

## Supplementary information

**Synthesis of diamines monomer (Am2):** (a) 4-(but-3-enyloxy)-nitrobenzene (**1**): A mixture of 4-nitrophenol (5 g, 35.9 mmol), 4-bromo-1-butene (7.28 g, 53.9 mmol), K<sub>2</sub>CO<sub>3</sub> (7.5 g, 53.9 mmol) and 100 ml acetone was reflux with stirring under nitrogen for overnight. The white solids in the reaction mixture were then filtered by the filter paper. The filtrate acetone was then reduced to 0 ml. The oily crude product was then purified by extraction the diethyl ether (100 ml) phase with water (3 X 100 ml). The organic phase was collected and concentrated. Brown oil was obtained (80 %). ES-MS (+ve mode): m/z 194 [M+H]<sup>+</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.21 (d, *J* = 9.26 Hz, 2H), 6.97 (d, *J* = 9.27 Hz, 2H), 5.91 (tdd, *J* = 17.02, 10.25, 6.72 Hz, 1H), 5.19 (dddd, *J* = 16.27, 10.26, 2.90, 1.52 Hz, 2H), 4.13 (t, *J* = 6.66 Hz, 2H), 2.61 (q, *J* = 6.67 Hz, 2H). Anal. Calcd. for C<sub>10</sub>H<sub>11</sub>NO<sub>3</sub>: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.20; H, 5.73; N, 7.23. (b)

Tetradimethylsiloxanes- $\alpha,\omega$ -bis[4-(but-3-enyloxy)-nitrobenzene] (**2**): 4-(But-3-enyloxy)-nitrobenzene (2 g, 10.31 mmol) was added to a 20 mL of toluene 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (1.33 g, 4.71 mmol). 2 drops of Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene) was then added to the solution mixture. The reaction was stirred at room temperature under nitrogen for overnight. The reaction mixture was concentrated, giving crude brown oil which was then purified by silica gel column chromatography to give brown oil (98%). ES-MS (+ve mode): m/z 670 [M+H]<sup>+</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.21(d, *J* = 9.30 Hz, 4H), 6.96 (d, *J* = 9.27 Hz, 4H), 4.08 (t, *J* = 6.39 Hz, 4H), 1.96-1.75 (m, 4H), 1.67-1.46 (m, 4H), 0.72-0.55 (m, 4H), 0.11 (m, 24H). Anal. Calcd. for C<sub>28</sub>H<sub>48</sub>N<sub>2</sub>O<sub>9</sub>Si<sub>4</sub>: C, 50.27; H, 7.23; N, 4.19. Found: C, 50.33; H, 7.30; N, 4.12. (c)

Tetradimethylsiloxanes- $\alpha,\omega$ -bis[4-(butyloxy)-aminobenzene] (**Am2**): Tetradimethylsiloxanes- $\alpha,\omega$ -bis[4-(buten-4-oxy)-nitrobenzene] (1.667 g, 2.49 mmol) and 10 % Pd-C (0.32 g) were added to a 40 mL of methanol. Then hydrazine monohydrate (1.25 g, 25 mmol) was slowly added to the solution mixture. The reaction was stirred at room temp under N<sub>2</sub> for overnight. The reaction mixture was concentrated, giving yellow oil (100 %). ES-MS (+ve mode): m/z 610 [M+H]<sup>+</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 6.79 (d, *J* = 8.81 Hz, 4H), 6.65 (d, *J* = 8.81 Hz, 4H), 3.93 (t, *J* = 6.50 Hz, 4H), 1.95-1.72 (m, 4H), 1.56 (tt, *J* = 9.36, 6.53 Hz, 4H), 0.77-0.55 (m, 4H), 0.14 (m, 24H). Anal. Calcd. for C<sub>28</sub>H<sub>52</sub>N<sub>2</sub>O<sub>5</sub>Si<sub>4</sub>: C, 55.22; H, 8.61; N, 4.60. Found: C, 55.11; H, 8.70; N, 4.62.

