

Supporting Information

Contraction of Weak Polyelectrolyte Multilayers in Response to Organic Solvents of Widely Varying Properties

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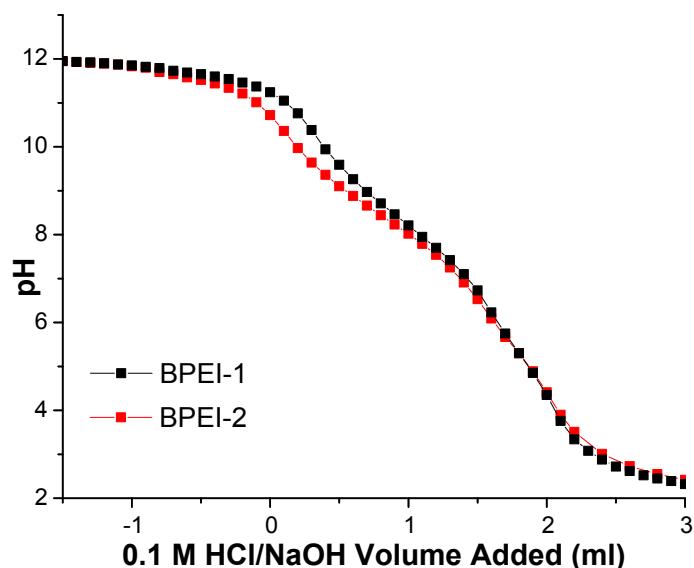


Fig. S1 Titration curve of 1 M BPEI-1 and BPEI-2 by addition of 0.1 M NaOH/HCl solution. Positive value represents addition of HCl, and negative values represent addition of NaOH. The three steps in the titration curve are associated with the pKa for the amines of BPEI-1 ($\text{pKa}= 11.4, 7.1, 3.0$) and BPEI-2 ($\text{pKa}=11.9, 7.3, 3.3$).

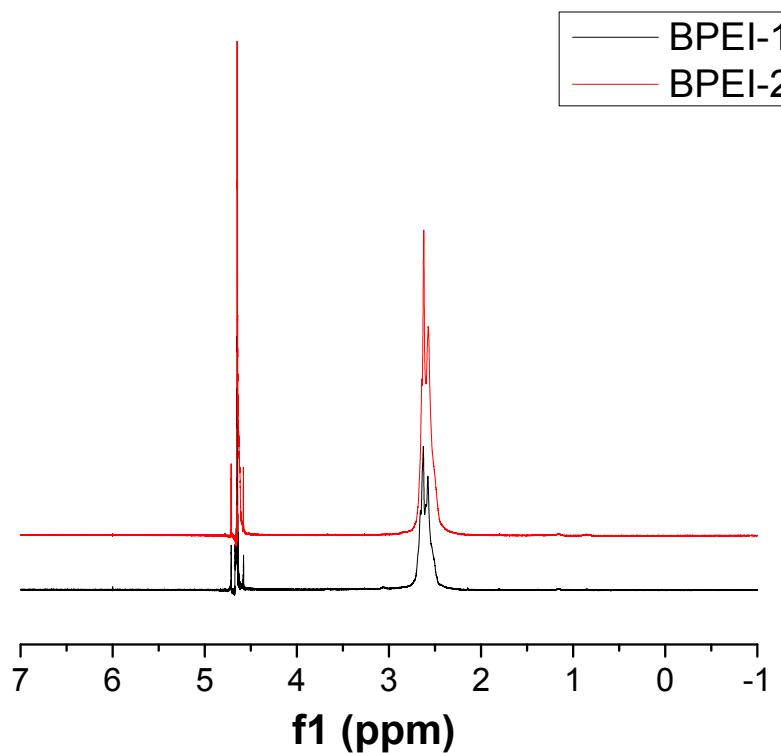


Fig. S2 ¹H NMR spectra of BPEI-1 (black line) and BPEI-2 (red line) in *D*₂O.

