Greener Dipolar Aprotic Solvents for the Dynamic Polycondensation of High-Performance Polyimide Membranes

E. San José[a,b], M.R. de la Viuda*[a,b], F.J. Carmona[a,b], C. Soto[a,b], L. Palacio[a,b], P. Prádanos[a,b],

A. Hernández[a,b], A. Tena*[a,b]

[a] Surfaces and Porous Materials (SMAP), CSIC-Associated Research Unit, Universidad de Valladolid, 47011, Valladolid, Spain;

[b] Institute of Sustainable Processes (ISP), 47011, Valladolid, Spain;

Email: monicarosa.viuda@uva.es

Email: a.tena@uva.es

Supporting information

The list of solvents analyzed in this work can be found in Table S1 and Table S2. While Table S1 is a general list of the solvents analyzed, including apolar and polar protic solvents, the Table S2 is including in detail the polar aprotic solvents analyzed as well as their dielectric constant, flash point.

The code of colors employed in this work is represented as follows:

Color	Reason to be excluded
	Safety Criteria
	Health Criteria
	Environmental Criteria
	Specific Criteria – synthesis and membrane formation
	Selected

Table S1. List of apolar and polar protic solvents analyzed in this work organized by alphabetical order.

Apolar solvents				Polar protic solvents			
1	1,4-Dioxane	20	Ethyl ether	1	Acetamide	20	Isobutanol
2	Anisole	21	Furan	2	Acetic acid	21	Isopropanol
3	Benzene	22	Heptane	3	Benzyl acetate	22	Isopropylamine
4	Biphenyl	23	Heptanoic acid	4	Benzyl alcohol	23	Lactic acid
5	Butanoic acid	24	Hexane	5	n-Butanol	24	Methanol
6	Butylamine	25	Isoamyl acetate	6	Chloroacetic acid	25	Methyl acetate
7	Butylbenzene	26	Isopentane	7	Cyanoacetic acid	26	Methyl lactate
8	Caproic acid	27	Linoleic acid	8	Ethanol	27	Methyk tert-butyl ether
9	Carbon disulfide	28	Naphtalene	9	Ethyl acetate	28	Pyridine
10	Carbon tetrachloride	29	*p*-Cymene	10	Ethyl lactate	29	tert-Butanol
11	Chloroform	30	Pentane	11	Ethylamine	30	Tetrahydrofurfuryl alcohol
12	Cumene	31	Succinimide	12	Ethylene glycol	31	Water
13	Cyclohexane	32	T-Amyl methyl ether	13	Formic acid		
14	Cyclohexanone	33	Toluene	14	Furfuryl alcohol		
15	Cyclopentane	34	Triethylamine	15	Glycerol		
16	Decane	35	Turpentine	16	Hydrazine		
17	Diethyl eter	36	Xylene	17	Hydrochloric acid		
18	Dimethyl ether	37	α-Pinene	18	Hydrogen peroxide		
19	D-Limonene			19	Isoamyl alcohol		

Table S2. List of the Polar Aprotic solvent analyzed in this work ordered by their dielectric constant. It is highlighted color the solvents excluded from the selection (attending to the Table 1 of the main text). The solvent selected are simple presented in highlighted in green.