**Synthesis of dialdehydes monomer (Ald1):** (a) 3,6,9,12,15-Pentaoxaheptadecane-1,17-diylbis(4-methylbenzenesulfonate) (**5**): A

mixture of hexaethylene glycol (3 g, 10.6 mmol) and triethylamine (10.7 g, 110 mmol) in 50 ml dry CH<sub>2</sub>Cl<sub>2</sub> was kept at 0 °C under N<sub>2</sub>. Solid *p*-toluenesulfonyl chloride (31.8 mmol) was slowly added to the mixture which was kept under 5 °C. The reaction mixture was stirred under nitrogen for 24 hour at room temp. The reaction mixture was then washed with pH 1 HCl (aq) 150 ml X 5. The filtrate CH<sub>2</sub>Cl<sub>2</sub> was then collected and reduced to 0 ml. The oily crude product was then purified by silica gel chromatography by using ethyl acetate:CH<sub>2</sub>Cl<sub>2</sub>(1:1). Colorless oil was obtained (60 %). ES-MS (+ve mode): m/z 592 [M+H]<sup>+</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.81 (d, *J* = 8.18 Hz, 4H), 7.35 (d, *J* = 8.18 Hz, 4H), 4.21-4.14 (m, 4H), 3.73-3.67 (m, 4H), 3.65-3.61 (br, 8H), 3.62-3.57 (br, 8H), 2.46 (s, 6H). Anal. Calcd. for C<sub>26</sub>H<sub>38</sub>O<sub>11</sub>S<sub>2</sub>: C, 52.87; H, 6.48. Found: C, 52.74; H, 6.42. (b) 4,4'-[3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(oxy)]dibenzaldehyde (**Ald1**): A mixture of 3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(4-methylbenzenesulfonate) (2.7 g, 4.57 mmol), 4-hydroxybenzaldehyde (1.67 g, 13.7 mmol), K<sub>2</sub>CO<sub>3</sub> (3.8 g, 27.4 mmol) and 30 ml anhydrous DMF was heat at 80 °C with stirring under nitrogen for overnight. The solids in the reaction mixture were then filtered. The filtrate was then concentrated. The crude product was then purified by silica gel chromatography by using pure CH<sub>2</sub>Cl<sub>2</sub>, then pure ethyl acetate, then MeOH to wash out the product. Colorless solid was then obtained (74%). <sup>1</sup>H-NMR (400 MHz, DMSO- d<sub>6</sub>) δ ppm = 9.90 (s, 2H), 7.84 (d, *J* = 8.78 Hz, 4H), 7.04 (d, *J* = 8.77 Hz, 4H), 4.28-4.15 (m, 4H), 3.96-3.83 (m, 4H), 3.80-3.57 (m, 16H). Anal. Calcd. for C<sub>26</sub>H<sub>34</sub>O<sub>9</sub>: C, 63.66; H, 6.99. Found: C, 63.53; H, 6.77.

