Supplementary information

Polymer Solubility in Ionic Liquids: Dominated by Hydrogen Bonding

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Supporting information content

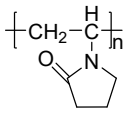
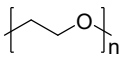
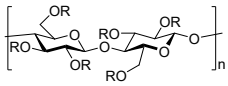
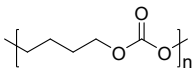
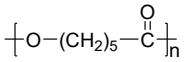
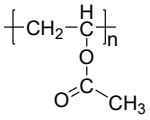
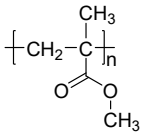
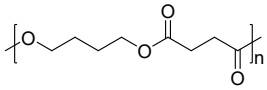
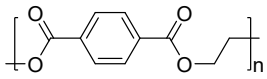
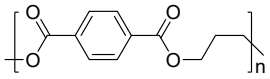
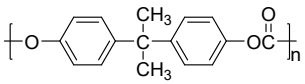
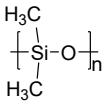
Number of pages: 9

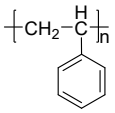
Number of tables: 4

1. Description of polymer samples

Structures, the Kamlet-Abraham-Taft (KAT) parameters α, β, π^* and weight average molecular weight (M_w) of 13 hydrogen bond (H-bond) basicity polymers are provided in Table S1, and 14 H-bond acidity polymers in Table S2.

Table S1 The chemical structure and the KAT parameters of H-bond basicity polymers

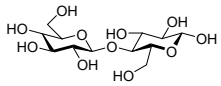
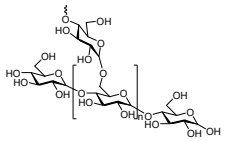
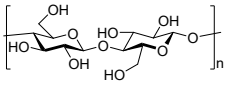
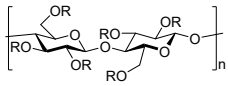
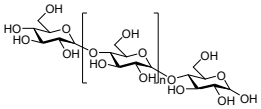
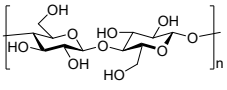
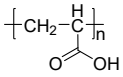
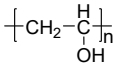
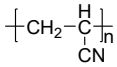
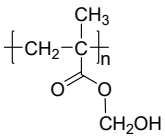
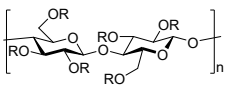
No.	Structure	Name	Abbreviation	M_w (kg/mol)	α_p	β_p	π^*	Ref.
1		Poly(vinyl pyrrolidone)	PVP	58	0.01 (-0.12)	0.93 (0.78)	0.93 (0.91)	1 (2)
2		Poly(ethylene oxide)	PEO	30	0.00	0.65	0.86	1
3	 R= -$COCH_3$	Cellulose triacetate	CTA[a]	200	0.00	0.45	0.45	3
4		Poly (butylene carbonate)	PBC	50	-[b]	-	-	
5		Poly(caprolactone)	PCL	80	0.00	0.41	0.63	1
6		Poly(vinyl acetate)	PVAc	100	0.00 (0.02)	0.40 (0.44)	0.77 (0.76)	1 (2)
7		Poly(methyl methacrylate)	PMMA	200	0.00 (0.24)	0.38 (0.38)	0.71 (0.76)	1 (2)
8		Poly (butylene succinate)	PBS	40	-	-	-	
9		Poly(ethylene terephthalate)	PET	35	-	-	-	
10		Poly(trimethylene terephthalate)	PTT	38	-	-	-	
11		Bisphenol a polycarbonate	BAPC	26	-0.03 (0.14)	0.21 (0.41)	0.76 (0.61)	2 (1)
12		Poly(dimethyl siloxane)	PDMS	115	-	-	-	

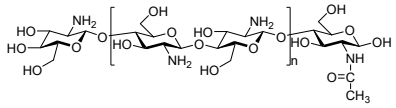
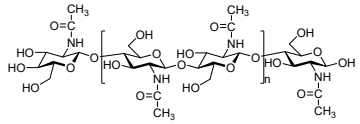
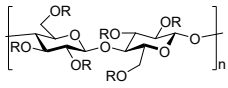
13		Polystyrene	PS	200	0.08	0.06	0.65	2

[a]The substitution degree of acetate is 3.0.

[b]The value is absent.

Table S2 The chemical structure and the KAT parameters of H-bond acidity polymers.