Number	Solvent name	CAS number	Dielectric constant	Flash Point / °C	Boiling Point / °C	H3xx statement
1	Diethyl carbonate	96-49-1	2.8	143	248	None
2	Diisopropyl ether	108-20-3	3.9	-28	69	H336
3	Dioctyl phthalate	117-84-0	5.1	221	386	H360
4	Isobutyl acetate	110-19-0	5.1	22	115	H336
5	n-Butyl acetate	123-86-4	5.1	22	126	H336
6	Glycol diacetate	111-55-7	5.1	82	186	None
7	Ethyl tert-butyl ether	637-92-3	5.2	-19	72	H336
8	Butyl acrylate	141-32-2	5.2	-65	145	H335
9	Chlorobenzene	108-90-7	5.6	29	132	H332
10	Diethyl sulfide	352-93-2	5.7	-7	92	H319
11	Dimethyl ether	115-10-6	6.2	-4	25	none
12	Isopropyl acetate	108-21-4	6.3	2	89	H319
13	Fluorobenzene	462-06-6	6.4	-15	85	H318
14	N-butyl 2-pyrrolidone	2687-91-4	6.5	108	241	H319
15	Cyclopentyl methyl ether	5614-37-9	6.7	-1	106	H302
16	Dibutyl phthalate	84-74-2	6.7	187	340	H360
17	Dimethyl carbonate	616-38-6	7.2	16	90	None
18	Tetrahydrofuran	109-99-9	7.6	-14	66	H351
19	Methyl tetrahydrofuran	96-47-9	7.6	-11	80	H318
20	N-Octyl pyrrolidone	2687-94-7	7.8	142	170	H314
21	Chlorocyclohexane	542-18-7	7.9	32	142	H335
23	Dichloromethane	75-09-2	8.9	n.a	40	H351
24	Bromoethane	74-96-4	9.0	-118	38	H351
25	Heptanal	111-71-7	9.1	48	153	H319
26	Diethyl succinate	123-25-1	10.4	90	217	None
27	p-Cresol	1319-77-3	10.6	85	202	H314
28	Dichloroethane	75-34-3	10.7	13	84	H350
29	Sulfolane	126-33-0	11.0	177	287	H360
30	Dimethyl isosorbide	5306-85-4	11.4	110	95	H335
31	Cyrene	53716-82-8	12.7	61	203	H319
32	Methylcyclohexanone	583-60-8	13.0	-4	101	H332
33	Methyl isobutyl ketone	108-10-1	13.1	13	117	H319
34	N-Ethyl pyrrolidone	2687-91-4	15.7	91	97	H360
35	Acetyl Bromide	506-96-7	16.2	110	74	H314
36	Benzaldehyde	100-52-7	17.9	63	170	H302
37	Acetophenone	98-86-2	18.0	105	202	H319
38	Methyl ethyl ketone	78-93-3	18.5	-6	80	H319
39	Ethyl isocyanate	109-90-0	19.7	-1	60	None
40	Acetone	67-64-1	20.7	-18	6	H319
41	Acetic anhydride	108-24-7	21.0	49	139	H314
42	Acetaldehyde	75-07-0	21.8	-40	21	H350
43	Acetylacetone	123-54-6	23.0	38	138	H302
44	Methyl nitrate	598-58-3	23.9	24	65	H336
45	Benzonitrile	100-47-0	25.9	70	375	H312
46	Hexamethylphosphoramide	680-31-9	30	144	>200	H350
47	Pentaborane	19624-22-7	31.1	30	60	H336
48	1.3-Propanediol	504-63-2	32.0	>100	214	None
49	2-Pyrrolidone	616-45-5	32.2	129	245	H360
50	N-methyl-2-pyrrolidone	872-50-4	32.2	96	202	H360
51	Acrylonitrile	107-13-1	33.0	-5	77	H350

52	Nitrobenzene	98-95-3	35.6	88	211	H360
53	Acetonitrile	75-05-8	36.6	2	82	H319
54	Dimethylformamide	68-12-2	36.7	58	153	H360
55	γ-Valerolactone	108-29-2	36.7	100	207	None
56	Nitromethane	75-52-5	37.3	35	101	H302
57	Dimethylacetamide	127-19-5	37.8	70	166	H360
58	N.N-dimethyl lactamide[a]	35123-06-9	37.8	109	223	H319
59	1.3-Dimethyl-3.4.5.6-tetrahydro-2(1H)-pyromidinone	7226-23-5	38.8	121	246	H361
60	γ-Butyrolactone	96-48-0	40.0	98	204	H332
61	Furfural	98-01-1	42.1	60	162	H351
62	Dimethyl sulfoxide	67-68-5	46.7	95	189	None
63	Propylene carbonate	108-32-7	64.0	116	242	H319
64	3-Methoxy-N,N-dimethylpropanamide	53185-52-7	nd	99	215	H361
65	Ethyl-5-(dimethylamino)-2-methyl-5-oxopentanoate	1174627-68-9	nd	119	214	H319

Chemicals: 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, >99%), 3,3′-Dihydroxybenzidine (HAB, >99%), 2,2-bis(4-aminophenyl)hexafluoropropane (6FpDA, >98%) and 2,4-Diaminomesitylene (DAM, >99%) were purchased from Apollo Scientific (Apollo Scientific, Manchester, United Kingdom) and used without additional purification. Anhydrous N-methyl-2-pyrrolidone (NMP), γ-Valerolactone (GVL), Dihydrolevoglucosenone (Cyrene), Dimethyl Isosorbide (DMI) and Dimethyl Carbonate (DMC) were purchased from Merck (Germany). 3-Methoxy-N,N-dimethylpropanamide (KJCMPA-100®) and Dimethylsulfoxide (DMSO) were kindly donated by AlephChem (Alephchem, Milano, Italy) and IMCD Pharmaceuticals (IMCD, Cleveland, Ohio, USA) respectively. The solvents were used as received. Imidization method was carried out through addition of acetic anhydride (Ac_2O) and pyridine (Py), both purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, Missouri, USA).

