	0.92	1
8	<i>N</i> -acetyl-2-pyrrolidone (NAP)	5	○ ²⁰	23.6	n/a	n/a	n/a	-
9	Dimethylformamide (DMF)	5	○	24.9	0	0.69	0.88	1
10	Dimethyl sulfoxide (DMSO)	5	○	26.7	0	0.76	1.00	1
<u>HBA Solvent</u> (PAA-insoluble)								
11	Acetonitrile (ACN)	5	×	16.1	0.19	0.40	0.66	1
12	Cyclopentyl methyl ether (CPME)	5	×	17.2	0	0.53	0.42	1
13	Eucalyptol (Euc)	5	×	17.7	0	0.61	0.36	1
14	2-methyl tetrahydrofuran (MTHF)	5	×	18.1	0	0.45	0.48	1
15	Ethyl acetate (EtAc)	5	×	18.2	0	0.45	0.45	1
16	2-Pentanone (MPK)	5	×	18.3	0.05	0.5	0.65	1
17	Dimethyl carbonate (DMC)	5	×	18.7	0	0.38	0.47	1
18	2-Butanone (MEK)	5	×	19.1	0.06	0.48	0.60	1
19	Acetone (Ace)	5	×	19.4	0.08	0.48	0.62	1
20	Anisole (Ans)	5	×	19.5	0	0.32	0.70	1
21	Cyclohexanone (CHN)	5	×	19.6	0	0.55	0.68	1
22	Tetrahydrofuran (THF)	5	×	19.8	0	0.55	0.55	1
23	Cyclopentanone (CPN)	5	×	22.1	0	0.52	0.71	1
24	γ -valerolactone (GVL)	5	×	23.7 ^d	0	0.60	0.83	2
25	γ -butyrolactone (GBL)	5	×	26.3	0	0.53	0.85	1
26	Propylene carbonate (PPC)	5	×	27.2	0	0.40	0.83	1

Table S1. (Cont.)

No.	Pure Solvent	Conc. (wt%)	PAA ^a	δ (MPa ^{0.5}) ^e	K-T Parameters			Ref.	
					α	β	π^*		
HBD Solvent (PAA-insoluble)									
27	1-Pentanol (PeOH)	5	×	21.9	0.84	0.86	0.40	1	
28	1-Butanol (BuOH)	5	×	23.2	0.84	0.84	0.47	1	
29	1-Propanol (PrOH)	5	×	24.6	0.84	0.90	0.52	1	
30	2-methoxyethanol (MxOH)	5	×	25.1 ^d	0.72	0.72	0.77	3	
31	Ethanol (EtOH)	5	×	26.5	0.86	0.75	0.54	1	
32	Methanol (MeOH)	5	×	29.6	0.98	0.66	0.60	1	
33	Water (H ₂ O)	5	×	47.8	1.17	0.47	1.09	1	
No.	Literature Solvent-Pairs	Weight Ratio	Conc. (wt%)	PAA ^a	δ (MPa ^{0.5}) ^e	K-T Parameters			
						α	β	π^*	
34	THF-MeOH	8/2	15	×	21.7	0.75	0.67	0.67	This work ^b
		8/2	10	○	21.7	0.75	0.67	0.67	This work ^b
		8/2	5	○	21.7	0.75	0.67	0.67	This work ^b
35	THF-EtOH	7/3	5	○	21.8	0.65	0.67	0.67	This work ^b
36	THF-H ₂ O	9.5/0.5	5	○	20.7	0.26	0.69	0.64	4, 5
		9/1	5	○	22.0	0.46	0.69	0.68	4, 5
		8/2	5	○	24.9	0.48	0.69	0.72	4, 5
		7.5/2.5	5	○	25.9	0.50	0.69	0.74	4, 5
		7/3	5	○	27.3	0.50	0.68	0.76	4, 5
		6/4	5	×	29.9	0.51	0.68	0.81	4, 5
37	Ace-H ₂ O	9/1	5	×	22.2	0.57	0.56	0.75	4, 5
	Ace-H ₂ O	8/2	5	×	24.5	0.70	0.58	0.81	4, 5
	Ace-H ₂ O	7/3	5	×	27.0	0.75	0.59	0.87	4, 5
	Ace-H ₂ O	6/4	5	×	29.5	0.95	0.58	0.93	4, 5
No.	Replacement Solvent-Pairs	Weight Ratio	Conc. (wt%)	PAA ^a	δ (MPa ^{0.5}) ^e	K-T Parameters			
						α	β	π^*	
38	CHN-MeOH	7/3	5	○	22.9	0.80	0.64	0.77	This work ^b
39	CHN-EtOH	7/3	5	○	21.9	0.66	0.66	0.75	This work ^b
40	CPN-MeOH	6/4	5	○	25.5	0.82	0.64	0.76	This work ^b
41	CPN-EtOH	6/4	5	○	24.1	0.71	0.66	0.74	This work ^b
42	EtAc-MeOH	8/2	5	×	20.6	0.85 ⁶	0.59	0.61	This work ^b
		5.5/4.5	5	×	23.8	0.95 ⁶	0.64	0.63	This work ^b
		4/6	5	×	25.3	0.97 ⁶	0.66	0.64	This work ^b
43	GVL-MeOH	8/2	5	○	25.2	0.62	0.62	0.86	This work ^b
44	GVL-EtOH	7/3	5	○	24.7	0.58	0.64	0.84	This work ^b
45	GVL-H ₂ O	9.5/0.5	5	○	25.0	0.18	0.62	0.93	This work ^b
46	GBL-MeOH	7/3	5	○	27.6	0.82	0.61	0.87	This work ^b
47	GBL-EtOH	7/3	5	○	26.4	0.66	0.61	0.88	This work ^b
48	GBL-H ₂ O	9.5/0.5	5	○	27.5	0.35	0.59	0.96	This work ^b

Table S1. (Cont.)

No.	Replacement Solvent-Pairs	Weight Ratio	Conc. (wt%)	PAA ^a	δ (MPa ^{0.5}) ^e	K-T Parameters			Ref.
						α	β	π^*	
49	DMF-H ₂ O	9.5/0.5	5	○	26.1	0.19	0.76	0.92	4, 5
		9/1	5	○	26.9	0.27	0.76	0.94	4, 5
		8.5/2	5	○	27.9	0.32	0.73	0.96	4, 5
		8/2	5	○	29.2	0.36	0.71	1.00	4, 5
		6.5/3.5	5	×	32.6	0.46	0.66	1.07	4, 5
		5/5	5	×	35.5	0.57	0.62	1.12	4, 5
50	DMSO-H ₂ O	9.5/0.5	5	○	27.9	0.13	0.78	1.00	4, 5
		9/1	5	○	28.7	0.20	0.71	1.01	4, 5
		8.5/2	5	×	30.1	0.30	0.70	1.04	4, 5

Note: a = the appearances of PAA solutions in pure solvent and solvent-pair mixtures:

○ = Homogeneous solution;

× = Heterogeneous solution.

b = π^* of literature solvent-pairs and replacement solvent-pairs measured in this work is the average value of π^* from N, N-dimethyl-4-nitroaniline and 4-nitroanisole indicators.

β of literature solvent-pairs and replacement solvent-pairs obtained in this work is the average value of β from 4-nitroaniline and 4-nitrophenol indicators.

c = The δ values of monomers and PAA were estimated by group contribution method⁷ using equations 8 and 9 in table S4 with parameters of F_{di} , F_{pi} , E_{hi} , and V_i , which relate to their molecular structures (Fig. S1).

d = The δ values of GVL and MxOH were estimated by group contribution method.⁸

e = The δ values of pure solvents were obtained from literature,¹⁶ while δ values of solvent mixtures were estimated from volume fraction average of pure solvents as shown in equation 10 (Table S4).

According to literature solvent-pair mixtures (Table S1), Echigo et al.⁹ reported the homogeneous PAA solutions of 15 wt% in THF-MeOH mixture at a weight ratio of 8/2 and 25°C, while Sysel et al.¹⁹ reported that homogeneous PAA solutions in THF-MeOH mixtures could only be obtained at PAA concentration of 5 wt%. In this work, results for solvent-pairs, THF-EtOH and THF-H₂O (Fig.1 and Table S1), reported in the literature,¹⁵ could be reproduced for 5 wt% PAA concentrations, except for acetone-water mixtures

Table S2. Indicator relationships used to determine Kamlet-Taft solvatochromic parameters.

No.	Indicator Relationship	Ref.
1	$N, N\text{-dimethyl -4-nitroaniline}$ $-\pi^* = 0.314 \times (27.52 - v_{\max})$	[17]
2	4-nitroanisole $-\pi^* = 0.427 \times (34.12 - v_{\max})$	[18]
3	4-nitroaniline $-\beta = 0.358 \times (31.10 - v_{\max}) - 1.125 \times \pi_{\text{average}}^*$	[18]
4	4-nitrophenol $-\beta = 0.346 \times (35.04 - v_{\max}) - 0.57 \times \pi_{\text{average}}^*$	[18]
5	$2,6\text{-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate}$ $-\alpha = 0.0649 \times E_T(30) - 2.03 - 0.72 \times \pi_{\text{average}}^*$ $-E_T(30), \text{kcal}\cdot\text{mol}^{-1} = 28591.5/\lambda_{\max} (\text{nm})$	[18]

Note: v_{\max} = Maximum wavenumber of absorption of indicator i in term of kilokaiser
($1\text{kK}=10,000/\lambda_{\max} (\text{nm})$).

π_{average}^* is the average value of π^* from indicators 1 and 2.

Table S3. Experimental results for preparation of homogeneous (\circ) and heterogeneous (\times) poly(amic acid) (PAA) solutions of 5 wt % in literature and replacement hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) solvent-pairs at 25 °C with Kamlet-Taft solvatochromic parameters measured in this work unless noted.

Literature Solvent-pairs	Weight ratio	Conc. (mol%) ^e	Phase	δ (MPa ^{0.5}) ^f	K-T parameters			Δ K-T values ^c		
					α	β	π^*	α	β	π^*
▲ THF-MeOH	8/2	1.4	\circ	21.7	0.75	0.67	0.67	0.39	0.08	0.10
△ THF-MeOH	4/6	1.0	\times	25.8	0.94	0.72	0.68	0.18	0.09	0.09
▲ THF-MeOH	7/3	1.5	\circ	21.8	0.65	0.67	0.67	0.46	0.05	0.13
▲ THF- H ₂ O	9.5/0.5	1.5	\circ	20.7	0.26	0.69	0.64	0.06	0.15	0.00
▲ THF- H ₂ O	9/1	1.4	\circ	22.0	0.46 ^a	0.69 ^a	0.68 ^a	0.10	0.16	-0.04
▲ THF- H ₂ O	8/2	1.1	\circ	24.9	0.48 ^a	0.69 ^a	0.72 ^a	-0.11	0.18	-0.10
▲ THF- H ₂ O	7.5/2.5	1.0	\circ	25.9	0.50 ^a	0.69 ^a	0.74 ^a	-0.17	0.19	-0.12
▲ THF- H ₂ O	7/3	0.90	\circ	27.3	0.50 ^a	0.68 ^a	0.76 ^a	-0.24	0.18	-0.13
△ THF-H ₂ O	5/5	0.70	\times	32.7	0.54 ^a	0.68 ^a	0.86 ^a	-0.40	0.19	-0.12
Replacement Solvent-pairs (HBA-HBD)										
▼ CHN-MeOH	7/3	1.5	\circ	22.9	0.80	0.64	0.77	0.23	0.02	0.10
▼ CHN-EtOH ^d	7/3	1.8	\circ	21.9	0.66	0.66	0.75	0.23	0.00	0.10
◆ CPN-MeOH ^d	6/4	1.3	\circ	25.5	0.82	0.64	0.76	0.19	0.02	0.10
◆ CPN-EtOH ^d	6/4	1.6	\circ	24.1	0.71	0.66	0.74	0.23	-0.01	0.12
◆ GVL-MeOH	8/2	1.7	\circ	25.2	0.62	0.62	0.86	0.19	0.00	0.11
◆ GVL-EtOH	7/3	1.8	\circ	24.7	0.58	0.64	0.84	0.16	-0.03	0.13
◆ GVL-H ₂ O	9.5/0.5	2.0	\circ	25.0	0.18	0.62	0.93	-0.02	0.06	0.01
★ GBL-MeOH	7/3	1.4	\circ	27.6	0.82	0.61	0.87	0.30	0.01	0.12
★ GBL-EtOH	7/3	1.7	\circ	26.4	0.66	0.61	0.88	0.28	-0.02	0.12
★ GBL-H ₂ O	9.5/0.5	1.8	\circ	27.5	0.35	0.59	0.96	0.27	0.07	0.01
▽ EtAc-MeOH	8/2	1.2	\times	20.6	0.85 ^b	0.59	0.61	0.57	0.10	0.11
	5.5/4.5	0.8	\times	23.8	0.95 ^b	0.64	0.63	0.20	0.03	0.04
	4/6	0.7	\times	25.3	0.97 ^b	0.66	0.64	0.06	0.00	0.02

Note: ^aRef. [4-5]

^bRef. [6]

^c Δ K-T values represent the difference between the K-T parameters (θ) of the mixture and that of their mole fraction (x) average, e.g., $\theta = \theta_{mixture} - (x_1\theta_{pure1} + x_2\theta_{pure2})$.

^dPrecipitation occurred after 24 h.

^eConcentration of pyromellitic dianhydride (PMDA) and 4, 4'-oxidianiline (ODA) monomers in 10 g of solvent mixture.

^fvalues estimated from volume fraction average of pure solvents at 25 °C (Table S4).

Table S4. Solubility parameter group contribution method⁷ used for pyromellitic dianhydride (PMDA), 4,4'-oxidianiline (ODA), and poly(amic acid) (PAA).

Structural Groups	F_{di} (MJ/m ³)·mol ⁻¹	F_{pi} (MJ/m ³)·mol ⁻¹	E_{hi} J·mol ⁻¹	V cm ³ ·mol ⁻¹
-NH ₂	280	0	8400	17.00
-O-	100	400	3000	6.45
para- Phenylene	1270	110	0	68.52
-CO-	290	770	2000	17.30
Phenyl (tetra substituted)	1270	110	0	56.52
-COOH	530	420	10000	26.10
-NH-	160	210	3100	11.00

Equations

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (8)$$

$$\delta_d = \sum F_{di}/V \quad (9a)$$

$$\delta_p = \sqrt{\sum F_{pi}^2}/V \quad (9b)$$

$$\delta_h = \sqrt{\sum E_{hi}/V} \quad (9c)$$

$$V = \sum N_i V_i \quad (9d)$$

$$\delta = \varphi_1 \delta_1 + \varphi_2 \delta_2 \quad (10)$$

δ_i = solubility parameter of pure component i ; and φ_i = volume fraction of pure component i .