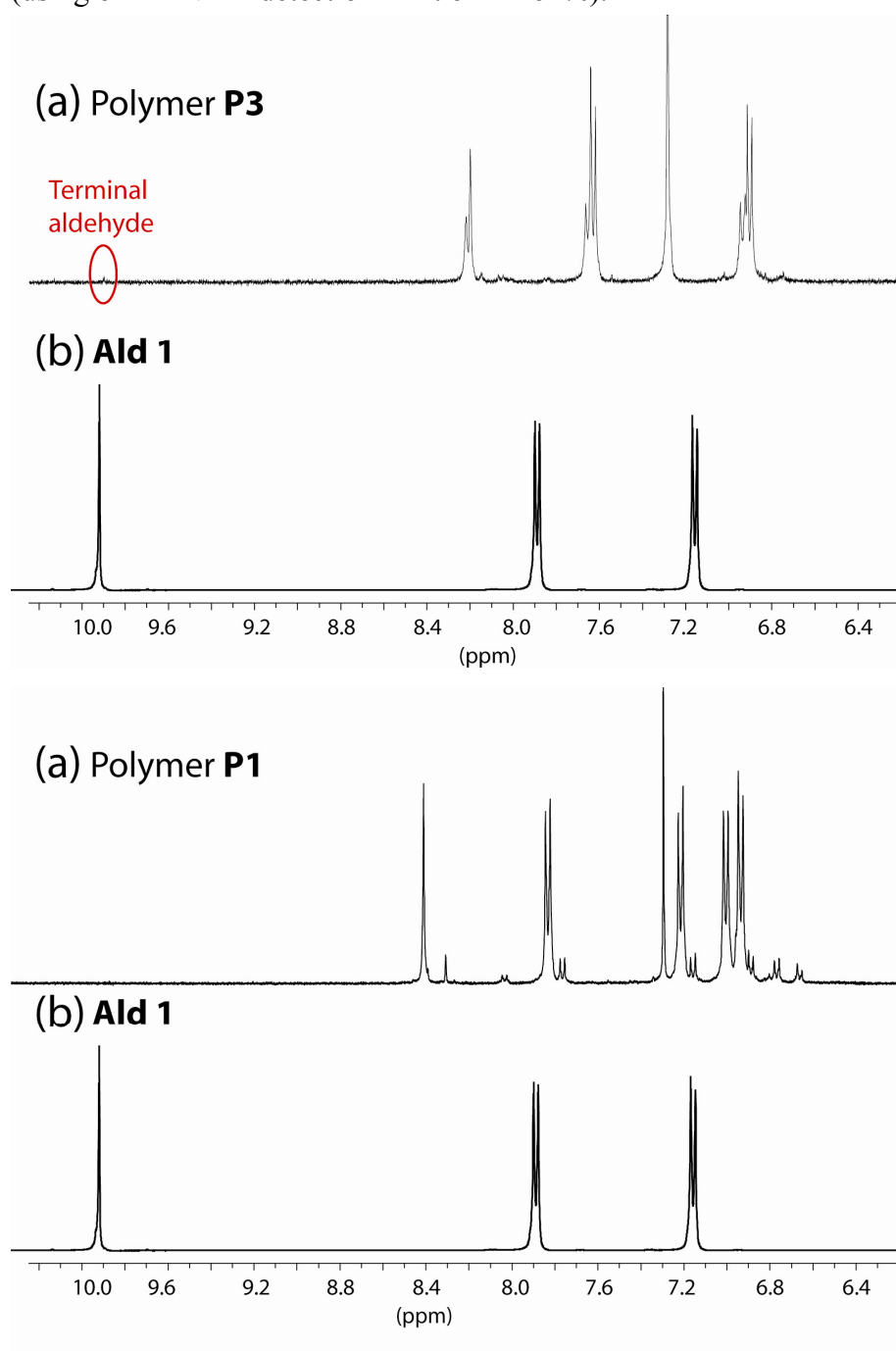
**Synthesis of dialdehydes monomer (Ald2):** (a) 4-(but-3-enyloxy)phenyl-4'-formylazobenzene (**7**): A mixture of 4'-formyl-4-hydroxyphenylazobenzene, **6**, (4.07 g, 18 mmol), 4-bromo-1-butene (4.85 g, 36 mmol), K<sub>2</sub>CO<sub>3</sub> (10 g, 72 mmol) and 30 ml anhydrous DMF was heated at 80 °C with stirring under nitrogen for overnight. The solids in the reaction mixture were then filtered by the filter paper. The filtrate DMF was then reduced to 0 ml. The crude product was then purified by silica chromatography by using pet heptane:acetone (5:1). Orange solid was then obtained (93%). ES-MS (+ve mode): m/z 281 [M+H]<sup>+</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 10.17 (s, 1H), 8.14 (d, *J* = 8.66 Hz, 2H), 8.07 (d, *J* = 8.66 Hz, 2H), 8.01 (d, *J* = 9.06 Hz, 2H), 7.19 (d, *J* = 9.05 Hz, 2H), 5.98 (m, 1H), 5.29-5.08 (m, 2H), 4.23 (t, *J* = 6.62 Hz, 2H), 2.62 (q, *J* = 6.65 Hz, 2H). Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.99; H, 5.73; N, 9.93. (b) Tetradimethylsiloxanes- $\alpha,\omega$ -bis[4-(butyloxy)phenyl-4'-formylazobenzene] (**Ald2**): 4-(But-3-enyloxy)phenyl-4'-formylazobenzene, **7**, (0.7373 g, 2.63 mmol) was added to a 6 mL of toluene 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (0.35 g, 1.25 mmol). 2