The general polymerization protocol is showed in Figure 1. An excess of acetic anhydride (20 mmol) and pyridine (15 mmol) were added to the poly(amic) acid solution.

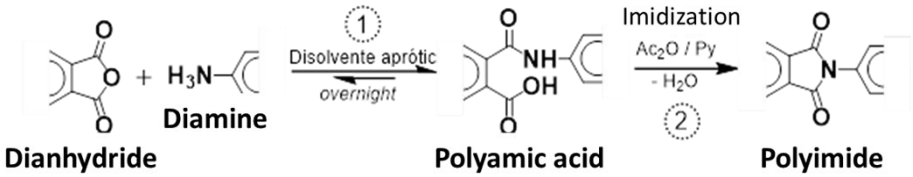

Figure S1. Scheme of the reactions involved in the synthesis of the polymers.

Polymer characterization: The molecular structure of polymers was confirmed by ^{1}H-NMR using the Agilent AV-400 spectrometer. The samples were dissolved in deuterated DMSO-d_6 and the measurements were taken at room temperature. Approximately, 10 mg of each polymer was dissolved in 0.6 mL of solvent. Molecular weights of the polyimides were determined by using gel permeation chromatography (GPC) after calibration with polystyrene standards. GPC measurements were performed at 40 °C using DMF as eluent on a Water 1525 Binary HPLC Pump equipped with polystyrene gel columns with different pore sizes, using a refractive index (RI) detector. The peak-average molecular weight (M_p), number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) were determined. The chemical structure of polymers was

performed by attenuated total internal reflectance−Fourier transform infrared spectroscopy (ATR-FTIR) experiments at room temperature on a FT-IR Bruker Tensor 27 in a spectral range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Characterization of the polymers:

^{1}H-NMR of the synthetized polymers

6FDA-AcHAB: ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.23 (d, J = 8.0 Hz, 2H, H_b), 8.00 (d, J = 8.0 Hz, 2H, H_c), 7.86 (s, 2H, H_d), 7.81 (d, J =8.2 Hz, 2H, H_e), 7.79 (s, 2H, H_g), 7.68 (d, J = 8.2 Hz, 2H, H_f), 2.17 (s, 6H, H_a). FTIR-ATR ν(C=O symmetric) 1778 cm^{-1}, ν(C=O asymmetric) 1721 cm^{-1}, ν(C-N) 1366 cm^{-1} and ν(C-N-C) 1086 cm^{-1}.

6FDA-6FpDA: ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 8.19 (d, J = 8.1 Hz, 2H, H_b), 7.96 (d, J = 8.1 Hz, 2H, H_c), 7.77 (s, 2H, H_d), 7.63 (d, J = 8.6 Hz, 4H, H_a y H_e), 7.56 (d, J = 8.6 Hz, 4H, H_f y H_g). FTIR-ATR ν(C=O symmetric) 1787 cm^{-1}, ν(C=O asymmetric) 1725 cm^{-1}, ν(C-N) 1364 cm^{-1} and ν(C-N-C) 1083 cm^{-1}.

6FDA-DAM: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 7.6 Hz, 2H, H_b), 7.91 (m, 4H, H_c y H_d), 7.31 (s, 1H, H_a), 2.13 (s, 6H, H_f), 1.91 (s, 3H, H_e). FTIR-ATR ν(C=O symmetric) 1787 cm^{-1}, ν(C=O asymmetric) 1721 cm^{-1} , ν(C-N) 1366 cm^{-1} and ν(C-N-C) 1086 cm^{-1}.