Table S5. Correspondence of FT-IR wavenumber and functional groups of poly(amic acid) (PAA).^{9, 10}

Functional Groups	Wave number ($\nu_{\max}/\text{cm}^{-1}$)
C=O stretching of amide PAA	1661 (strong signal)
N-H bending of 2nd amide PAA	1550-1510 (strong signal)
O-H stretching of carboxylic in PAA	3400-2400 (very strong and broad signal)
N-H stretching of amide PAA	3400-3200 (broad signal)
N-H bending of 1st amide PAA	1620-1590 (strong signal)
C=O stretching of imide PI	1778 (medium signal)

Table S6. Differential thermogravimetric analysis (DTGA) temperature of Poly(amic acid) (PAA) in the replacement solvent-pairs.

PAA in the replacement solvent-pairs	DTGA Temperature (°C)	
	First	Second
CHN-MeOH	189	611
CHN-EtOH	185	602
CPN-MeOH	160	598
CPN-EtOH	155	583
GVL-MeOH	155	573
GVL-EtOH	163	593
GVL-water	154	586
GBL-MeOH	162	598
GBL-EtOH	155	591
GBL-water	159	590
Commercial PAA	169	586
Polyimide (Kapton)	600	-
ODA monomer	316	-
PMDA monomer	350	-

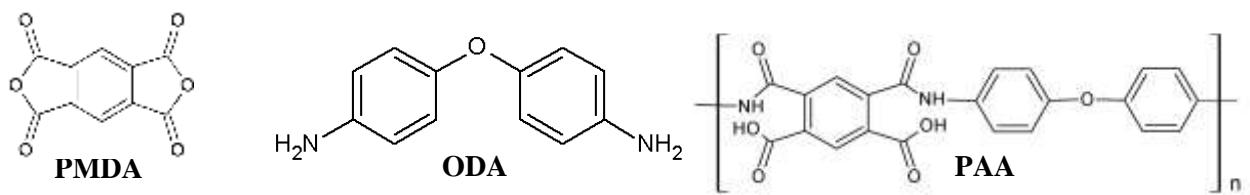


Figure S1. Chemical structures of pyromellitic dianhydride (PMDA), 4,4'-oxidianiline (ODA), and poly(amic acid) (PAA).

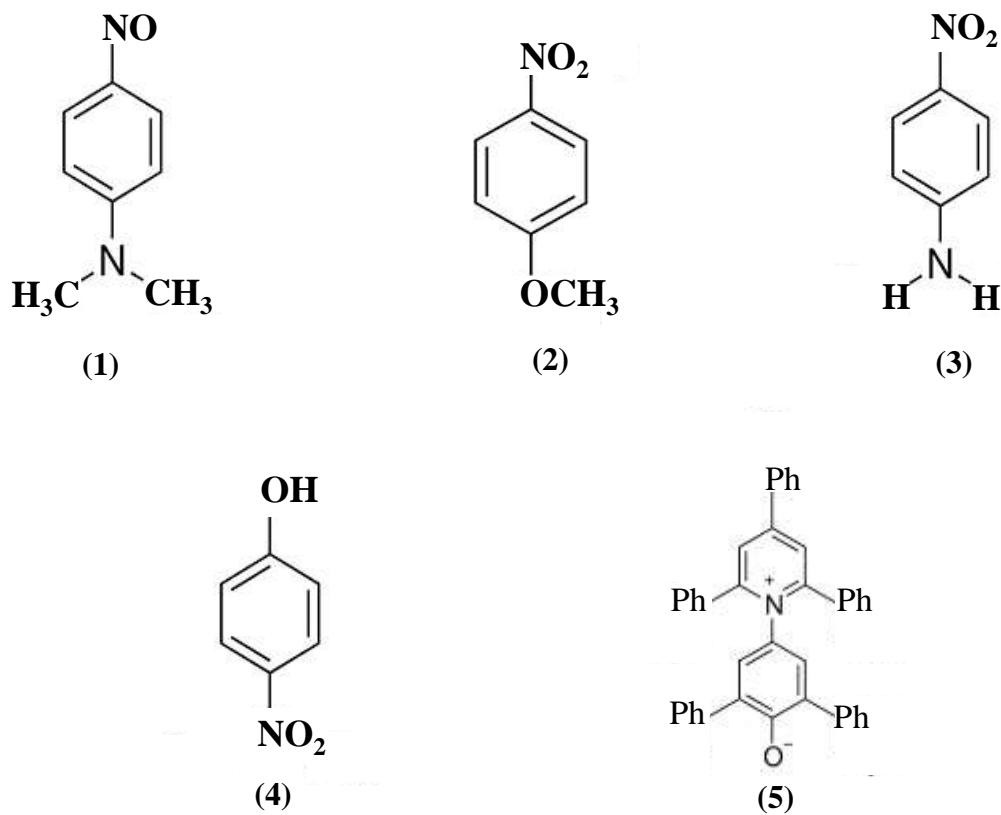
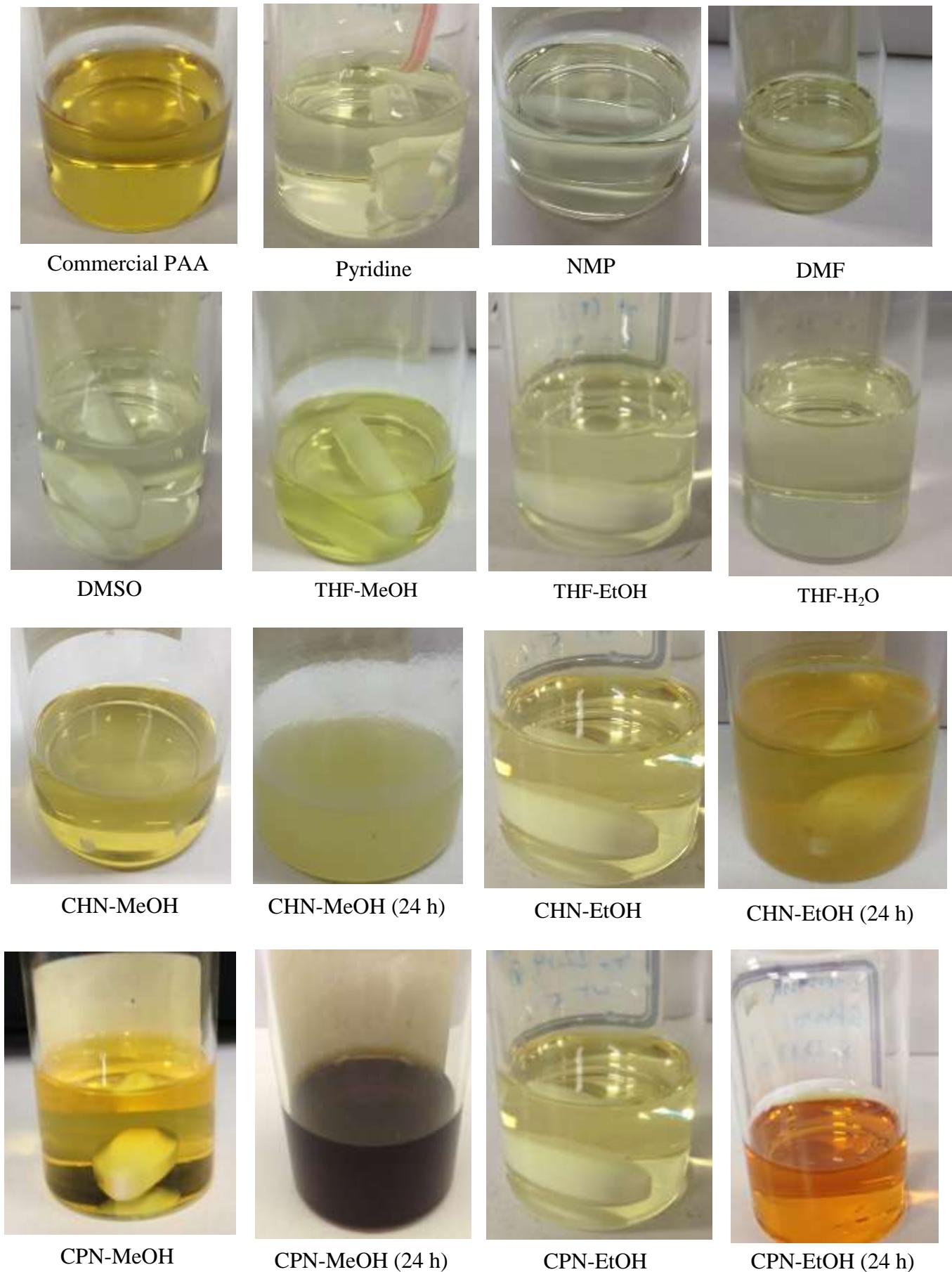


Figure S2. Molecular structures of solvatochromic indicators used in this work:

- (1) N,N -dimethyl-4-nitroaniline; (2) 4-nitroanisole; (3) 4-nitroaniline;
- (4) 4-nitrophenol; and (5) 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate.

Figure S3. a) Solution appearance of homogeneous solutions after 3 h reaction time unless stated.



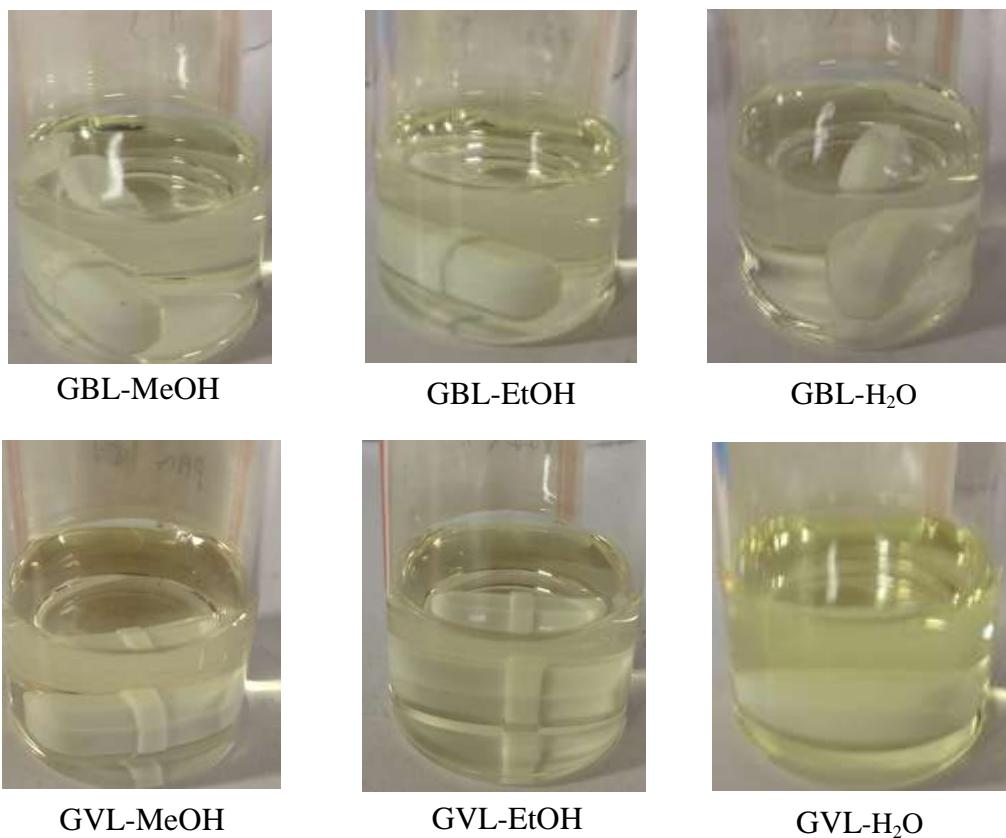
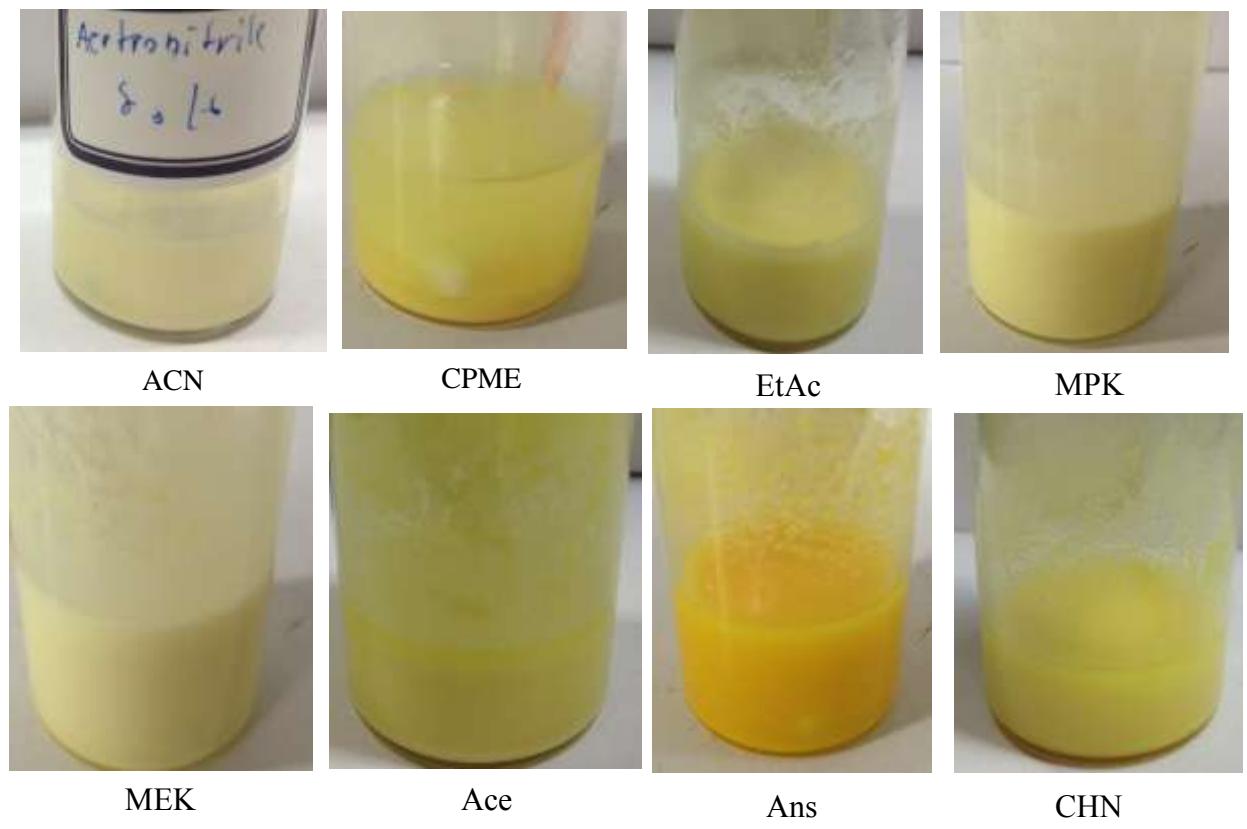


Figure S3. b) Solution appearance of heterogeneous solutions after 3 h reaction time.





