Supporting information for

Soluble and processable thermoplastic hybrid polyimides containing POSS in main chains

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Synthesis of polymers.

Synthesis of 3 / PMDA-polyimide (6a)

A mixture of **3** (0.15 g, 0.1 mmol) and PMDA (**4a**) (0.026 g, 0.1 mmol) in dehydration tetrahydrofuran (THF) (1.0 mL) was stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **3**/PMDA-polyimide precursor (**5a**).

5a: FT-IR (KBr): v = 1059 (Si-O-Si), 1260 (Si-CH₃), 1646(amide C=O), 1719 (imide C=O) cm⁻¹. ¹H-NMR (DMSO, 400 MHz): δ = 0.33-0.37 (d, *CH*₃-Si, 6H), 0.80-0.842 (t, *CH*₂-Si, 4H), 1.72-1.74 (m, Si-CH₂*CH*₂*CH*₂, 4H), 3.12-3.16 (t, Si-CH₂CH₂*CH*₂, 4H), 7.20-7.54 (m, protons of DDSQ phenyl groups, 40H), 7.67 (s, Ar-*H*, 2H), 8.11 (s, -N*H*, 2H), 13.31 (br, -O*H*, 2H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -16.32, -78.15, -78.22, -79.29, -79.35 ppm.

The cast film of **3**/PMDA-polyimide precursor (**5a**) was heated at 200 °C for 3 h under reduced pressure to obtain **3** / PMDA-polyimide (**6a**).

6a: FT-IR (KBr): v = 1071 (Si-O-Si), 1262 (Si-CH₃), 1359 (C-N), 1719, 1771 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.29 (s, *CH*₃-Si, 6H), 0.70-0.74 (t, *CH*₂-Si, 4H), 1.71-1.79 (m, Si-CH₂*CH*₂CH₂, 4H), 3.59-3.62 (t, Si-CH₂CH₂CH₂, 4H), 7.16-7.49 (m, protons of DDSQ phenyl groups, 40H), 8.07-8.10 (t, Ar-*H*, 2H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -18.43, -78.40, -79.34 -79.41, -79.46 ppm.

Synthesis of **3** / 6FDA-polyimide (**6b**)

A mixture of **3** (0.15 g, 0.1 mmol) and 6FDA (**4b**) (0.031 g, 0.1 mmol) in dehydration tetrahydrofuran (THF) (1.0 mL) was stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **3**/6FDA-polyimide precursor (**5b**).

5b: FT-IR (KBr): v = 1076 (Si-O-Si), 1257 (Si-CH₃), 1648(amide C=O), 1722 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.36 (s, *CH*₃-Si, 6H), 0.82-0.87 (t, *CH*₂-Si, 4H), 1.63-1.64 (m, Si-CH₂*CH*₂*CH*₂, 4H), 3.14-3.16 (t, Si-CH₂CH₂*CH*₂, 4H), 7.26-7.53 (m, protons of DDSQ phenyl groups, 40H), 7.72-7.75 (t, Ar-*H*, 2H), 7.88-7.90 (m, Ar-*H*, 2H), 8.45 (s, -N*H*, 2H), 13.32 (br, -O*H*, 2H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -16.29, -78.21, -79.26 -79.31, -79.40 ppm.

The cast film of **3**/6FDA-polyimide precursor (**5b**) was heated at 200 °C for 3 h under reduced pressure to obtain **3** / 6FDA-polyimide (**6b**).

6b: FT-IR (KBr): v = 1073 (Si-O-Si), 1256 (Si-CH₃), 1363 (C-N), 1719, 1778 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): $\delta = 0.30$ (s, *CH*₃-Si, 6H), 0.72-0.76 (t, *CH*₂-Si, 4H), 1.70-1.78 (m, Si-CH₂*CH*₂*CH*₂, 4H), 3.56-3.60 (t, Si-CH₂CH₂*CH*₂, 4H), 7.16-7.51 (m, protons of DDSQ phenyl groups, 40H), 7.65-7.67 (t, Ar-*H*, 2H), 7.81-7.83 (t, Ar-*H*, 4H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): $\delta = -18.32$, -78.20, -79.25, -79.30, -79.36 ppm.