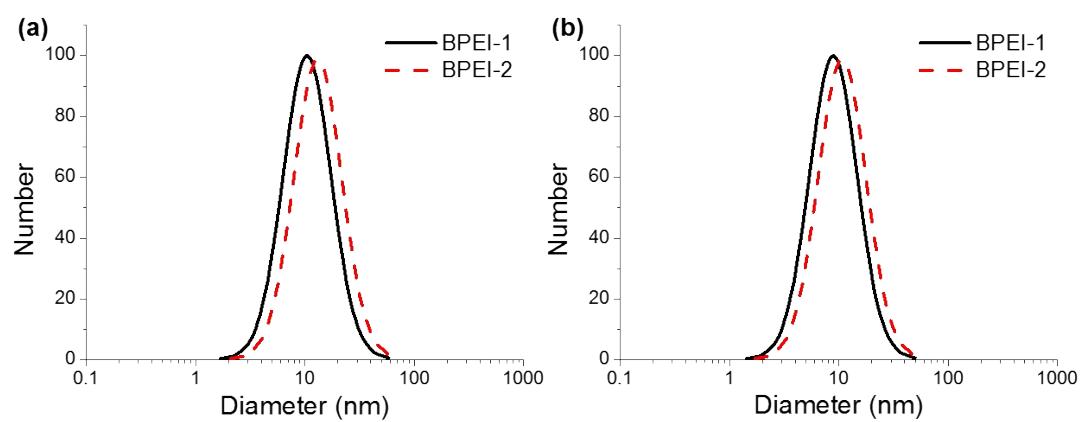


Fig. S3 Hydrodynamic radii of BPEI-1 (black solid line) and BPEI-2 (red dashed line) determined by DLS. The sample concentrations are (a) 1 mg/mL and (b) 0.5 mg/mL in DI water.