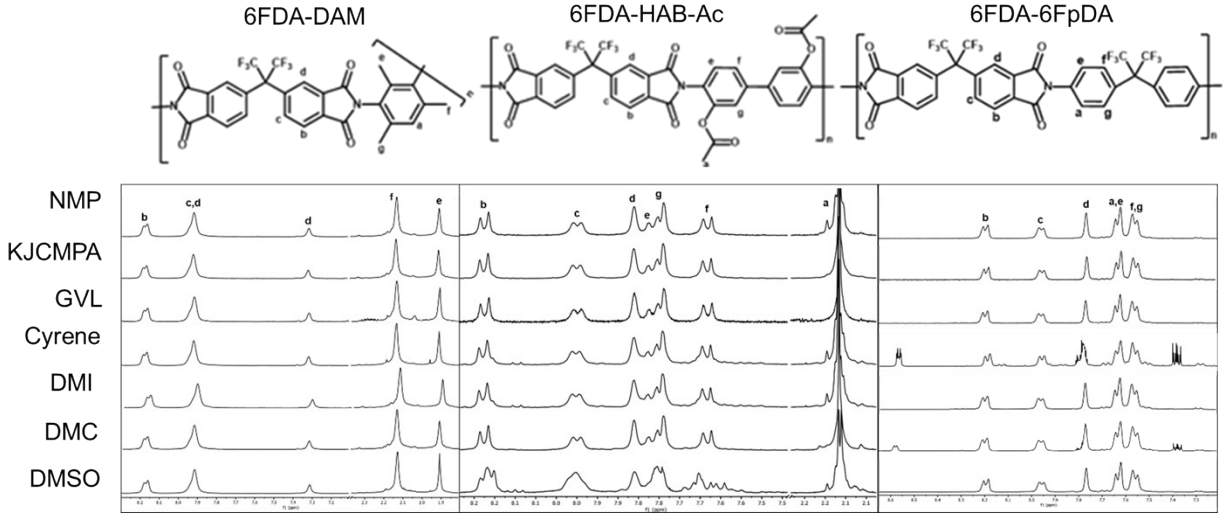

Figure S2. *^{1}H-NMR in d_6-DMSO for the polymers synthesized in the different solvents*

Solubility parameters reported in literature for the DMSO solvent.

Table S3. Some examples of reported HSP values for DMSO.

Reference	Method	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	δ_T ($MPa^{1/2}$)
[1-3]*	Solubility poly(ether sulfone) by DataFit	18.4	16.4	10.2	26.6
[4]	HSPiP software	18.4	10.1	11.1	23.7
[5]	Solubility test for a chemical	17.4	14.2	7.3	23.6
[6]	Group contribution	18.4	13.7	11.3	24.86

[7]	Cohesive energy	9.0	8.0	6.0	13.45
[6]	Solubility test for a chemical	19.3	16.4	10.2	27.3

* This is the most repeated and employed value over the literature review.

FTIR analysis

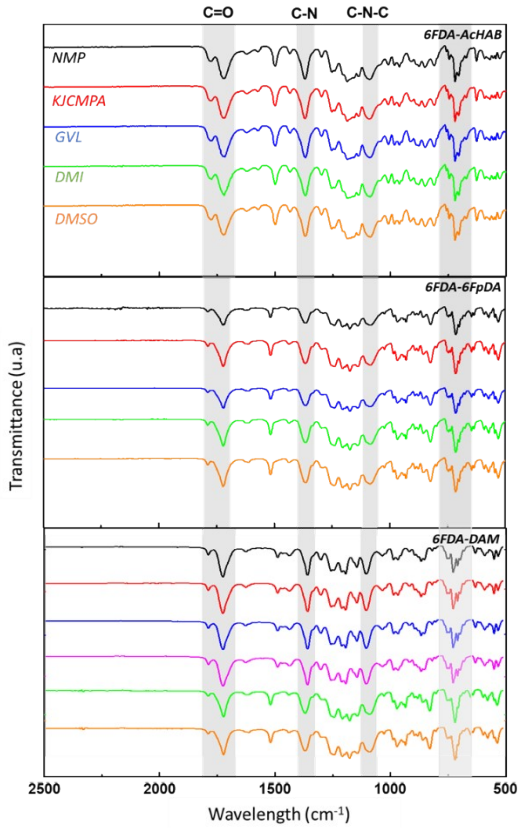

Figure S3. FTIR-ATR spectrum of the three polymers synthesized in the 6 selected solvents using NMP as reference.

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