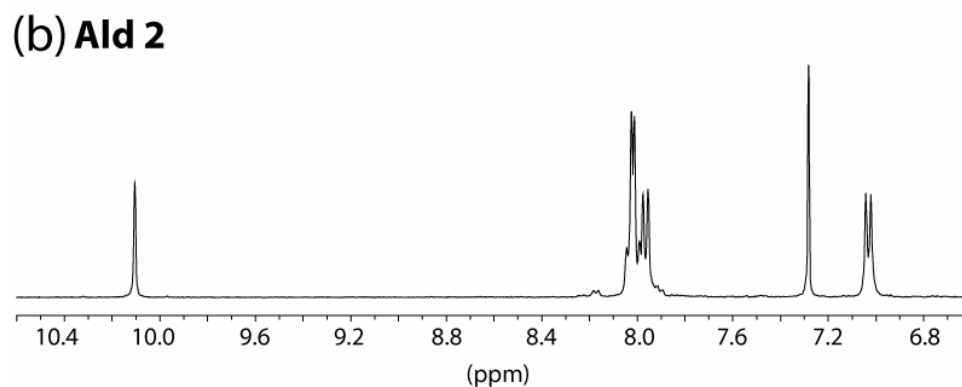
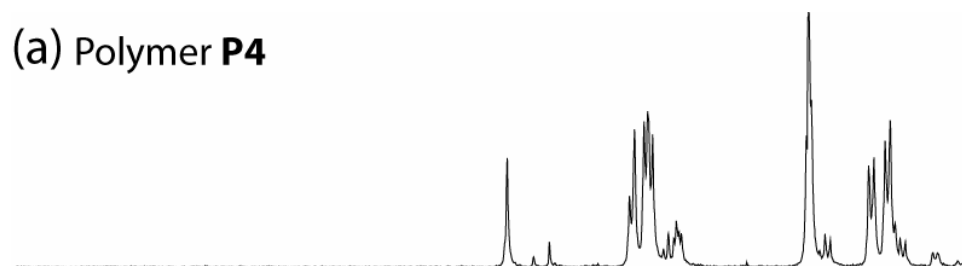
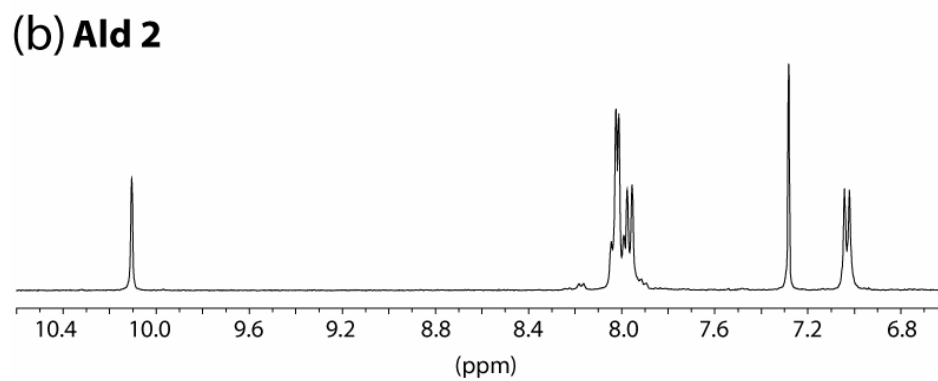
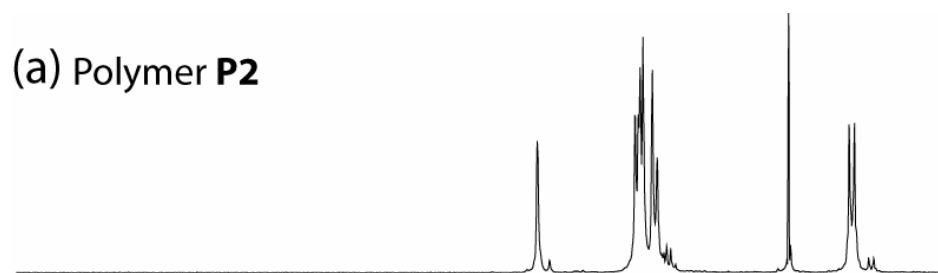
drops of Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene) was then added to the solution mixture. The reaction was stirred at room temperature under nitrogen for overnight. The reaction mixture was concentrated, giving crude red oil which was then purified by silica gel column chromatography [heptane:CH<sub>2</sub>Cl<sub>2</sub>:acetone (3:2:0.2)] to give red solid (98%). ES-MS (+ve mode): *m/z* 843 [M+H]<sup>+</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm = 10.15 (s, 2H), 8.12 (d, *J* = 8.64 Hz, 4H), 8.04 (d, *J* = 8.63 Hz, 4H), 7.99 (d, *J* = 9.04 Hz, 4H), 7.15 (d, *J* = 9.03 Hz, 4H), 4.17 (t, *J* = 6.37 Hz, 4H), 1.98-1.81 (m, 4H), 1.64 (tt, *J* = 9.38, 6.50 Hz, 4H), 0.79-0.66 (m, 4H), 0.15 (m, 24H). Anal. Calcd. for C<sub>42</sub>H<sub>58</sub>N<sub>4</sub>O<sub>7</sub>Si<sub>4</sub>: C, 59.82; H, 6.93; N, 6.64. Found: C, 59.54; H, 6.95; N, 6.60.