Synthesis of 3 / BTDA-polyimide (6c)

A mixture of 3 (0.15 g, 0.1 mmol) and BTDA (4c) (0.038 g, 0.1 mmol) in dehydration tetrahydrofuran

(THF) (1.0 mL) was stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **3**/BTDA-polyimide precursor (**5c**).

5c: FT-IR (KBr): ν = 1073 (Si-O-Si), 1262 (Si-CH₃), 1664 (amide C=O), 1722 (imide C=O) cm⁻¹.

The cast film of **3**/BTDA-polyimide precursor (**5c**) was heated at 200 °C for 3 h under reduced pressure to obtain **3**/BTDA-polyimide (**6c**).

6c: FT-IR (KBr): v = 1066 (Si-O-Si), 1262 (Si-CH₃), 1362 (C-N), 1715, 1774 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.31(s, *CH*₃-Si, 6H), 0.73-0.77 (t, *CH*₂-Si, 4H), 1.72-1.80 (m, Si-CH₂*CH*₂*CH*₂, 4H), 3.60-3.64 (t, Si-CH₂CH₂*CH*₂, 4H), 7.20-7.51 (m, protons of DDSQ phenyl groups, 40H), 7.91-7.93 (d, Ar-*H*, 2H), 8.07-8.12 (t, Ar-*H*, 4H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -18.30, -78.39, -79.37, -79.40, -79.43 ppm.

Synthesis of 3 / HPMDA-polyimide (6d)

A mixture of **3** (0.15 g, 0.1 mmol) and HPMDA (**4d**) (0.027 g, 0.1 mmol) in dehydration tetrahydrofuran (THF) (1.0 mL) was stirred at 40 °C for 3 h and the solvent was removed under reduced pressure to obtain **3**/HPMDA-polyimide precursor (**5d**).

5d: FT-IR (KBr): v = 1072 (Si-O-Si), 1261 (Si-CH₃), 1665 (amide C=O), 1729 (imide C=O) cm⁻¹.

The cast film of **3**/HPMDA-polyimide precursor (**5d**) was heated at 200 °C for 3 h under reduced pressure to obtain **3** / HPMDA-polyimide (**6d**).

6d: FT-IR (KBr): v = 1065 (Si-O-Si), 1261 (Si-CH₃), 1361 (C-N), 1707, 1774 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): $\delta = 0.27$ (s, *CH*₃-Si, 6H), 0.63-0.67 (t, *CH*₂-Si, 4H), 1.15 (br, f, 4H), 1.58 (m, Si-CH₂CH₂CH₂, 4H), 2.36-2.50 (br, e, 4H), 3.25-3.36 (t, Si-CH₂CH₂CH₂, 4H), 7.17-7.48 (m, protons of DDSQ phenyl groups, 40H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): $\delta = -18.32$, -78.45, -79.40, -79.45, -79.50 ppm.

Synthesis of 3 / BTA-polyimide (6e)

A mixture of **3** (0.15 g, 0.1 mmol) and BTA (**4e**) (0.029 g, 0.1 mmol) in dehydration tetrahydrofuran (THF) (1.0 mL) was stirred at 40 °C for 3 h and the solvent was removed under reduced pressure to obtain **3**/BTA-polyimide precursor (**5e**).

5e: FT-IR (KBr): v = 1070 (Si-O-Si), 1261 (Si-CH₃), 1674 (amide C=O), 1729 (imide C=O) cm⁻¹.

The cast film of **3**/BTA-polyimide precursor (**5e**) was heated at 200 °C for 3 h under reduced pressure to obtain **3** / BTA-polyimide (**6e**).