CPN



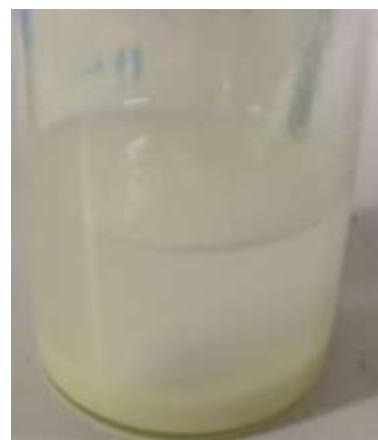
GVL



GBL



PPC



PrOH

Functional Groups Analysis by FT-IR

Table S5 tabulates the significant spectra of PAA corresponding to its structure (Fig. S1) and Figure S4 shows FT-IR spectra of the PAA in all replacement solvent-pairs and commercial PAA solutions. FT-IR spectra of PAA in all replacement solvent-pairs agreed well with the results from commercial PAA solution, in which the absorption wavenumbers (ν_{max} , cm^{-1}) of 1661 (C=O stretching of amide), 1550 (N-H bending of 2nd amide PAA), 3400-2400 (O-H stretching of carboxylic in PAA) corresponded with those of commercial PAA solutions.

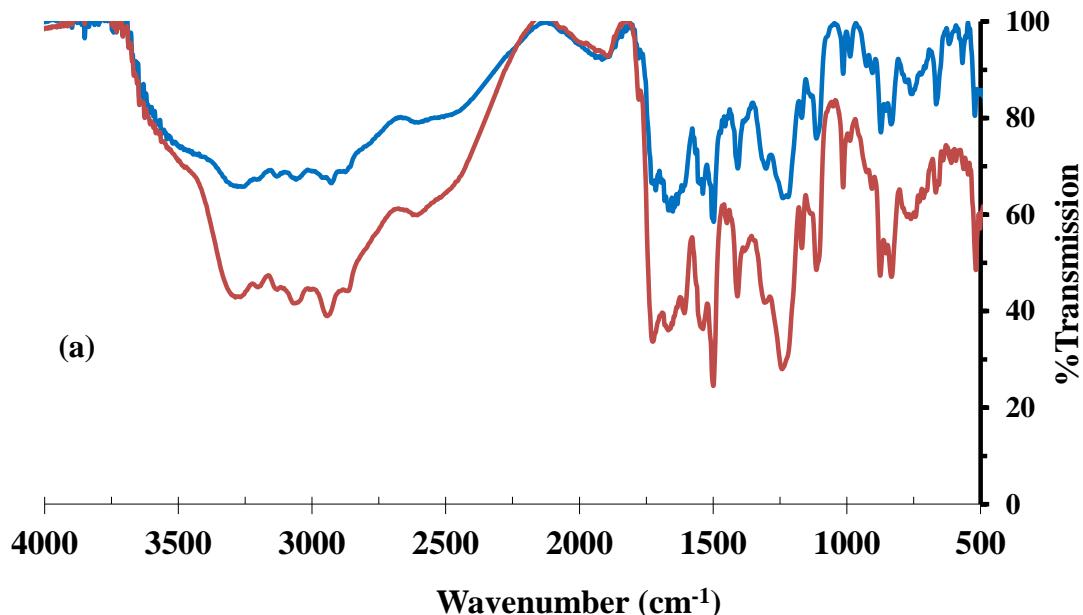


Figure S4. a) PAA in cyclohexanone-MeOH at weight ratio 7/3.

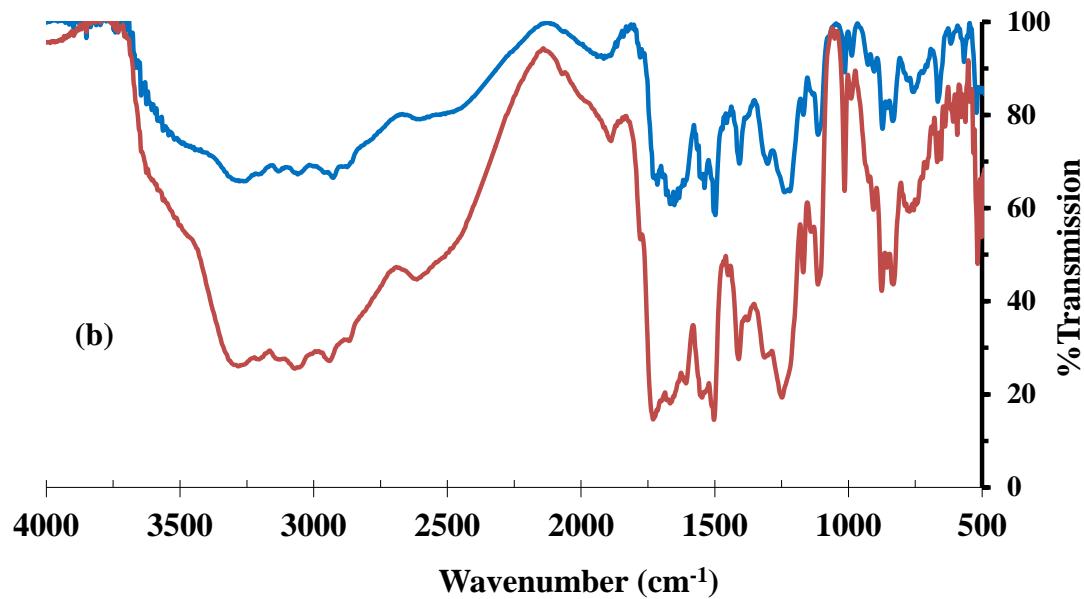


Figure S4. b) PAA in cyclohexanone-EtOH at weight ratio 7/3.

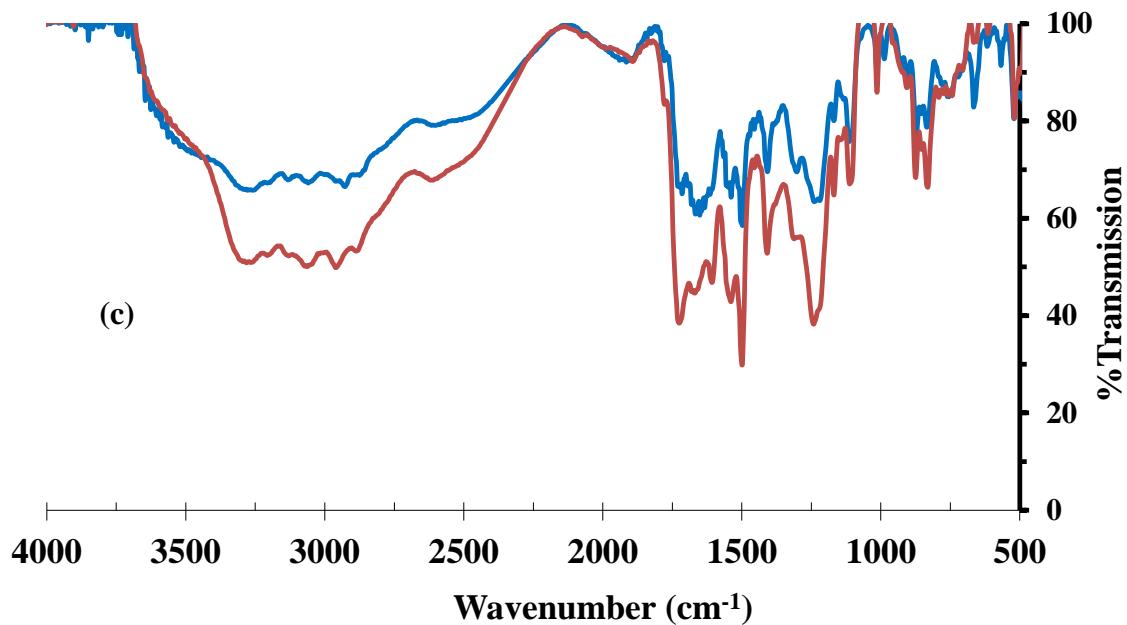


Figure S4. c) PAA in cyclopentanone-MeOH at weight ratio 6/4.

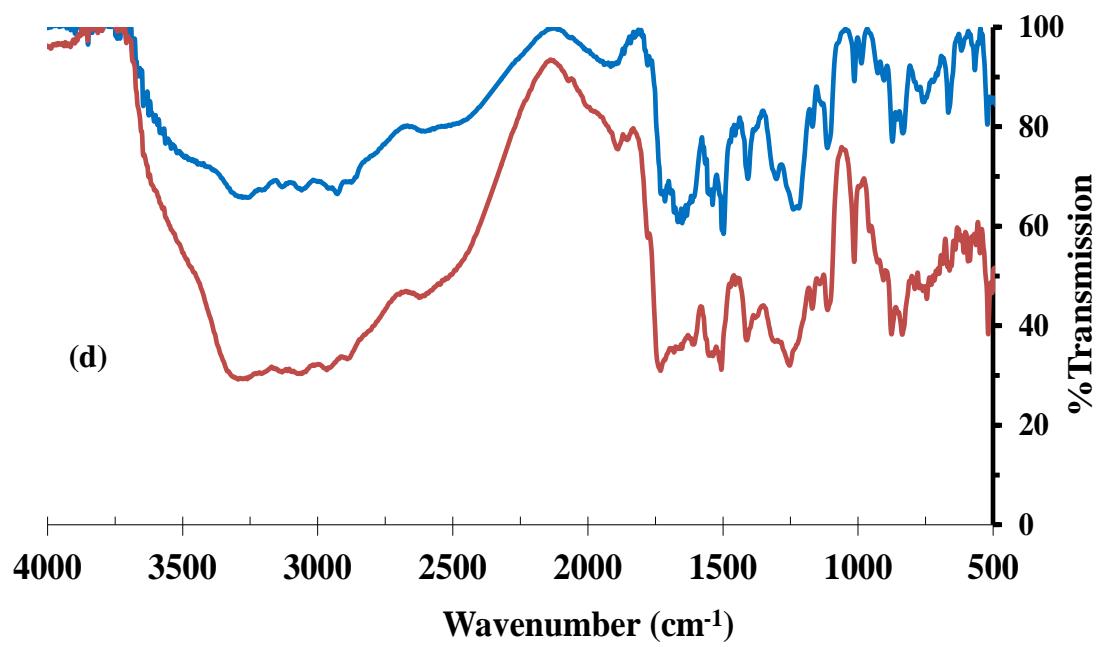


Figure S4. d) PAA in cyclopentanone-EtOH at weight ratio 6/4.

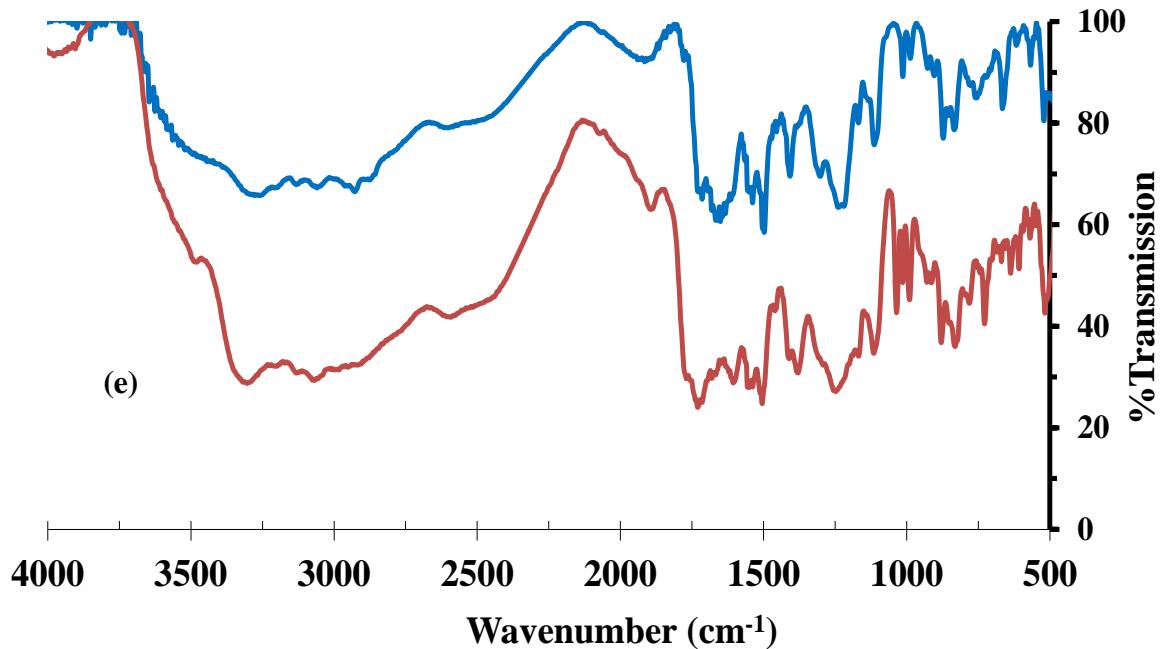


Figure S4. e) PAA in γ -butyrolactone-MeOH at weight ratio 7/3.