No.	Structure	Name	Abbreviation	M_w (kg/mol)	α_p	β_p	π^*	Ref.
1		Cellobiose	-[a]	0.342	1.44	0.66	0.16	4
2		Amylopectin	-	-	1.37	0.65	0.26	4
3		Microcrystalline cellulose	MCC	36	1.31	0.62	0.34	4
4	 R=H or -CH_2COONa, DS=0.7	Carboxymethylcellulose	CMC0.7[b]	700	0.94	0.91	0.43	5
5		Amylose	-	-	0.83	0.67	0.68	4
6	 PD=2000	Bacterial cellulose	BC	324	0.79	0.87	0.76	6
7		Poly(acrylic acid)	PAA	450	-[c]	-	-	
8		Poly(vinyl alcohol)	PVA[d]	250	0.66	0.52	1.11	2
9		Polyacrylonitrile	PAN	85	-	-	-	
10		Poly (2-hydroxyethyl methacrylate)	PHEMA	150	0.67	0.43	0.98	2
11	 R=H or -$COCH_3$, DS=2.36	Cellulose acetate	CA2.36[e]	200	0.63	0.53	0.60	3

12		Chitosan[f]	-	80	0.49 1.46	0.98 0.27	0.66 0.15	4
13		Chitin	-	90	0.67	0.86	0.91	4
14	 R=H or -CH_2COONa, DS=1.2	Carboxymethylcellulose	CMC1.2[b]	250	0.63	0.87	0.63	5

[a]No abbreviation.

[b]The substitution degree of carboxymethyl samples (No. 4 and 14) is 0.7 and 1.2, respectively.

[c]The value is absent.

[d]α of PVA derived from model solvents in ref. 2.

[e]The substitution degree of acetate is 2.36.

[f]Chitosan exhibits totally different KAT parameters for two samples with different MW (600 Kg/mol vs 150 Kg/mol). The degree of deacetylation also influences the value of KAT parameters.

2. The conditions and methods of solubility tests

We followed the methods of solubility tests of polymer solubility in ILs reported in literature.[7,8] Due to the high viscosity of ILs, the speed of polymer dissolution is very slow, so the heating or a cosolvent evaporation method[8] was used to help the dissolution. The dissolution was carried out at 150 °C for 10 h for synthetic polymers and 120 °C for 10 h for natural polymers (polysaccharides with corresponding derivatives) for avoiding the degradation. Then cooled under room temperature, and phase changes in the ILs-polymer solutions (3 wt% concentration) were monitored over a course of 72 h. The polymer was regarded as soluble in ILs when the ILs-polymer solutions (3 wt% concentration) was homogeneous and transparent, otherwise, the polymer was regarded as insoluble.

The general procedure for cosolvent evaporation based on the characteristic nonvolatile nature of ILs is as follows[8]: (1) an organic solvent was used to prepare a homogeneous solution of a polymer; (2) an IL was added to the polymer organic solvent solution; and (3) after ensuring the transparency of the three-component mixture, the organic solvent was evaporated. In the study, tetrahydrofuran or dichloromethane were used as volatile organic solvents. The solubility results of co-solvent evaporation method were consistent with those of the heating method. It is known that that the molecular weight and the molecular weight distribution (MWD) of polymers also influence results of solubility tests. Most polymers using in the solubility test were commercial polymers normally having their MW of 30 to 500 Kg/mol (seeing Table S1 and Table S2) and MWD of 2 - 5.

3. Data of polymer Solubility in Ionic Liquids

The solubility data of basicity polymers in 11 ILs (7 acidity, and 4 basicity) are collected in Table S3, and the solubility data of acidity polymers in Table S4. Solid symbols "●" represents solubilization, half-filled symbols "◓" represents solubilization at high temperatures only, and open symbols "○" represents insolubilization.

In the text, it has been suggested that the solubility of polymers in ILs is related to value of the product of $\Delta\alpha\Delta\beta$, which is called as the quantitative hydrogen bonding (QHB) analysis. Here, the values of QHB analysis, as $\Delta\alpha\Delta\beta \times 10^3$, are also listed in Table S3 and Table S4. As an indicator of H-bond strength, the negative QHB value is proportional to the solubility of polymers in ILs. For instance, the poly(vinyl pyrrolidone) can be dissolved up to 40 wt% in $[C_4mim][Tf_2N]$ or $[C_4mim][PF_6]$, while the QHB factor is -462 and -488, respectively. Celluloses can be dissolved up to 25 wt% in $[C_2mim][Ac]$ (QHB factor = -307) while only 0.5 wt% in [Amim][Br] (-32). Last, although KAT parameters of some polymers (Table S1 and Table S2) are absent, their solubility data (Table S3 and Table S4) still supported the solubility criteria qualitatively.

Table S3 Results of solubility tests and values[a] of QHB analysis for H-bond basicity polymers in different ILs. Repetitions of experimental observations in refs. 7,8 were marked in blue text. The other data (in black text) are new results tested in this work.