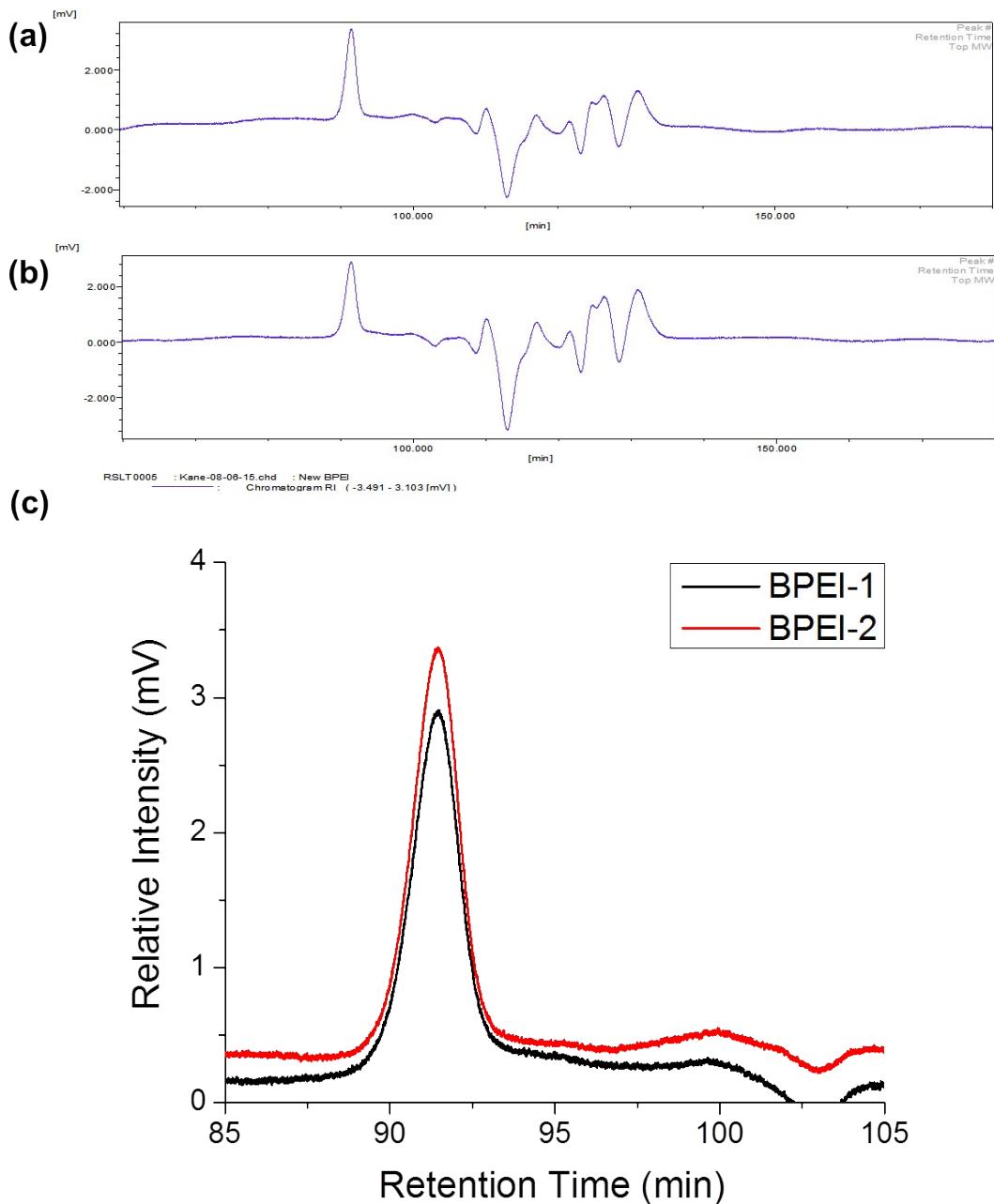


Fig. S4 GPC traces of (a) BPEI-1 and (b) BPEI-2. An enlarged area (c) provides direct comparison between BPEI-1 (black line) and BPEI-2 (red line).

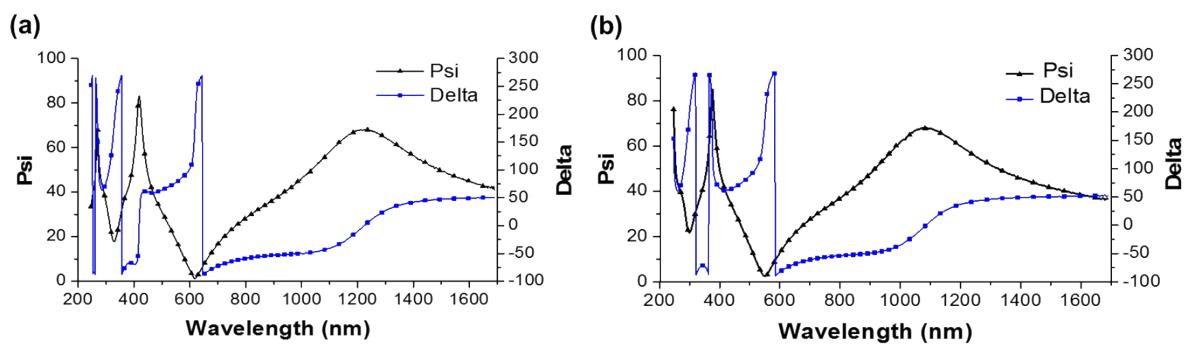


Fig. S5 Representative spectroscopic ellipsometry data of (a) BPEI-1/PAA and (b) BPEI-2/PAA films; Ψ (black line with \blacktriangle) and Δ (blue line with \blacksquare). The typical quality of the fit using a Cauchy layer to describe the optical properties of the BPEI/PAA is shown by solid lines.

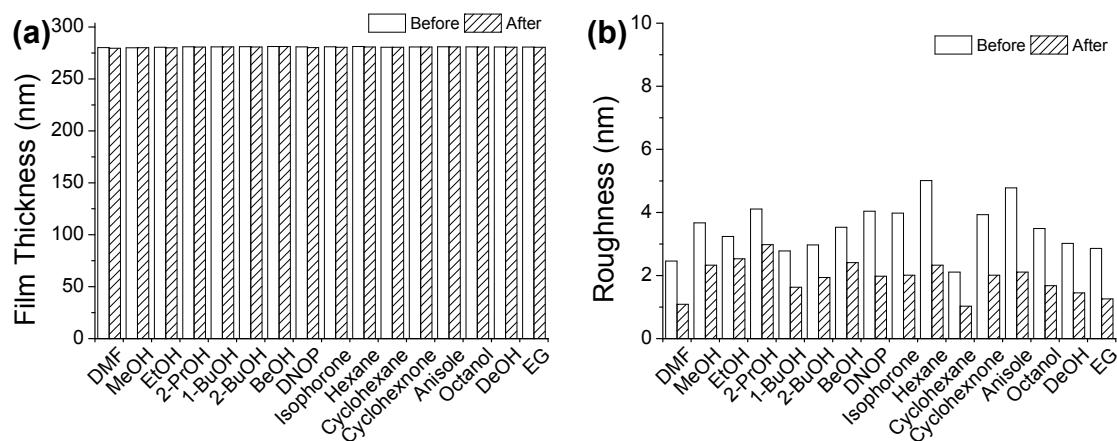


Fig. S6 Film thickness (a) and roughness (b) of BPEI/PAA film before and after organic liquid treatment and drying.