**General procedure for the preparation of the dynamic imine polymers (P1-P4):**

Condensation polymerization reaction was performed by mixing diamine (**Am1** or **Am2**) (0.20 mmol), dialdehyde (**Ald1** or **Ald2**) (0.20 mmol) and anhydrous Na<sub>2</sub>SO<sub>4</sub> (2 mmol) in 4 ml CHCl<sub>3</sub>. The reaction mixture was stirred and refluxed under N<sub>2</sub> for 24 hrs. The solution mixture was then concentrated after the filtration of Na<sub>2</sub>SO<sub>4</sub>. Polymer was obtained by casting in a petri dish (2.5 cm diameter), by redissolving the polymer product in CH<sub>2</sub>Cl<sub>2</sub> and then letting the solution slowly evaporate under atm/50 °C temp. **Polymer P1 (Ald1/Am2)**: <sup>1</sup>H-NMR spectrum (400 MHz, 5 mM, CDCl<sub>3</sub>):δ ppm = 8.41 (s, 2H), 7.82 (d, *J* = 8.69 Hz, 4H), 7.20 (d, *J* = 8.77 Hz, 4H), 6.99 (d, *J* = 8.63 Hz, 4H), 6.92 (d, *J* = 8.80 Hz, 4H), 4.24-4.16 (m, 4H), 3.98 (t, *J* = 6.51 Hz, 4H), 3.92-3.86 (m, 4H), 3.78-3.63 (m, 16H), 1.94-1.74 (m, 4H), 1.62-1.47 (m, 4H), 0.72-0.54 (m, 4H), 0.10 (m, 24H). M.W. = 38000 gmol<sup>-1</sup>. **Polymer P2 (Ald2/Am1)**: <sup>1</sup>H-NMR spectrum (400 MHz, 5 mM, CDCl<sub>3</sub>):δ ppm = 8.36 (s, 2H), 7.98-7.88 (m, *J* = 8.67, 5.31 Hz, 8H), 7.86 (d, *J* = 8.56 Hz, 4H), 7.01 (d, *J* = 9.03 Hz, 4H), 4.06 (t, *J* = 6.41 Hz, 4H), 3.75 (t, *J* = 6.52 Hz, 4H), 3.71-3.66 (m, 4H), 3.65-3.56 (m, 8H), 2.03 (quin, *J* = 6.48 Hz, 4H), 1.93-1.79 (m, 4H), 1.62-1.48 (m, 4H), 0.73-0.57 (m, 4H), 0.10 (m, 24H). M.W. = 53000 gmol<sup>-1</sup>. **Polymer P3 (Ald1/Am1)**: <sup>1</sup>H-NMR spectrum (400 MHz, 5 mM, CDCl<sub>3</sub>):δ ppm = 8.22, 8.20 (s, 2H), 7.69-7.57 (m, 4H), 6.96-6.87 (m, 4H), 4.20-4.07 (m, 4H), 3.92-3.81 (m, 4H), 3.78-3.63 (m, 24H), 3.63-3.53 (m, 8H), 2.04-1.93 (m, 4H). M.W. = 34000 gmol<sup>-1</sup>. **Polymer P4 (Ald2/Am2)**: <sup>1</sup>H-NMR spectrum (400 MHz, 5 mM, CDCl<sub>3</sub>):δ ppm = 8.55, 8.37 (s, 2H), 8.02 (d, *J* = 8.42 Hz, 4H), 7.96 (d, *J* = 6.50 Hz, 4H), 7.94 (d, *J* = 6.56 Hz, 4H), 7.29-7.25 (m, 4H), 7.02 (d, *J* = 8.57 Hz, 4H), 6.95 (d, *J* = 8.59 Hz, 4H), 4.06 (t, *J* = 6.33 Hz, 4H), 4.00 (t, *J* = 6.41 Hz, 4H), 1.96-1.75 (m, 8H), 1.62-1.50 (m, 8H), 0.71-0.54 (m, 8H), 0.10 (m, 48H). M.W. = 54000 gmol<sup>-1</sup>.