No.	ILs	[C_2mim][Ac]	[Amim][Cl]	[C_4mim][Cl]	[Amim][Br]	[C_4mim][TfO]	[C_8mim][PF_6]	[C_4mim][BF_4]	[C_8mim][BF_4]	[C_8mim][Tf_2N]	[C_4mim][Tf_2N]	[C_4mim][PF_6]
	α_+	0.51	0.47	0.45	0.50	0.62	0.58	0.64	0.62	0.60	0.69	0.67
1	PS (β_p= 0.06)	○, 400	○, 304	○, 285	○, 252	○, 216	○, 200	○, 196	○, 189	○, 120	○, 116	○, 77
2	PDMS	○	○	○	○	○	○	○	○	●	○	○
3	BAPC (β_p= 0.21)	●, 421	○, 315	○, 298	○, 239	○, 163	○, 153	○, 134	○, 130	○, 50	○, 29	○, -14
4	PTT	○	○	○	○	○	○	○	○	○	○	○
5	PET	○	○	○	○	○	○	○	○	○	○	○
6	PBS	○	○	○	○	◓	◓	○	◓	○	◓	◓
7	PMMA (β_p= 0.38)	○, 311	○, 216	○, 203	○, 140	●, 50	●, 46	○, 19	○, 19	●, -54	●, -90	●, -127
8	PVAc (β_p= 0.40)	○, 301	○, 207	○, 194	○, 130	●, 37	●, 35	○, 6	◓, 6	●, -66	●, -104	●, -141
9	PCL (β_p= 0.41)	○, 296	○, 202	○, 189	○, 125	○, 31	◓, 29	○, 0	○, 0	●, -72	◓, -110	○, -147
10	PBC	○	○	○	○	●	●	○	●	●	●	●
11	CTA (β_p= 0.45)	-[b]	○, 183	○, 171	○, 105	●, 6	●, 6	●, -26	●, -25	○, -96	●, -138	●, -174
12	PEO (β_p= 0.65)	○, 173	○, 89	○, 81	○, 5	●, -118	●, -110	●, -154	●, -149	●, -216	●, -276	●, -308
13	PVP (β_p= 0.93)	○, 30	○, -41	○, -44	●, -132	●, -287	●, -268	●, -328	●, -317	●, -378	●, -462	●, -488

Solid symbols ●: solubilization; half-filled symbols ◓: solubilization at high temperatures only; open symbols ○: insolubilization.

[a]QHB factor as $\Delta\alpha\Delta\beta \times 10^3$.

[b]Decomposition in the IL at 120 °C.

Table S4 Results of solubility tests and values[a] of QHB analysis for H-bond acidity polymers in different ILs. Repetitions of experimental observations in refs. 7,8 were marked in blue text. The other data (in black text) are new results tested in this work.

No.	ILs	[C_2mim][Ac]	[Amim][Cl]	[C_4mim][Cl]	[Amim][Br]	[C_4mim][TfO]	[C_8mim][PF_6]	[C_4mim][BF_4]	[C_8mim][BF_4]	[C_8mim][Tf_2N]	[C_4mim][Tf_2N]	[C_4mim][PF_6]
	β	0.99	0.84	0.83	0.66	0.46	0.46	0.41	0.41	0.29	0.25	0.19
1	Cellobiose (α_p= 1.44)	●, -307	●, -175	●, -168	●, 0	○, 164	○, 172	○, 200	○, 205	○, 311	○, 308	○, 362
2	Amylopectin (α_p= 1.37)	●, -292	●, -171	●, -166	●, -9	○, 143	○, 150	○, 175	○, 180	○, 277	○, 272	○, 322
3	MCC (α_p= 1.31)	●, -296	●, -185	●, -181	○, -32	○, 110	○, 117	○, 141	○, 145	○, 234	○, 229	○, 275
4	CMC0.7 (α_p= 0.94)	●, -34	○, 33	○, 39	○, 110	○, 144	○, 162	○, 150	○, 160	○, 211	○, 165	○, 194
5	Amylose (α_p= 0.83)	●, -102	●, -61	●, -61	●, 3	○, 44	○, 53	○, 49	○, 55	○, 87	○, 59	○, 77
6	BC (α_p= 0.79)	●, -34	●, 10	●, 14	○, 61	○, 70	○, 86	○, 69	○, 78	○, 110	○, 62	○, 82
7	*PAA	●	●	●	●	◒	○	○	○	○	○	○
8	PVA(α_p= 0.66)	●, -71	●, -61	●, -65	●, -22	○, 2	○, 5	○, 2	○, 4	○, 14	○, -8	○, -3
9	PAN	-[b]	●	●	●	○	○	○	○	○	○	○
10	PHEMA (α_p= 0.67)	●, -90	●, -82	●, -88	●, -39	●, -2	○, -3	◒, 1	◒, 1	○, 10	○, -4	○, 0
11	CA2.36 (α_p= 0.63)	●, -55	●, -50	●, -54	●, -17	●, 1	◒, 4	●, -1	●, 1	○, 7	◒, -17	◒, -14
12	Chitosan	●	○	○	○	○	○	○	○	○	○	○
13	Chitin (α_p= 0.67)	●, -21	○, 4	○, 7	○, 34	○, 20	○, 36	○, 14	○, 23	○, 40	○, -12	○, 0
14	CMC1.2 (α_p= 0.63)	●, -14	○, 5	○, 7	○, 27	○, 4	○, 21	○, -5	○, 5	○, 17	○, -37	○, -27

Solid symbols ●: solubilization; half-filled symbols ◒: solubilization at high temperatures only; open symbols ○: insolubilization.

[a]QHB factor as $\Delta\alpha\Delta\beta \times 10^3$.

[b]Decomposition in the IL at 150 °C.

References

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