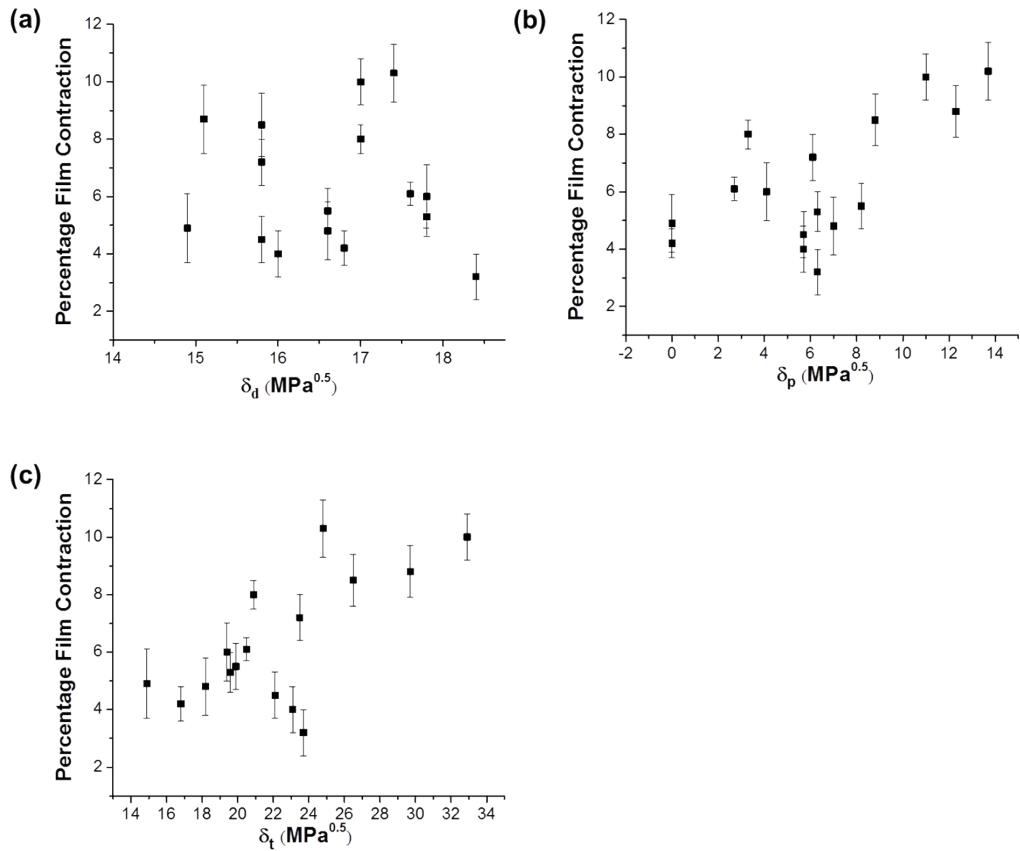


Fig. S7 Correlation between the components of the Hansen solubility parameters; (a) dispersion, (b) polarity, and (c) total (Hildebrandt); with contraction of the BPEI/PAA films in different organic liquid.