6e: FT-IR (KBr): v = 1065 (Si-O-Si), 1262 (Si-CH₃), 1349 (C-N), 1705, 1780 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.258 (s, *CH*₃-Si, 6H), 0591-0.611 (t, *CH*₂-Si, 4H), 1.506-1.525 (m, Si-CH₂*CH*₂*CH*₂, 4H), 2.525-2.605 (m, Ar-*H*), 3.261-3.321 (t, Si-CH₂*CH*₂*CH*₂, 4H), 3.450-3.520 (m, Ar-*H*), 5.595-5.768 (m, Ar-*H*), 7.203-7.467 (m, protons of DDSQ phenyl groups, 40H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -18.40, -78.49, -79.40, -79.47, -79.54 ppm.

Synthesis of **1** / PMDA-polyimide (**8a**)

A mixture of **1** (0.1381 g, 0.1 mmol) and PMDA (**4a**) (0.0225 g, 0.1 mmol) in dehydration tetrahydrofuran (THF) (1.5 mL) was stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **1**/PMDA-polyimide precursor.

1/PMDA-polyimide precursor: FT-IR (KBr): v = 1070 (Si-O-Si), 1260 (Si-CH₃), 1686 (amide C=O), 1723 (imide C=O) cm⁻¹.

The cast film of **1**/PMDA-polyimide precursor was heated at 200 °C for 3 h under reduced pressure to obtain **1** / PMDA-polyimide (**8a**)

8a: FT-IR (KBr): v = 1062 (Si-O-Si), 1263 (Si-CH₃), 1365 (C-N), 1728 (imide C=O), 1779 (imide C=O) cm⁻ ¹. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.57-0.58 (d, *CH*₃-Si, 6H), 6.95-7.55 (m, protons of DDSQ phenyl groups, 44H), 7.81-7.83 (d, Ar-Si, 4H), 8.50-8.52 (m, Ar-*H*, 2H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -16.32, -78.15, -79.22, -79.28, -79.35, ppm.

Synthesis of **1** / 6FDA-polyimides (**8b**)

A mixture of **1** (0.1354 g, 0.1 mmol) and 6FDA (**4b**) (0.0452 g, 0.1 mmol) in dehydration tetrahydrofuran (THF) (1.5 mL) was stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **1**/6FDA-polyimide precursor.

1/6FDA-polyimide precursor: FT-IR (KBr): v = 1068 (Si-O-Si), 1257 (Si-CH₃), 1689 (amide C=O), 1722 (imide C=O) cm⁻¹.

The cast film of 1/6FDA-polyimide precursor was heated at 200 °C for 3 h under reduced pressure to obtain 1/6FDA-polyimides (**8b**)

8b: FT-IR (KBr): v = 1062, 1117 (Si-O-Si), 1255 (Si-CH₃), 1365 (C-N), 1736 (imide C=O), 1784 (imide C=O) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ /= 0.56-0.57 (d, *CH*₃-Si, 6H), 7.09-7.54 (m, protons of DDSQ phenyl groups, 44H), 7.78-7.79 (d, Ar-Si, 4H), 7.80-8.05(m, Ar-*H*, 6H) ppm; ²⁹Si-NMR (CDCl₃, 80 MHz): δ = -31.43, -78.08, -79.19, -79.24, -79.25 ppm.

Synthesis of 10 / PMDA-polyimide (11a)

A mixture of **10** (0.0519 g, 0.4 mmol) and PMDA (**4a**) (0.0981 g, 0.4 mmol) in dehydration tetrahydrofuran (THF) (3.5 mL) were stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **10**/PMDA-polyimide precursor.

10/PMDA-polyimide precursor: ¹H-NMR (CDCl₃, 400 MHz): δ = 1.46 (br, *CH*₃CH₂CH₂-NH, 4H), 1.64 (br, CH₃CH₂CH₂-NH, 4H), 3.35 (br, CH₃CH₂CH₂-NH, 4H), 3.96 (br, -N*H*, 2H), 7.39 (s, Ar-*H*, 1H), 8.44 (s, Ar-*H*, 1H) ppm.

The cast film of **10**/PMDA-polyimide precursor was heated at 200 °C for 3 h under reduced pressure to obtain **10**/PMDA-polyimide (**11a**)

11a: FT-IR (KBr): v = 1362 (C-N), 1698, 1770 (imide C=O) cm⁻¹.