**Detection of the molecular weight of polymer P3 by its terminal group in  $^1\text{H-NMR}$  at 1 mM in  $\text{CDCl}_3$ .** Integration of the very small remaining  $^1\text{H-NMR}$  signal for terminal aldehyde protons gave a molecular weight of  $34000 \text{ gmol}^{-1}$  (~50 repeating units) for **P3**. On the other hand, this signal was not observable for **P1**, **P2** and **P4**. The ratio between the signals of their new imine proton and of the  $\alpha\text{-CH}_2$  of siloxane moiety for **P1**, **P2** and **P4**,  $\alpha\text{-CH}_2$  of oligo ethylene oxa moiety was exactly 2:4, indicating that polymerization was proceeded beyond the NMR detection limit. The molecular weights of these polymers were roughly estimated as  $\geq 50,000 \text{ gmol}^{-1}$  (using on  $^1\text{H-NMR}$  detection limit of 1 mol %).





GPC measurements on polymers **P1-P4** showed only peaks corresponding to monomers (their molecular weights were below  $1000 \text{ gmol}^{-1}$ ) due to dissociation on dilution.

**Synthesis of polymer blend – (a) B1<sub>sol</sub>:** polymers **P1** (0.005 mmol), **P2** (0.005 mmol) and pentadecafluorooctanoic acid ( $2 \times 10^{-7}$  mol, 1 % per imine unit) were dissolved in 1.00 ml of deuterated chloroform. The mixture was kept for 24 hrs. <sup>1</sup>H-NMR was used to identify the composition in the mixture.

**Synthesis of polymer blend – B1<sub>neat</sub>:** polymers **P1** (0.005 mmol), **P2** (0.005 mmol) and pentadecafluorooctanoic acid ( $2 \times 10^{-7}$  mol, 1 % per imine unit) were dissolved in 1.00 ml of dichloromethane. The mixture was dried up immediately at 80°C in vacuum oven for 24 hrs. <sup>1</sup>H-NMR was used to identify the composition in the neat polymer blend.