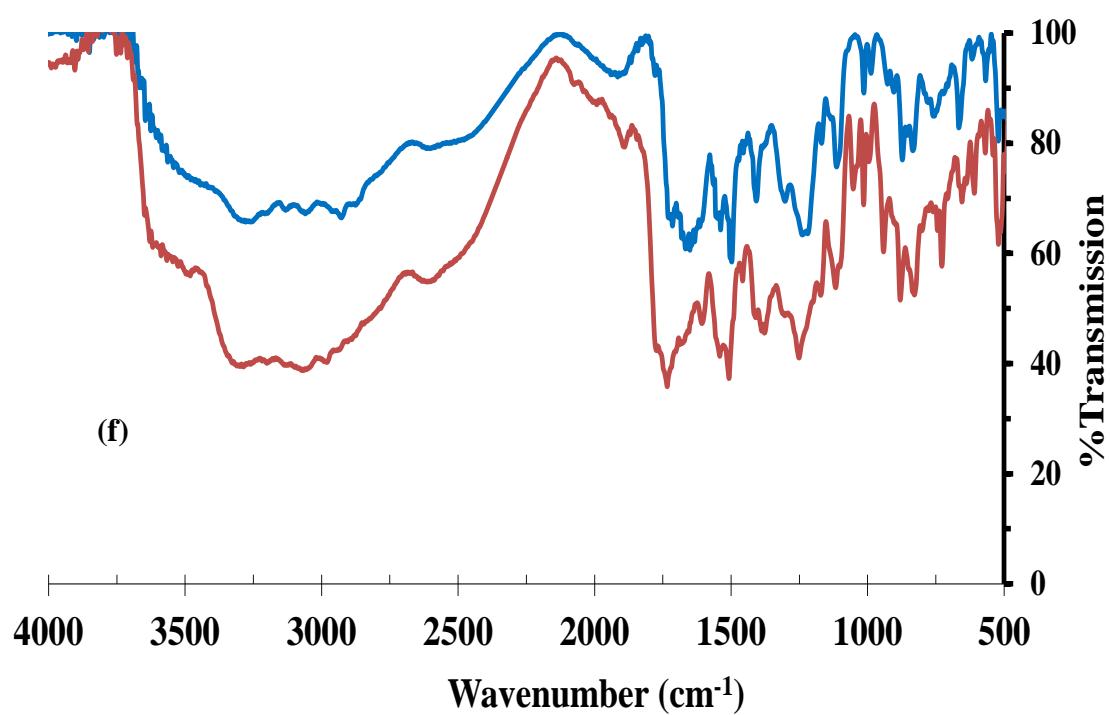


Figure S4. f) PAA in γ -butyrolactone-EtOH at weight ratio 7/3.

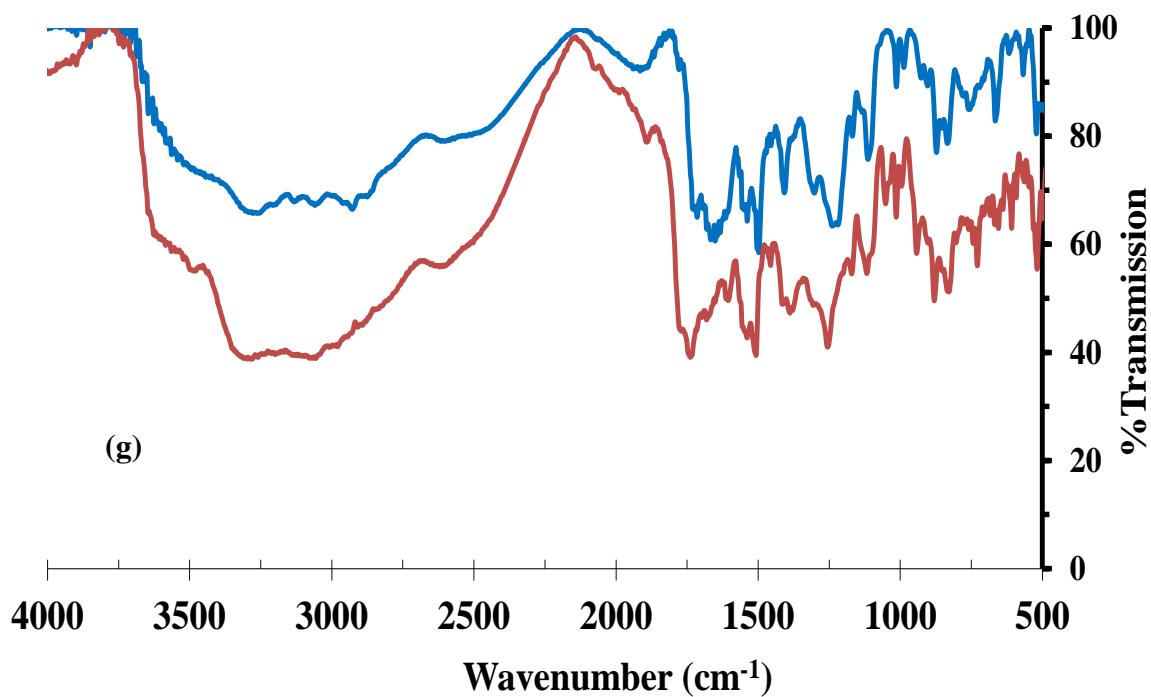


Figure S4. g) PAA in γ -butyrolactone-water at weight ratio 9.5/0.5.

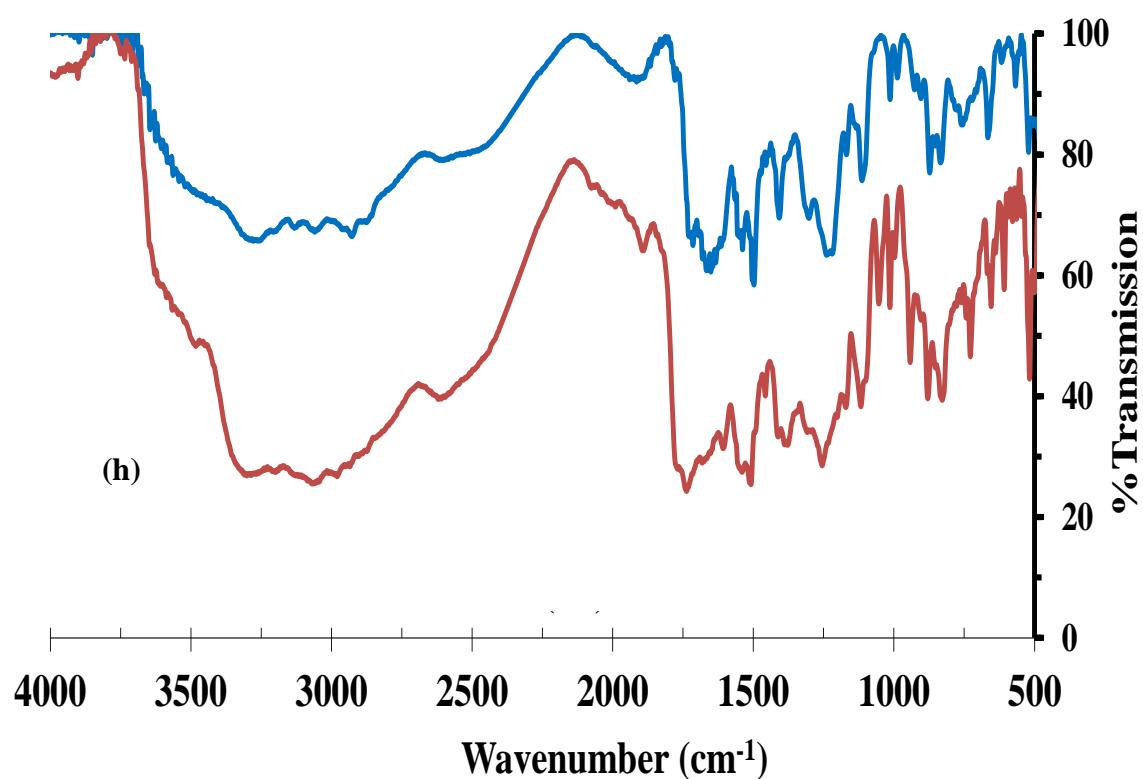


Figure S4. h) PAA in γ -valerolactone-MeOH at weight ratio 8/2.

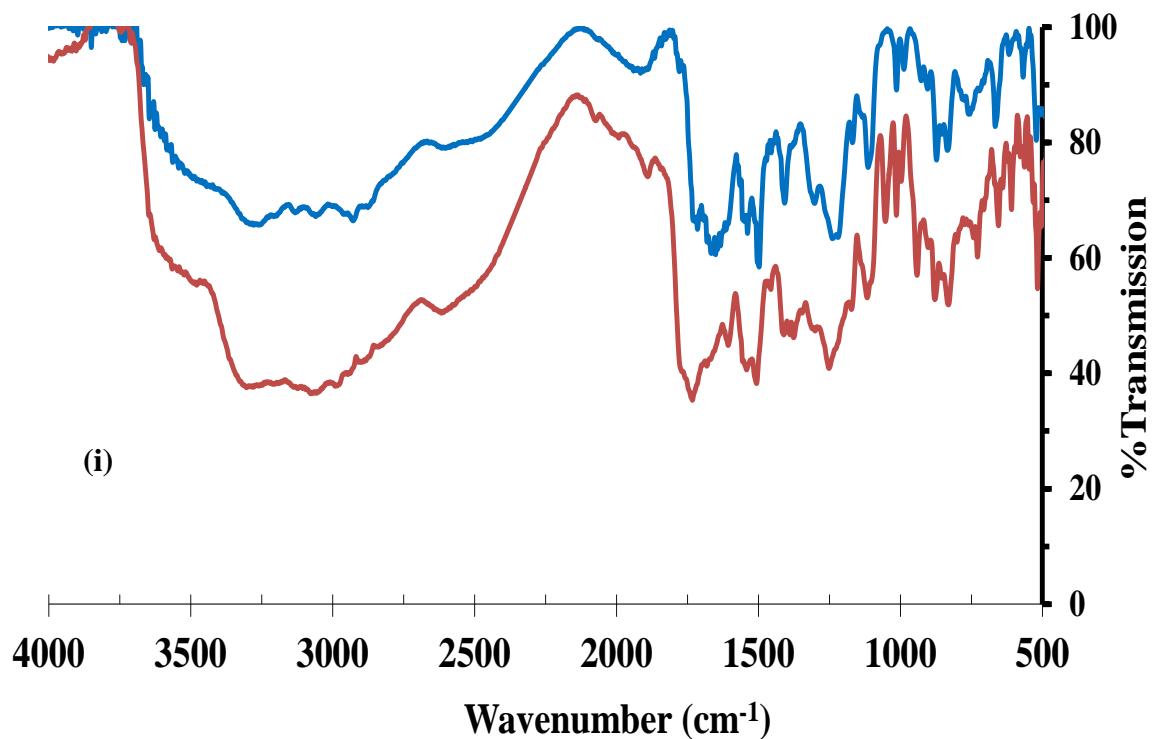


Figure S4. i) PAA in γ -valerolactone-EtOH at weight ratio 7/3.

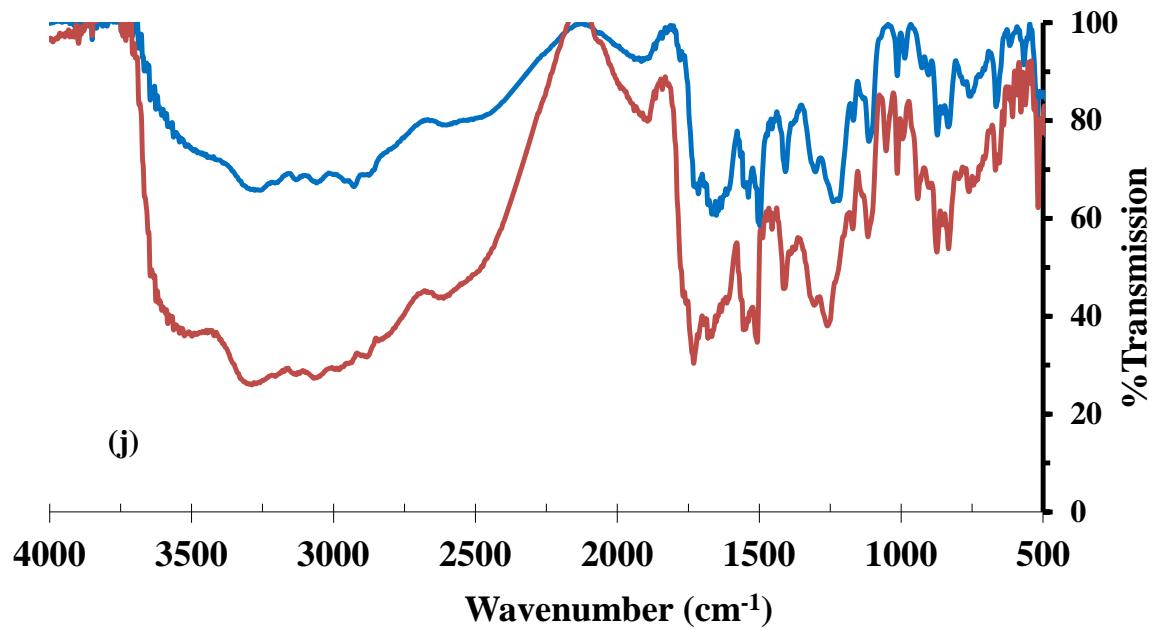


Figure S4. j) PAA in γ -valerolactone-water at weight ratio 9.5/0.5.

Figure S4. FT-IR spectra of poly(amic acid) (PAA) solutions for (red line) PAA in the replacement solvent-pairs and (blue lines) commercial PAA solution.

Functional Groups Analysis by $^1\text{H-NMR}$

Chemical structures of soluble-PAA solutions in the replacement solvent-pairs were analyzed by $^1\text{H-NMR}$. For $^1\text{H-NMR}$ of PAA from the literature,¹¹⁻¹⁴ the signals of protons of the amide group at 10.5 ppm and the aromatic protons of the polymer backbone appeared at 7.0-8.5 ppm. From this work, the $^1\text{H-NMR}$ of commercial PAA in Figure S5 (a) also exhibited the signals of protons of the amide group at 10.5 ppm and the aromatic protons of polymer backbone from 7.0 ppm to 8.5 ppm. Moreover, the two protons of five rings of NMP solvents were also detected at chemical shifts between 1.75 and 2.05 ppm^{13, 14} for the commercial PAA solution. In the case of $^1\text{H-NMR}$ of PAA in GVL-water mixture in Figure S5 (K), the signals of protons of amide group at 10.5 ppm and the aromatic protons of polymer backbone from 7.0 ppm to 8.5 ppm were clearly seen, whereas the signals of two protons from NMP solvents around 1.75-2.05 ppm disappeared. The signals of PAA in GVL-water mixtures at 1.3, 1.7, and 4.6 ppm were also detected, which represented the protons of GVL solvents as shown in Figure S5 (l).