Synthesis of **10** / 6FDA-polyimide (**11b**)

A mixture of **10** (0.0469 g, 0.4 mmol) and PMDA (**4b**) (0.177 g, 0.4 mmol) in dehydration tetrahydrofuran (THF) (3.5 mL) were stirred at room temperature for 3 h and the solvent was removed under reduced pressure to obtain **10**/6FDA-polyimide precursor.

10/6FDA-polyimide precursor: ¹H-NMR (CDCl₃, 400 MHz): δ = 1.33 (br, *CH*₃CH₂CH₂-NH, 4H), 1.49 (br, CH₃CH₂CH₂-NH, 4H), 3.18 (br, CH₃CH₂CH₂-NH, 4H), 7.29-7.95 (br, Ar-*H*, 6H), 8.45 (s, -N*H*, 1H), 8.44 (s, Ar-*H*, 1H) ppm.

The cast film of **10**/6FDA-polyimide precursor was heated at 200 °C for 3 h under reduced pressure to obtain **10**/6FDA-polyimide (**11b**).

11b: FT-IR (KBr): v = 1364 (C-N), 1705, 1776 (imide C=O) cm⁻¹.



Elusion volume (mL)

Figure S1 (a) SEC traces of the polyimide precursor (5) solutions from the polymerization at room temperature for **5a**, **5b**, and **5c** and at 40 °C for **5d** and **5e**, measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm. (b) SEC trace of the polymerization solutions of **7a** and **7b** in THF for 3h at room temperature, measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm.



Figure S2 FT-IR spectra of 3, 4a, 5a, and 6a.



Figure S3 FT-IR spectra of 3, 4b, 5b, and 6b.



Figure S4 FT-IR spectra of 8a, 7a, 8b, and 7b.





Figure S5 (a) $^1\text{H-}$ and (b) $^{29}\text{Si-NMR}$ spectra of 5a in DMSO-d_6



(b)



Figure S6 (a) $^1\text{H-}$ and (b) $^{29}\text{Si-NMR}$ spectra of 5b in DMSO-d_6



Figure S7 SEC traces of **6** measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm.



Figure S8 SEC traces of **8a** and **8b** measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm.



Figure S9 FT-IR spectra of 6.



Figure S10 (a) ¹H- and (b) ²⁹Si-NMR spectra of 6a in CDCl_{3.}



(b)



Figure S11 (a) 1 H- and (b) 29 Si-NMR spectra of **6b** in CDCl_{3.}



(b) а MMM. С -78 -79 80 δ**/ppm** -80 -10 -20 _40 δ/ppm -70 -50 -60 -30 0

Figure S12 (a) 1 H- and (b) 29 Si-NMR spectra of 8a in CDCl₃.



Figure S13 (a) 1 H- and (b) 29 Si-NMR spectra of **8b** in CDCl₃.



Figure S14 The FT-IR spectra of **5a** and **6a** after heating of **5a** at 200 °C for 3 h under reduced pressure. The imidization ratio was estimated by the intensity ratio of the peak at 1771 cm⁻¹ corresponding to C=O stretching against the peak at 1429 cm⁻¹ corresponding to C=C stretching of the dianhydride's benzene.



Figure S15 The FT-IR spectra of **5b** and **6b** after heating of **5b** at 200 °C for 3 h under reduced pressure. The imidization ratio was estimated by the intensity ratio of the peak at 1778 cm⁻¹ corresponding to C=O stretching against the peak at 1429 cm⁻¹ corresponding to C=C stretching of the dianhydride's benzene.