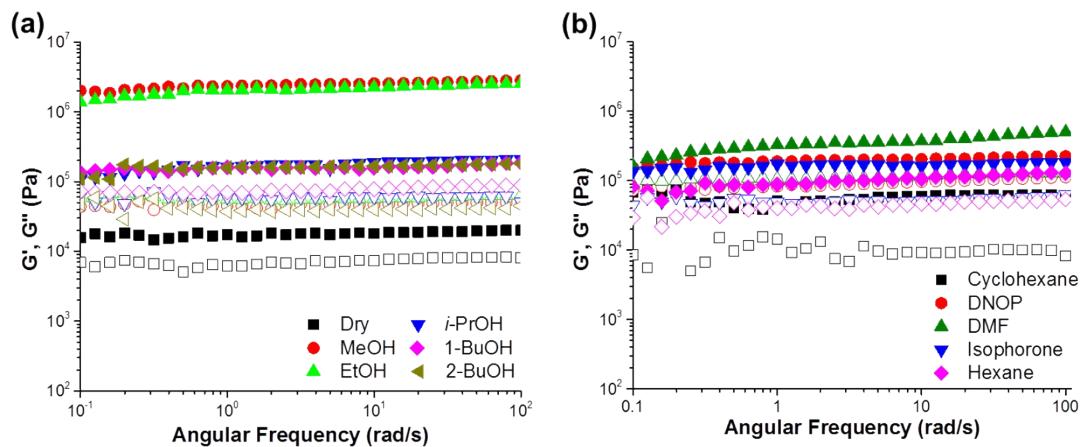


Fig. S8 Rheological properties of BPEI/PAA film while soaked in various organic solvents using angular frequency sweep scans. The solid symbols represent the storage modulus of the film, G' , while open symbols represent the loss modulus of the film, G'' .

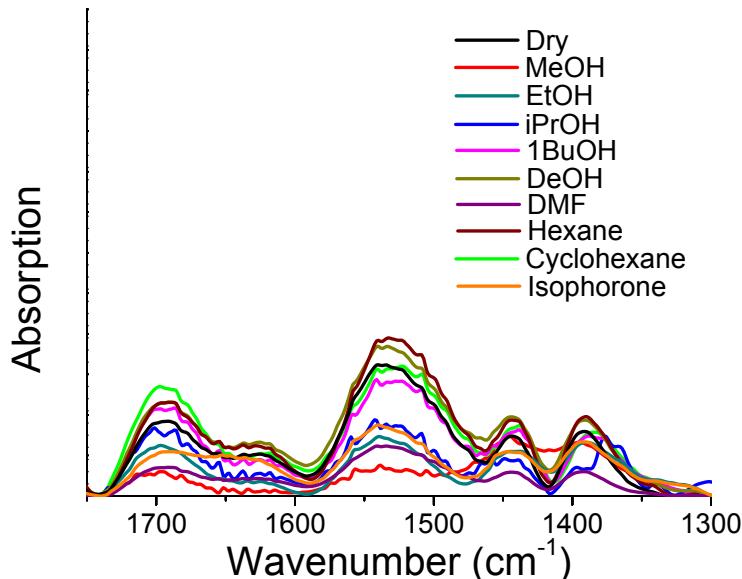


Fig. S9 ATR FTIR spectra of BPEI/PAA films in dry state and treated with methanol, ethanol, isopropanol, 1-butanol, decanol, DMF, hexane, cyclohexane, and isophorone.

Table S1. Hansen solubility for each organic liquid.^[1]

Solvent	δ_d	δ_p	δ_h	δ_t	Average Contraction %	Error
Dimethylformamide	17.4	13.7	11.3	24.8	10.3	0.81
Methanol	11.5	12.3	22.3	29.7	22.3	0.88
Ethanol	15.8	8.8	19.4	26.5	8.6	0.93
2-Propanol	15.8	6.1	16.4	23.5	7.6	0.68
1-Butanol	16	5.7	15.8	23.1	4.0	0.76
2-Butanol	15.8	5.7	14.5	22.1	4.5	0.74
Benzyl alcohol	18.4	6.3	13.7	23.7	3.2	0.78
Dioctyl phthalate	16.6	7	3.1	18.2	4.8	0.97
Isophorone	16.6	8.2	7.4	19.8	5.5	0.81
Hexane	14.9	0	0	14.9	4.9	0.94
Cyclohexane	16.8	0	0.2	16.8	4.2	0.62
Cyclohexnone	17.8	6.3	5.1	19.6	5.3	0.72
1-Octanol	17	3.3	11.9	20.9	8.0	0.43
Anisole	17.8	4.1	6.8	19.4	6.0	0.98
Decanol	17.6	2.7	10	20.5	6.1	0.53
Ethylene glycol	17	11	26	32.9	10.0	0.88

References

- (1) Hansen, C. M. Hansen solubility parameters: a user's handbook, CRC press, 2007.