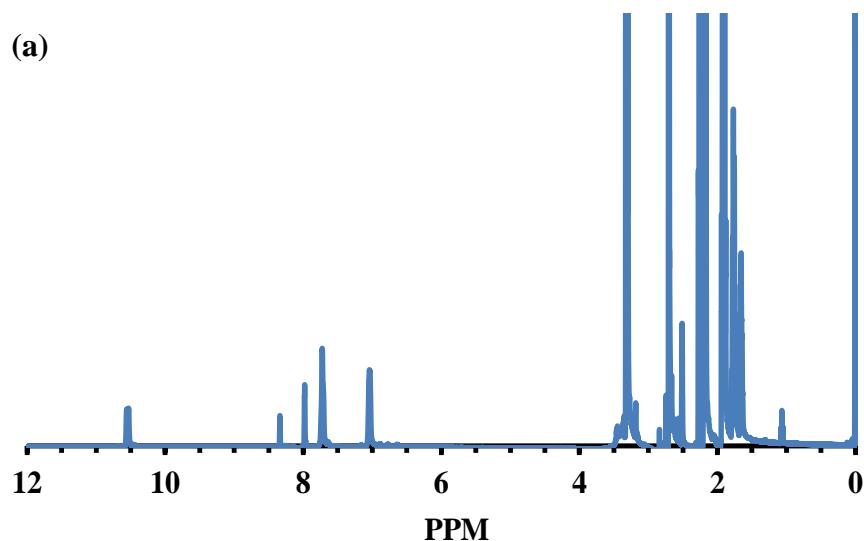


Figure S5. a) Commercial PAA.

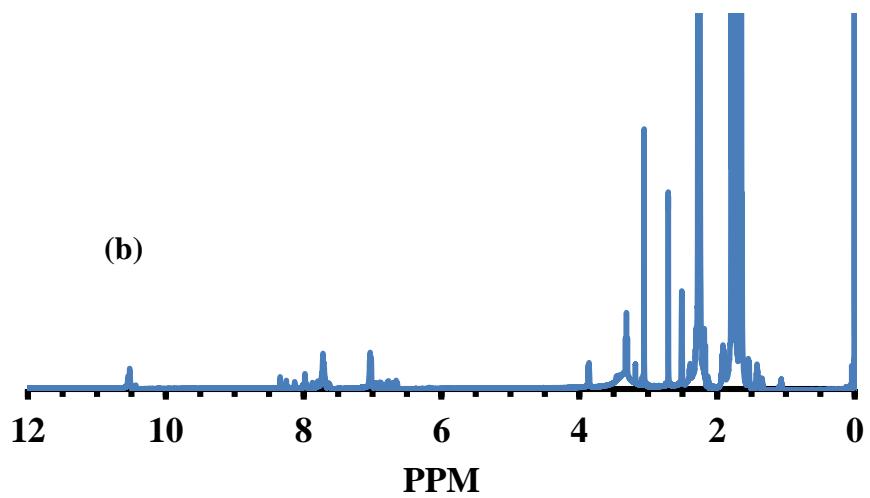


Figure S5. b) PAA in cyclohexanone-MeOH.

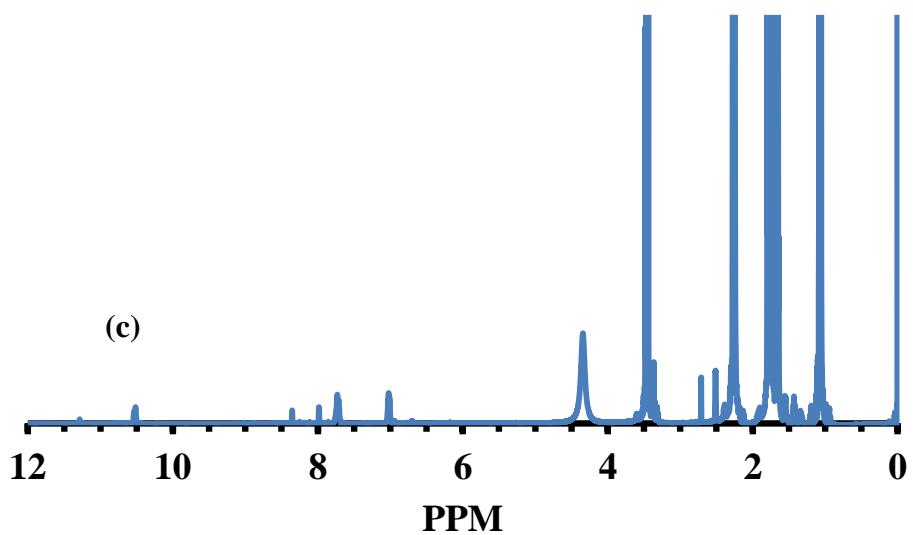


Figure S5. c) PAA in cyclohexanone-EtOH.

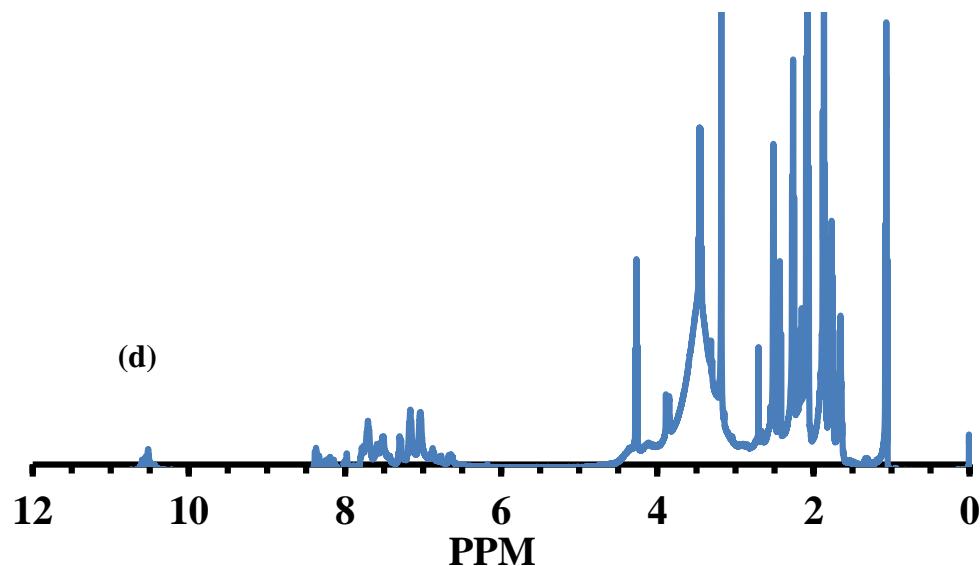


Figure S5. d) PAA in cyclopentanone-MeOH.

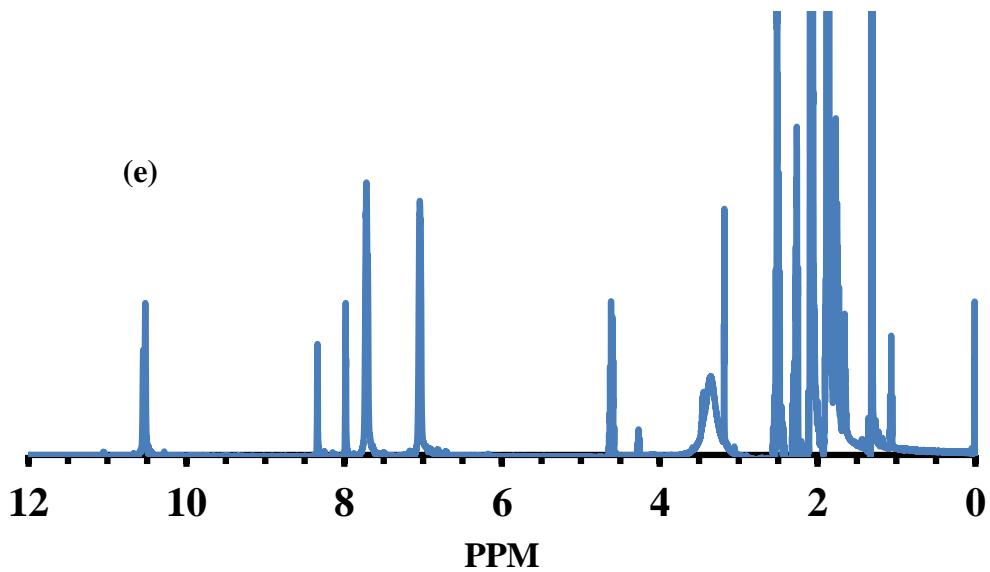


Figure S5. e) PAA in cyclopentanone-EtOH.

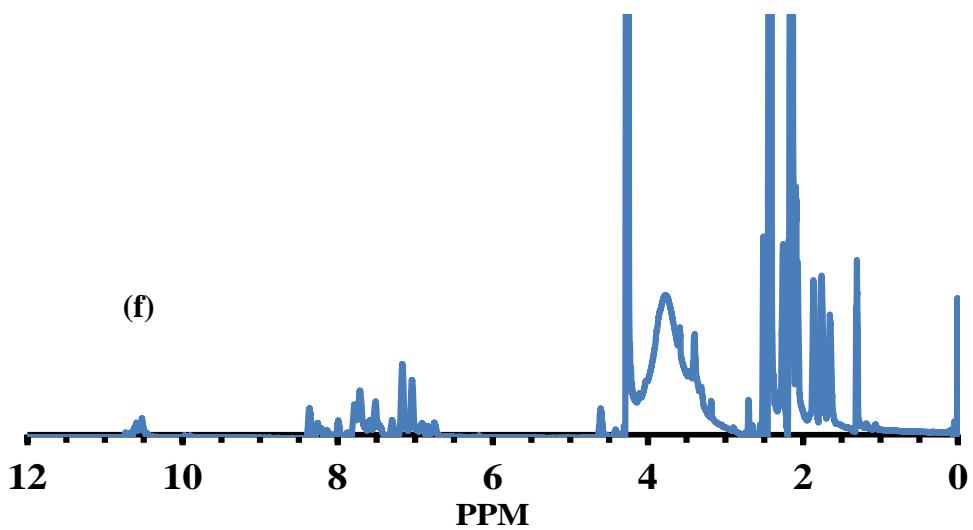


Figure S5. f) PAA in γ -butyrolactone-MeOH.

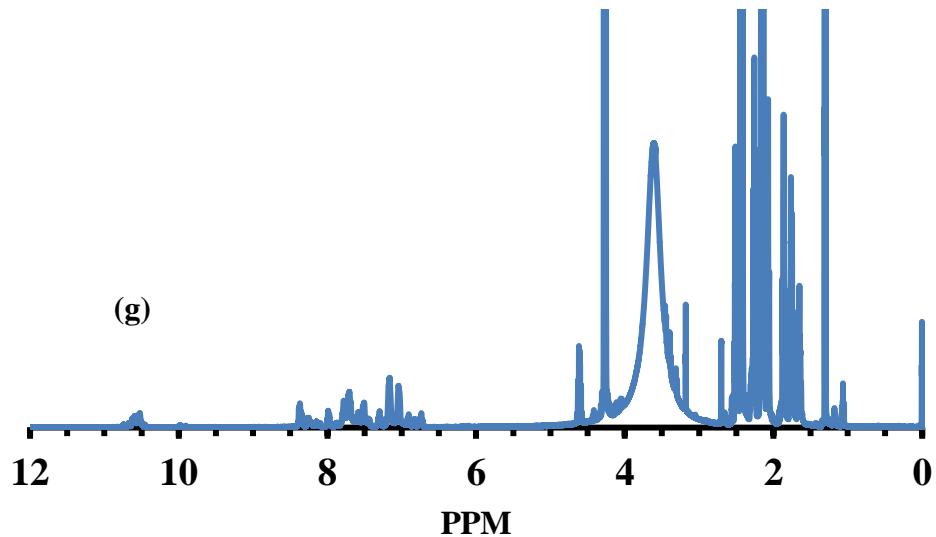


Figure S5. g) PAA in γ -butyrolactone-EtOH.

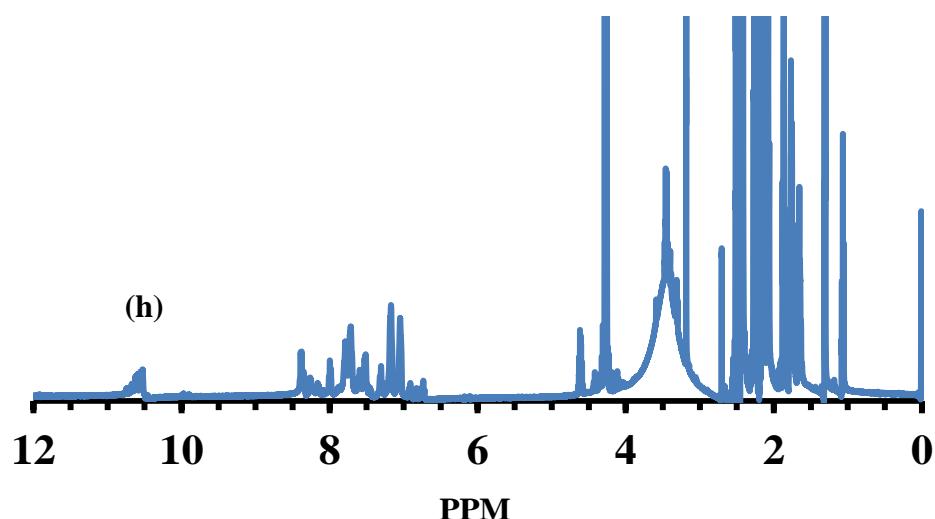


Figure S5. h) PAA in γ -butyrolactone-water.

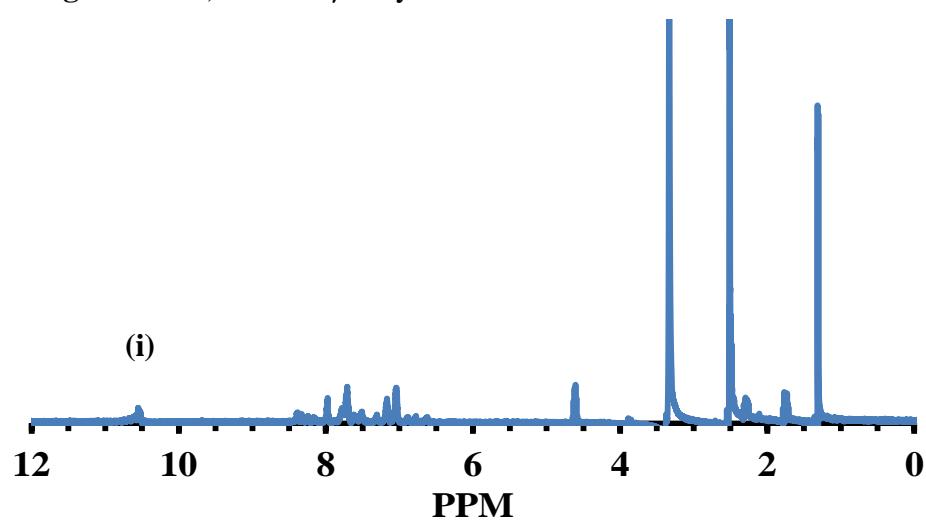


Figure S5. i) PAA in γ -valerolactone-MeOH.