Table S1 (a) The relative intensities of the peaks corresponding to the C=O stretching and the C=C stretching of the dianhydride's benzene in the FT-IR absorption spectra and their intensity ratios of the former against the latter of **6a** (b), **6b** (c), **8a**, and (d)**11a**.

a)				
	Wavenumber (cm ⁻¹) Absorbance		Intensity ratio (%)	
200 °C / 1 h	1430	0.0906	83	
	1771	0.0590		
200 °C / 2 h	1430	0.0495	99	
	1771	0.0390		
200 °C / 3 h	1430	0.0776	- 99	
	1771	0.0615		

(b)

	Wavenumber (cm ⁻¹)	Absorbance	Intensity ratio (%)	
200 °C / 1h	1778	0.0505	84	
	1430	0.0633		
200 °C / 2h	1777	0.0619	99	
	1431	0.0844		
200°C / 3h	1778	0.0879	99	
	1430	0.1120		

(c)

	Wavenumber (cm ⁻¹)	Absorbance	Intensity ratio (%)	
200 °C / 1h	1782	0.0528	72	
	1430	0.0761		
200 °C / 2h	1781	0.0488	83	
	1430	0.0824		
200°C / 3h	1780	0.0271	99	
	1430	0.0428		

(d)

	Wavenumber (cm ⁻¹)	Absorbance	Intensity ratio	
200 °C / 1h	1768	0.1667	80	
	1457	0.1349		
200 °C / 2h	1768	0.1667	88	
	1457	0.1594		
200°C / 3h	1769	0.1576	- 100	
	1457	0.1342		





Figure S16 (a) 1 H- and (b) 29 Si-NMR spectra of 6c in CDCl₃.



Figure S17 (a) 1 H- and (b) 29 Si-NMR spectra of **6d** in CDCl₃.



Figure S18 (a) ¹H- and (b) ²⁹Si-NMR spectra of **6e** in CDCl_{3.}



Figure S19 FT-IR spectra of 11a and 10/PMDA-polyimide precursor.



Figure S20 FT-IR spectra of 11b and 10/6FDA-polyimide precursor.



Figure S21 (a) ¹H-NMR spectrum of 10/PMDA-polyimide precursor in CDCl₃.



Figure S22 (a) ¹H-NMR spectrum of **10**/6FDA-polyimide precursor in CDCl₃.



Figure S23 (a)TGA thermograms of the films of 6 at a heating rate of 10°C min⁻¹ in N₂ flow, (b)TGA thermograms of the films of 6 at a heating rate of 10 °C min⁻¹ in air flow.



Figure S24 The Films heated and deformed of 6b at 150 °C above the glass transition.



Figure S25 Appearances of the films of 8a and 8b.



Figure S26 Photographs showing static contact angles of the cast films of 6a and 6b against water.

Table S2 Summary of the density data, contact angles against water, and Elastic modulus of the films of **6a**, **6b**, **9a**, **9b**, **11a**, **11b**, and **PMDA-ODA**.

Sample	Density (<i>d</i>) (g/cm ³)	Elastic modulus (GPa)	Contact angle (°)
6a	1.32 ± 0.00	3.2 ± 0.2	84 ± 1
9a	1.24 ± 0.00	3.7 ± 0.2	97± 2
11a	1.35 ± 0.01	5.4 ± 0.2	-
6b	1.39 ± 0.01	1.6 ± 0.1	87 ± 1
9b	1.12 ± 0.00	3.09 ± 0.08	96 ± 2
11b	1.45 ± 0.01	5.4 ± 0.1	-
PMDA-ODA polyimide	1.48 ± 0.01	8.28 ± 0.05	76 ± 2



Figure S27 ¹H-NMR spectra of 1 and 3 in CDCl_{3.}

Sample	M_n^{b}	M_{w}^{b}	M _w /M _n	<i>T</i> d1 (°C)	<i>T</i> d₅ (°C)
8b	5 500	13 300	2.4	431	522
6b	10 000	33 000	3.2	460	486
6b-Lª	4 000	10 800	2.7	403	467

Table S3 Summary of molecular weights and thermal properties of 6b, 6b-L, and 8b.

a A lower molecular weight of **6b** as labeled **6b-L** was prepared by changing the ratio of **3** against **4b** (1:0.8).

b Determined using SEC (THF 1.0 mL min⁻¹, UV detector).