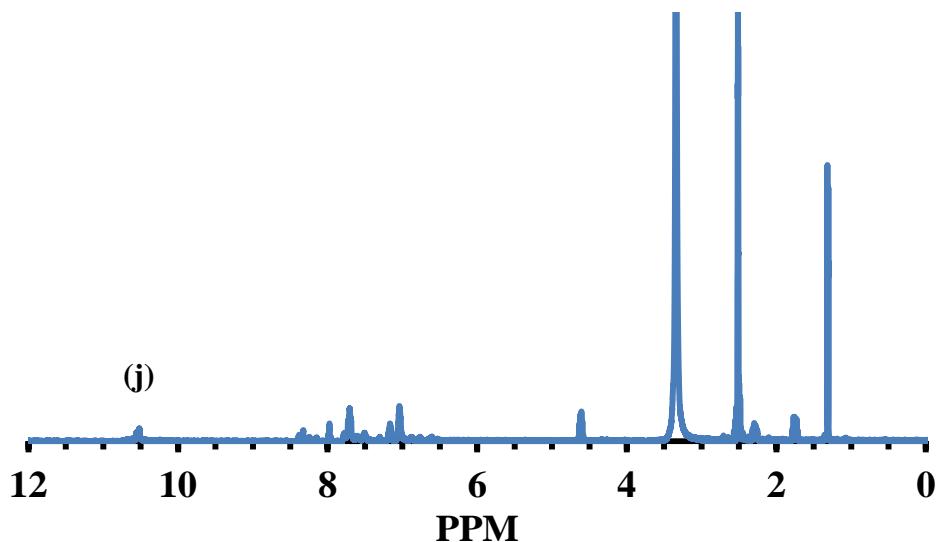


Figure S5. j) PAA in γ -valerolactone-EtOH .

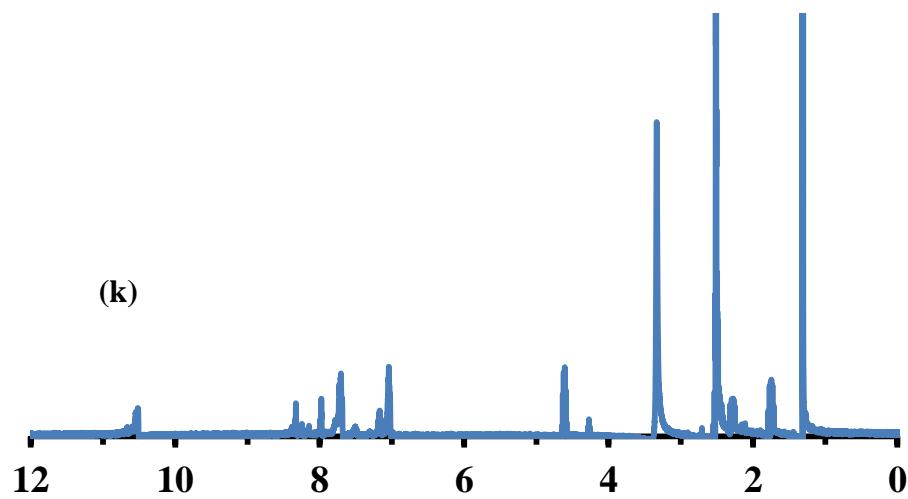


Figure S5. k) PAA s in γ -valerolactone-water.

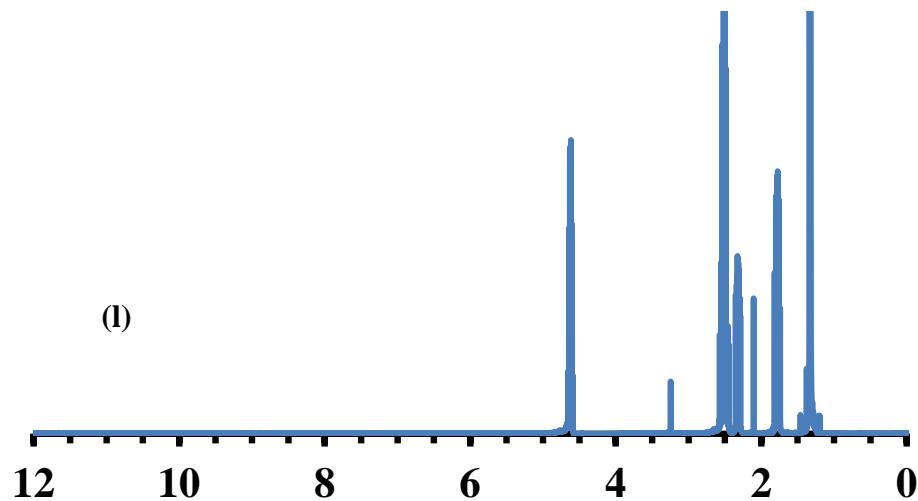


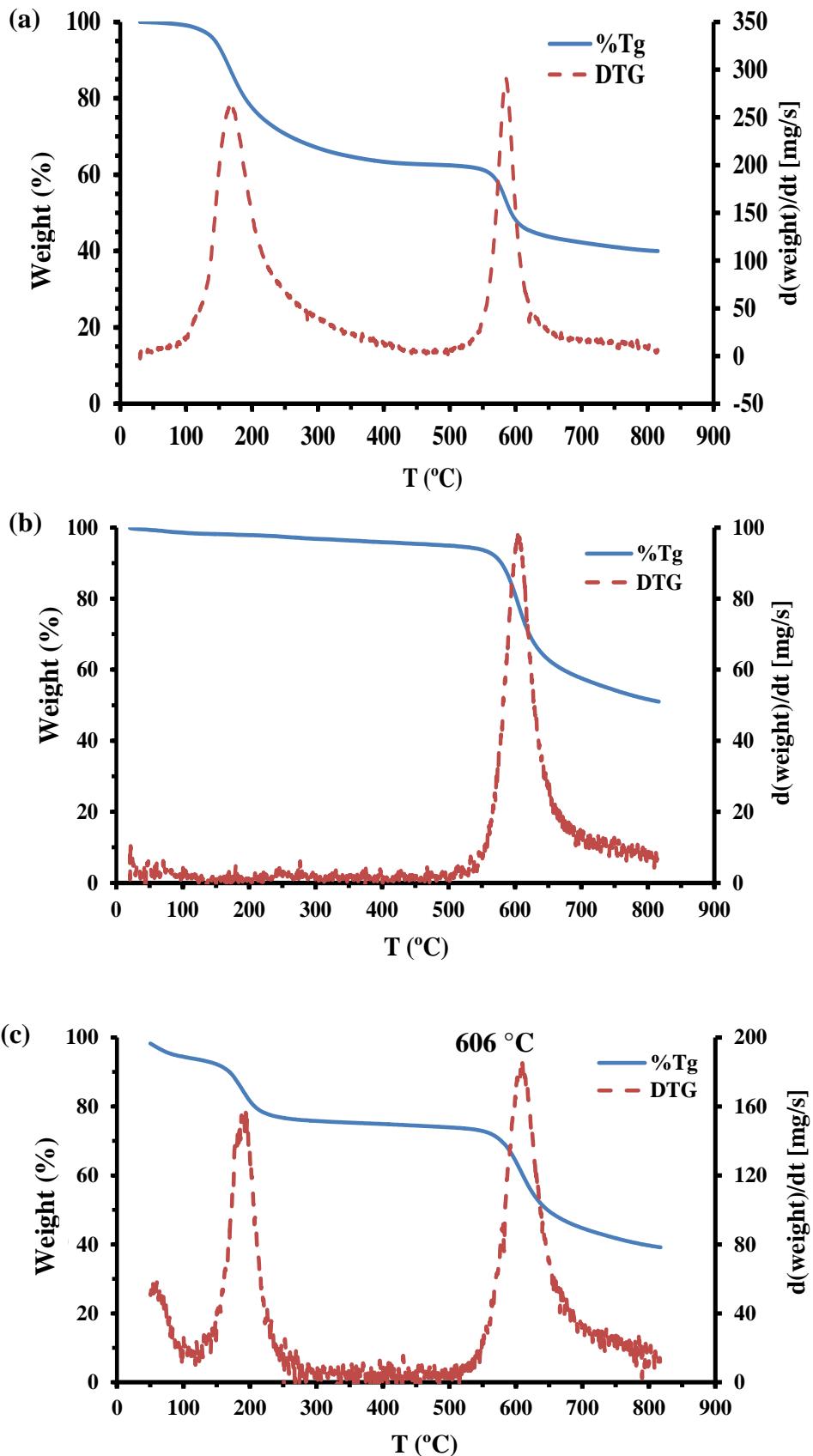
Figure S5. l) γ -valerolactone solvent.

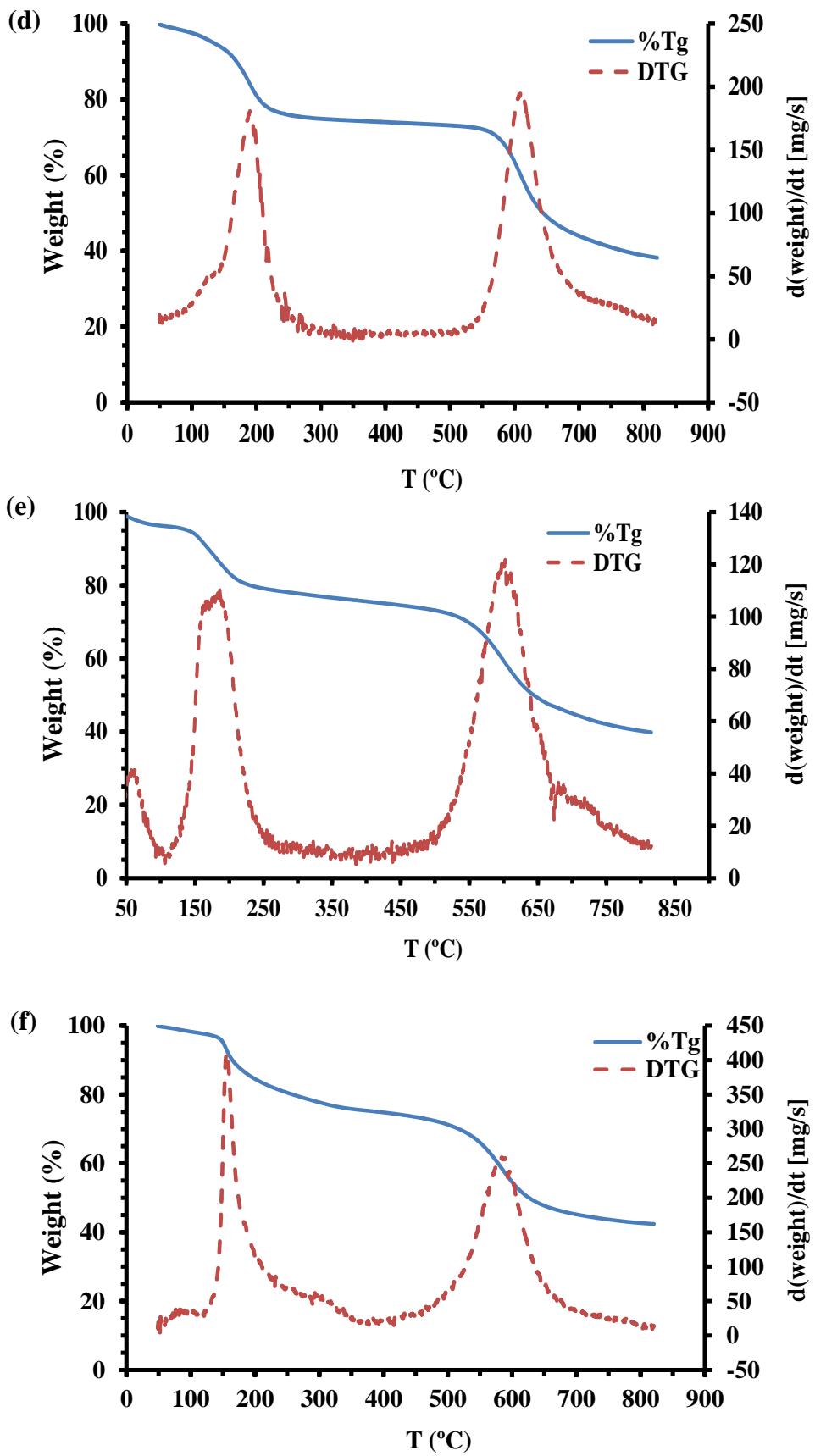
Figure S5. ^1H -NMR spectra of poly(amic acid) (PAA) synthesized in the replacement solvent-pairs: (a) commercial PAA in NMP solvent; (b) PAA in cyclohexanone-MeOH at weight ratio 7/3; (c) PAA in cyclohexanone-EtOH at weight ratio 7/3; (d) PAA in cyclopentanone-MeOH at weight ratio 6/4; (e) PAA in cyclopentanone-EtOH at weight ratio 6/4; (f) PAA in γ -butyrolactone-MeOH at weight ratio 7/3; (g) PAA in γ -butyrolactone-EtOH at weight ratio 7/3; (h) PAA in γ -butyrolactone-water at weight ratio 9.5/0.5; (i) PAA in γ -valerolactone-MeOH at weight ratio 8/2; (j) PAA in γ -valerolactone-EtOH at weight ratio 7/3; (k) PAA in γ -valerolactone-water at weight ratio 9.5/0.5; (l) γ -valerolactone solvent.

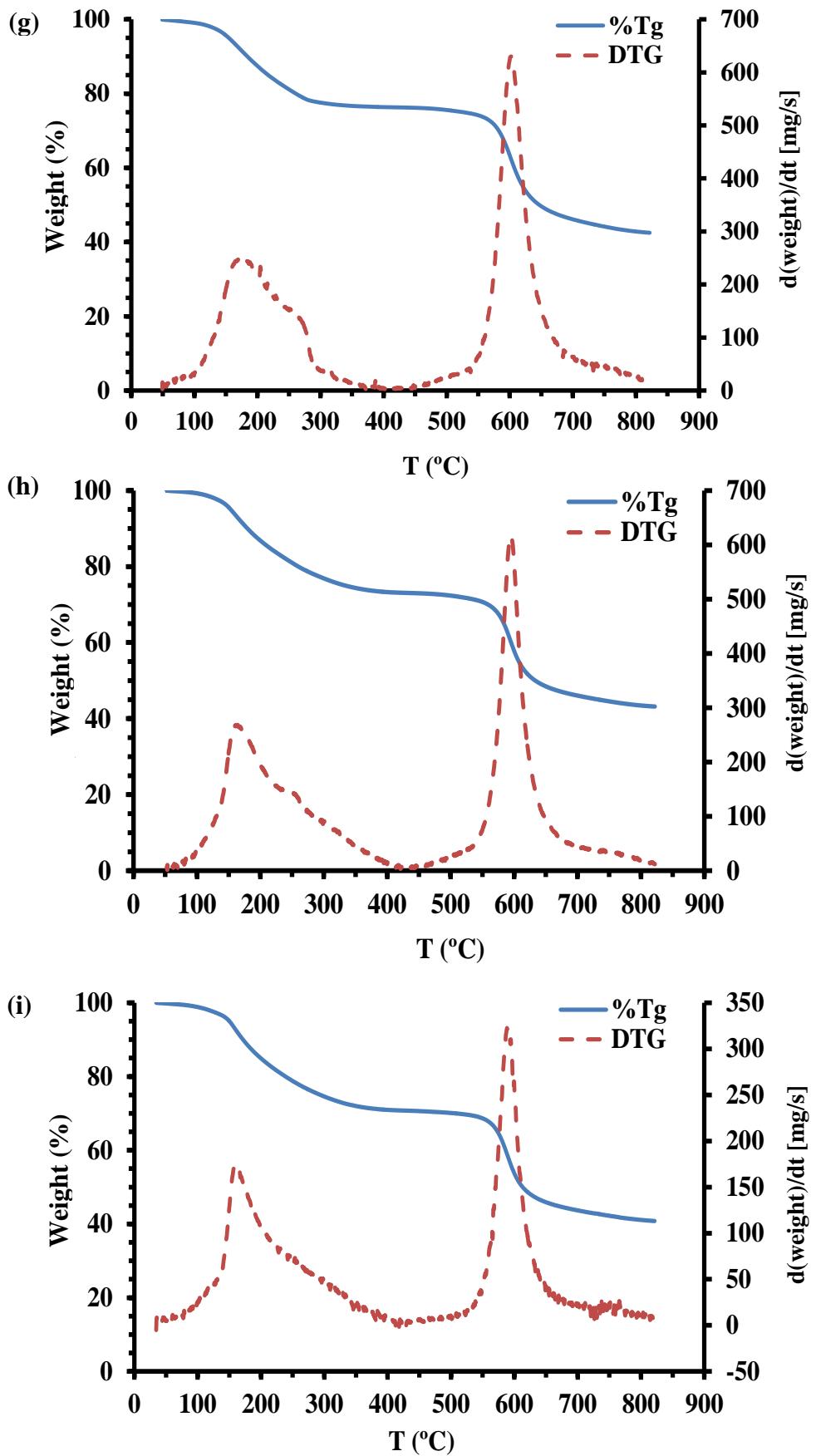
Thermal Stability Analysis

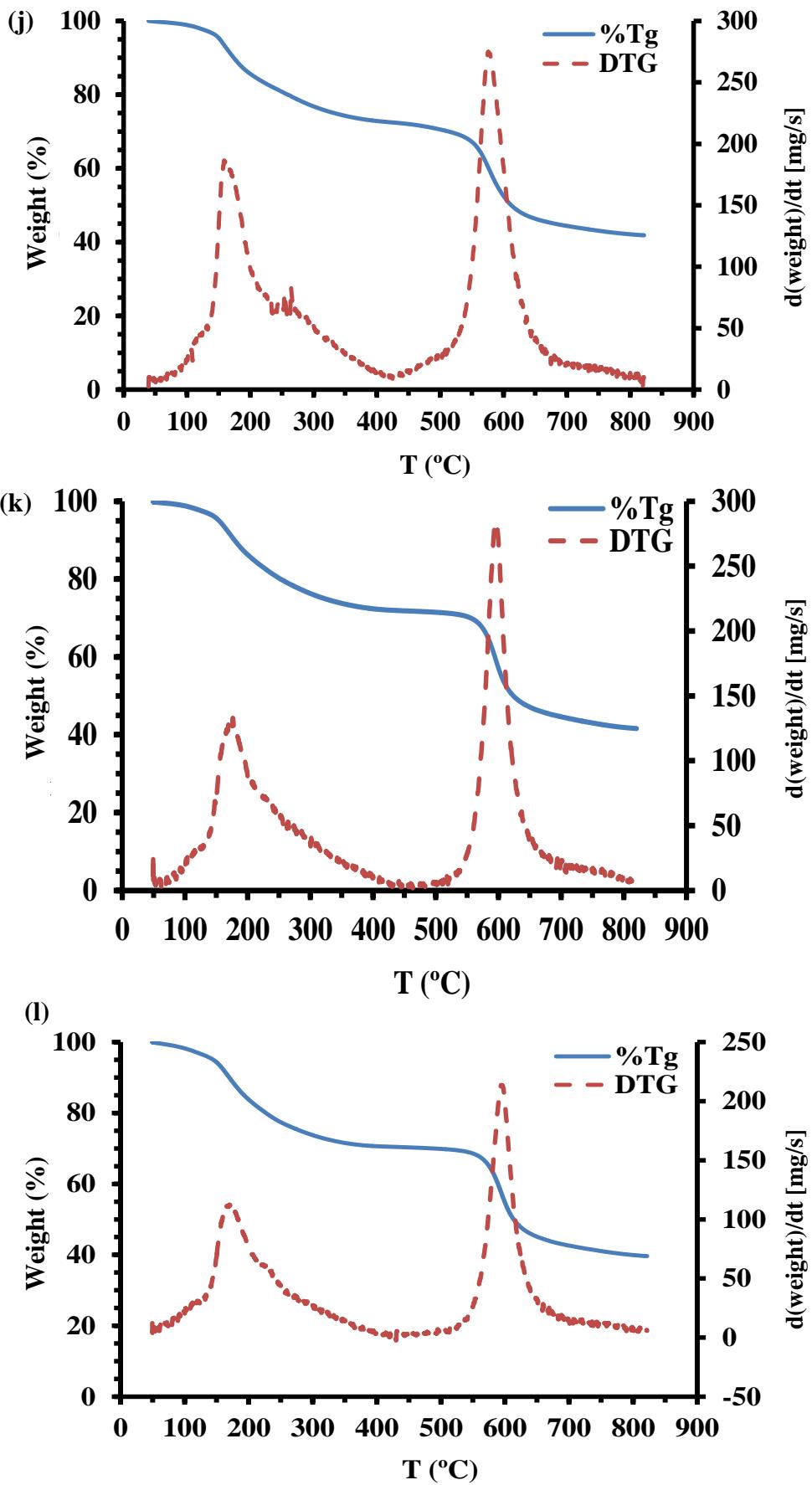
TGA results of PAAs synthesized in the replacement solvent-pairs, commercial PAA solution, commercial polyimide (Kapton®), and PMDA and ODA monomers are shown in Figure S6 and two differential thermogravimetric analysis (DTGA) peaks of all PAAs and monomers are tabulated in Table S6. Both PAA in the replacement solvent-pairs and commercial PAA exhibited two differential thermogravimetric analysis (DTGA) peaks below 800 °C. The first peak of DTGA around 150-170°C probably corresponds to the evaporation of solvent and by-product of water from condensation polymerization. After 380 °C, the PAA was converted completely to polyimide by thermal imidization. The second peak of DTGA was observed between 550 and 600 °C, which represents the degradation of polyimide. This degradation of polyimide between 550 and 600 °C agrees with that for commercial polyimide (Kapton®) from Dupont company (Fig. S6 (b)).

TGA results of ODA and PMDA monomers (Fig. S6 (m) and (n)) show that these monomers completely decompose at 316°C and 350°C, respectively. After ODA and PMDA react to form PAA, the PAAs in solvents do not readily decompose at 350°C, which indicates the occurrence of polymerization.









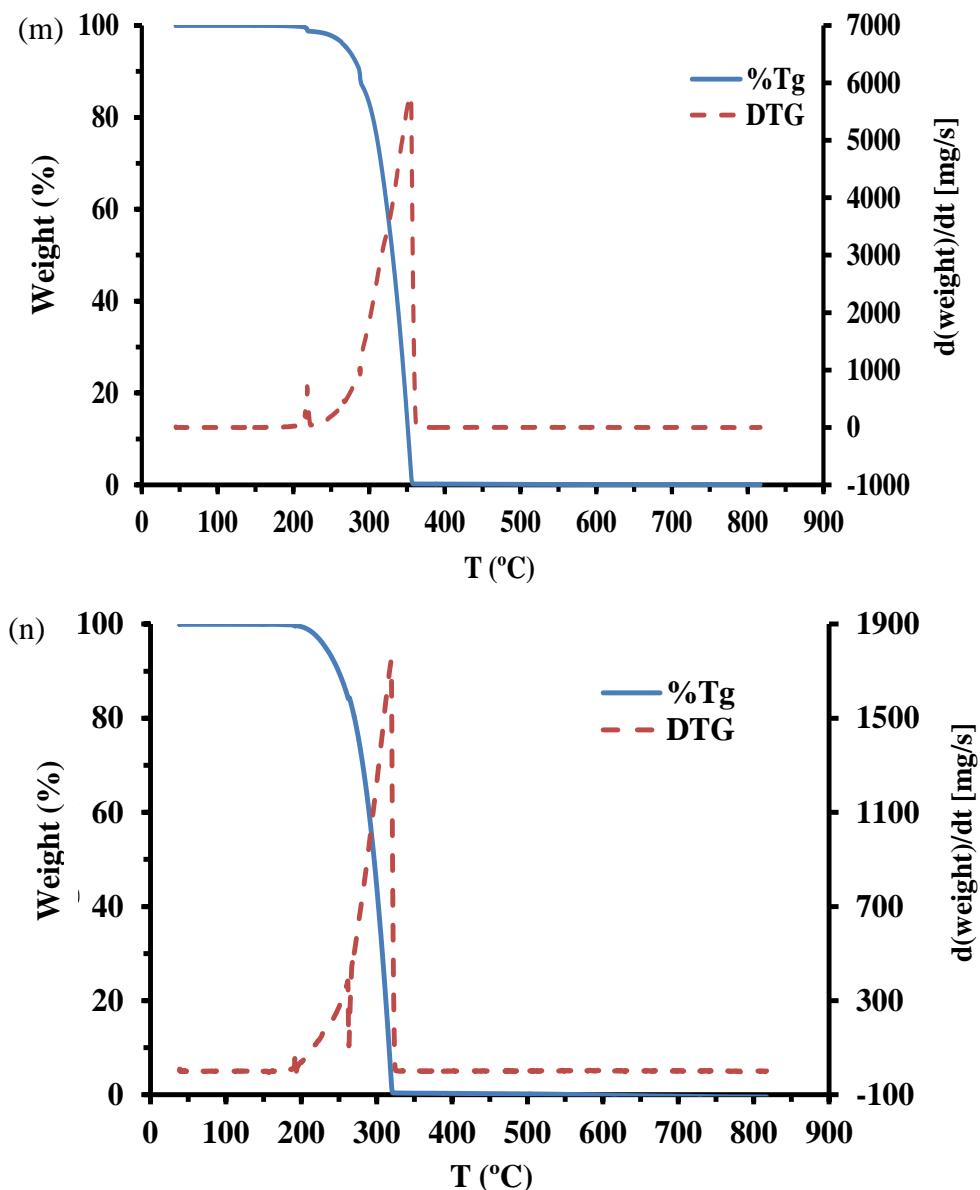


Figure S6. Thermogravimetric analysis (TGA) results of poly(amic acid) (PAA): (a) Commercial PAA solution; (b) Polyimide (Kapton); (c) PAA in PAA in cyclohexanone-MeOH at weight ratio 7/3; (d) PAA in cyclohexanone-EtOH at weight ratio 7/3; (e) PAA in cyclopentanone-MeOH at weight ratio 6/4; (f) PAA in cyclopentanone-EtOH at weight ratio 6/4; (g) PAA in γ -butyrolactone-MeOH at weight ratio 7/3; (h) PAA in γ -butyrolactone-EtOH at weight ratio 7/3; (i) PAA in γ -butyrolactone-water at weight ratio 9.5/0.5; (j) PAA in γ -valerolactone-MeOH at weight ratio 8/2; (k) PAA in γ -valerolactone-EtOH at weight ratio 7/3; (l) PAA in γ -valerolactone-water at weight ratio 9.5/0.5; (m) PMDA monomer; and (n) ODA monomer.

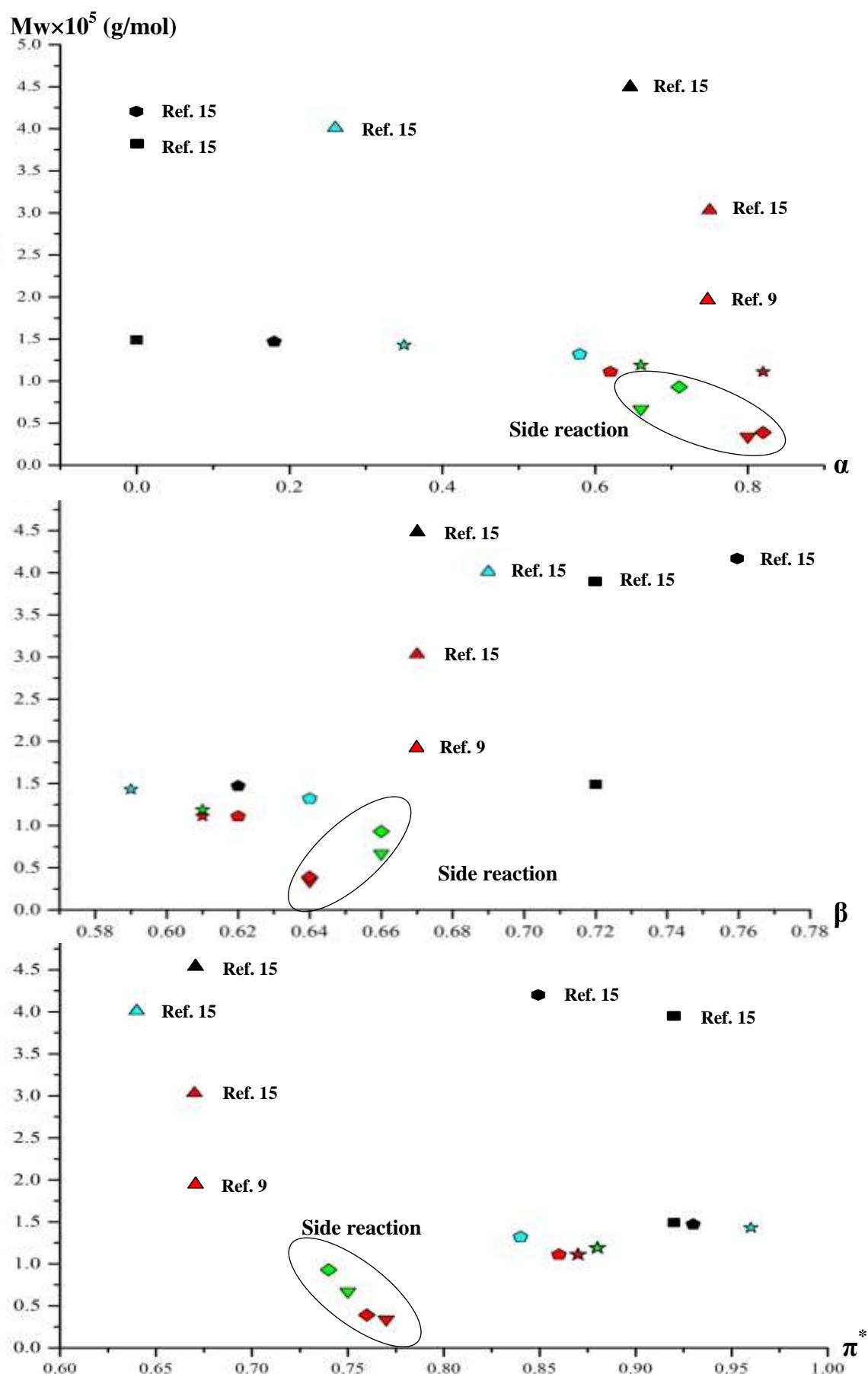


Figure S7. Molecular weight (\overline{M}_w) of poly(amic acid) (PAA) as a function of solvent or solvent mixture

GPC Results of poly(amic acid) (PAA) synthesized in the replacement solvent-pairs

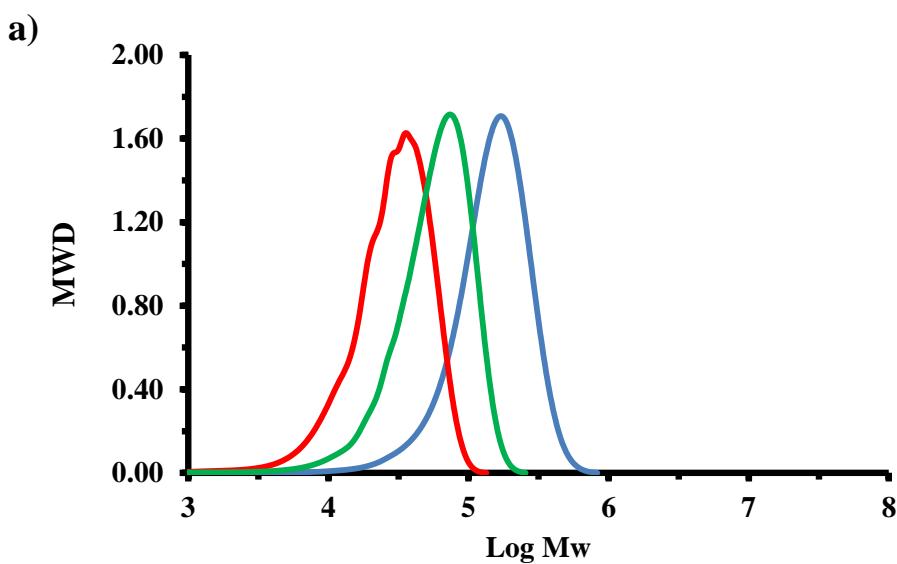


Figure S8. a) (Red line) PAA in cyclohexanone-MeOH, (green line) cyclohexanone-EtOH, (blue line) commercial PAA solution.

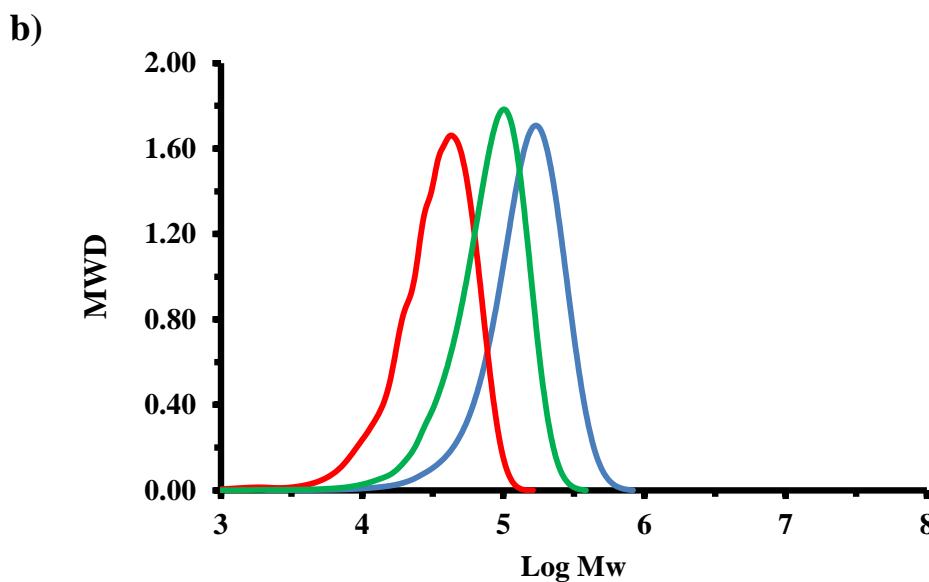


Figure S8. b) (Red line) PAA in cyclopentanone-MeOH, (green line) cyclopentanone-EtOH, (blue line) commercial PAA solution.

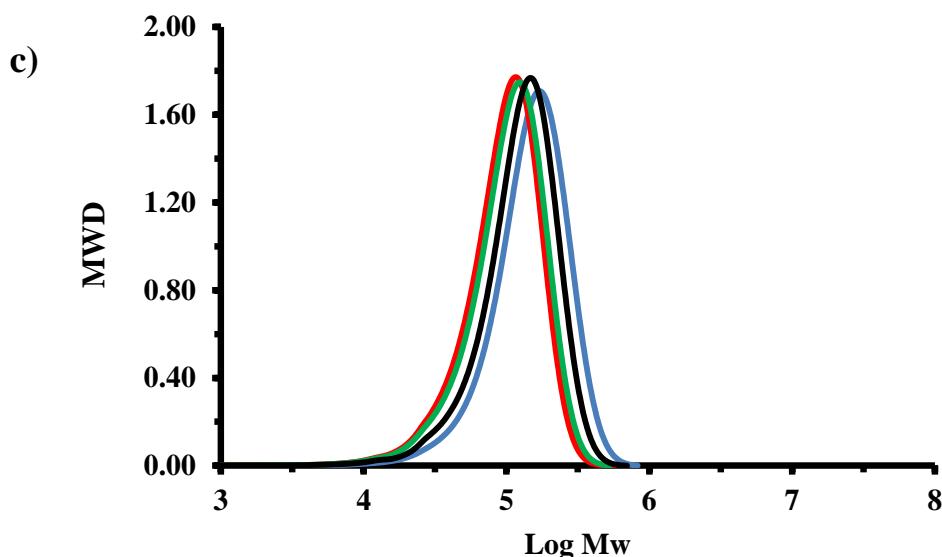


Figure S8. c) (Red line) PAA in γ -butyrolactone-MeOH, (green line) γ -butyrolactone-EtOH, (black line) γ -butyrolactone-water, (blue line) commercial PAA solution.

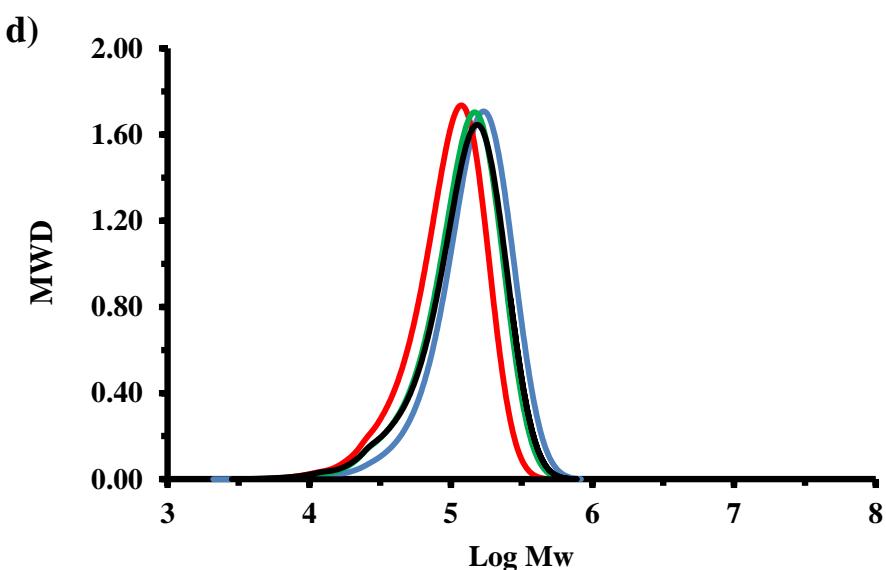


Figure S8. d) (Red line) PAA in γ -valerolactone-MeOH, (green line) γ -valerolactone-EtOH, (black line) γ -valerolactone-water, (blue line) commercial PAA solution.

Figure S8. Gel permeation chromatography (GPC) results for poly(amic acid) (PAA) synthesized in the replacement solvent-pairs in term of molecular weight distribution (MWD).

References for supporting information

1. Marcus, Y. *The Properties of Solvents*, John Wiley & Sons, England, 1998.
2. Jessop, P. G.; Jessop, D. A.; Fu, D.; Phan, L. Solvatochromic parameters for solvents of interest in green chemistry. *Green Chemistry* **2012**, 14, 1245-1259.
3. Rosés, M.; Ortega, J.; Bosch, E. Variation of ET(30) polarity and the Kamlet-Taft solvatochromic parameters with composition in alcohol-alcohol mixtures . *J Solution Chem* **1995**, 24, 51-63.
4. Marcus, Y. The use of chemical probes for the characterization of solvent mixtures. Part 2. Aqueous mixtures. *Journal of the Chemical Society, Perkin Transactions 2* **1994**, 1751-1758.
5. Migron, Y.; Marcus, Y. Polarity, hydrogen bonding, and structure of mixtures of water and cyanomethane. *Journal of the Chemical Society, Faraday Transactions 1* **1991**, 87, 1339-1343.
6. Mancini, P. M.; Adam, C.; Pérez, A. d. C.; Vottero, L. R. Solvatochromism in binary solvent mixtures. Response models to the chemical properties of reference probes. *Journal of Physical Organic Chemistry* **2000**, 13, 221-231.
7. Van Krevelen, D. W.; Nijenhuis, K. te. *Properties of Polymers: Their Correlation with Chemical Structure: their Numerical Estimation and Prediction from Additive Group Contributions*, Elsevier, Amsterdam, 2009.
8. Barton, A.F.M. Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, London, 2nd ed. 1991.
9. Echigo, Y.; Iwaya, Y.; Tomioka, I.; Furukawa, M.; Okamoto, S. A Novel Polymerization Process of Poly(4,4'-oxydiphenylenepyromellitic acid). *Macromolecules* **1995**, 28, 3000-3001.

10. Haruki, M.; Hasegawa, Y.; Fukui, N.; Kihara, S.-i.; Takishima, S. Production of polyamic acid in supercritical carbon dioxide with N,N-dimethylformamide. *Journal of Applied Polymer Science* **2014**, 131, 39878-39885.
11. Kim, B.-H.; Park, H.; Park, H.; Moon, D. C. Degree of imidization for polyimide films investigated by evolved gas analysis-mass spectrometry. *Thermochimica Acta* **2013**, 551, 184-190.
12. Cai, D.; Su, J.; Huang, M.; Liu, Y.; Wang, J.; Dai, L. Synthesis, characterization and hydrolytic stability of poly (amic acid) ammonium salt. *Polymer Degradation and Stability* **2011**, 96, 2174-2180.
13. Kim, S. I.; Pyo, S. M.; Kim, K.; Ree, M. Investigation of glass transition behaviours in aromatic poly(amic acid) precursors with various chain rigidities by oscillating differential scanning calorimetry. *Polymer* **1998**, 39, 6489-6500.
14. Kim, S. I.; Pyo, S. M.; Ree, M. Investigation of Glass Transition Behaviors in Poly(amic acid) Precursors of Semiflexible Polyimides by Oscillating Differential Scanning Calorimetry. *Macromolecules* **1997**, 30, 7890-7897.
15. Echigo, Y.; Furukawa, M.; Nakano, T.; Tomioka, I., US Patent no. 5466732, 1995.
16. Hansen, C. M., *Hansen Solubility Parameters: a User's Handbook*. CRC Press: Boca Raton, London, 2007.
17. Kamlet, M. J.; Taft, R. W. The solvatochromic comparison method. 6. The .pi.* scale of solvent polarities. *Journal of the American Chemical Society* **1977**, 99, 6027-6038.
18. Marcus, Y. The properties of organic liquids that are relevant to their use as solvating solvents. *Chemical Society reviews* **1993**, 22, 409-416.

19. Sysel, P.; Šindelář, V.; Chánová, E.; Wallin, B. Preparation of Polyimides by Using Mixtures of Tetrahydrofuran and Methanol and Their Properties. *Polymer Journal* **2002**, 34, 54-56.
20. Sroog, C. E. Polyimides. *Progress in Polymer Science* **1991**, 16, 561-694.