SUPPORTING INFORMATION

Dielectric Relaxation and Rheological Behavior of Supramolecular Polymeric Liquid

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Experimental:

Materials. 1,1,1,3,3,3-hexamethyldisilazane (HMDS, 98%, Acros Organics) was purified by distillation under reduced pressure prior to use. Chlorotrimethylsilane (TMSCl, 98%, Acros Organics) was purified by distillation under nitrogen gas. Chelidamic acid (95+, TCI), Decanoyl chloride (98+, Sigma-Aldrich), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Acros Organics), Ammonia, ca. 7 N solution in methanol (Acros Organics), 8-Bromo-1-octene(97%, Sigma-Aldrich), 10% Pd-C (Sigma-Aldrich), thymine (99+, Sigma-Aldrich), 1,6-Dibromohexane (97+, Alfa Aesar) were all used as received. All other reagents were of analytical grade and used as received. All solvents were purified according to literature procedures.

Synthesis:

**T-SH:** See Ref. S1.

**4-Oxybenzyl-2,6-Didecylamidopyridine (2):** A suspension of 4-Benzylxy-2,6-pyridinediamine 1 (6.0 g, 27.9 mmol) and triethylamine (7.8 mL, 55.7 mmol) in dry CH₂Cl₂ (600 mL) was stirred at room temperature under nitrogen atmosphere. To this was added decanoyl chloride (11.8 mL, 55.7 mmol) in dry CH₂Cl₂ (300 mL) dropwise, and the mixture was stirred for 4h. The resulting solution was then extracted with water (3 × 200 mL). Concentration in vacuum, followed by chromatography (SiO₂, Hex/EtOAc (1:1)) provided 12.7 g (87%) of the title compound as a cream-colored solid.

**1H NMR (400 MHz, CDCl₃, ppm)** δ: 7.62 (s, 2H, CONH), 7.58 (s, 2H, C₅H₂N), 7.45-7.31 (m, 5H, OCH₂ArH), 5.13 (s, 2H, OCH₂Ar) 2.36 (t, 4H, 2COCH₂), 1.70 (m, 4H, 2COCH₂CH₂), 1.26 (s, 24H, 2(CH₂)₆), 0.87 (t, 6H, CH₃).

**4-Hydroxyl-2,6-Didecylamidopyridine (3):** 4-Oxybenzyl-2,6-didecylamidopyridine 2 (4.0 g, 7.6 mmol) was stirred in the presence of 10% palladium on carbon (0.5 wt eq) in 60 mL of methanol for 6 h under hydrogen atmosphere. The suspension was filtered and the filtrate was evaporated to dryness in vacuum to obtain the title compound as white solid (3.0 g, 91%).

**1H NMR (400 MHz, DMSO-d₆, ppm)** δ: 10.45 (s, 1H, ArOH), 9.71 (s, 2H, CONH), 7.24 (s, 2H, C₅H₂N), 2.32 (t, 4H, 2COCH₂), 1.52 (m, 4H, 2COCH₂CH₂), 1.24 (s, 24H, 2(CH₂)₆), 0.83 (t, 6H, CH₃).

**4-Allyloctyl-2,6-Didecylamidopyridine (DAP9):** A solution of 4-Hydroxyl-2,6-Didecylamidopyridine 3 (2.5 g, 5.8 mmol), 8-bromo-1-octene (1.5 mL, 8.7 mmol), K₂CO₃ (0.82 g, 6.0 mmol) in 100 mL DMF was stirred at 65 °C for 24 h under nitrogen atmosphere. The solvent was removed under reduced pressure, then the solid was dissolved in CH₂Cl₂. After filtration, the liquid was concentrated in vacuo, followed by chromatography (SiO₂, CH₂Cl₂/Hexane (3:1)) provided 3.0 g (96%) of the title compound as light yellow solid.

**1H NMR (400 MHz, CDCl₃, ppm)** δ: 7.58 (s, 2H, CONH), 7.51 (s, 2H, C₅H₂N), 5.85-5.76 (m, 1H, CH=CH₂), 5.02-4.91 (m, 2H, CH=CH₂), 4.02 (t, 2H, CH₂O), 2.34 (t, 4H, 2COCH₂), 2.07-2.02 (q, 2H, CH₂CH₂), 1.77-1.65 (m, 6H, 2COCH₂CH₂, OCH₂CH₂), 1.48-1.32 (m, 6H, CH₂CH₂CH₂), 1.26 (s, 24H, 2(CH₂)₆), 0.87 (t, 6H, CH₃).

**2,6-Didecylamidopyridine-4-octyl-(N-1-mercapto-10-thymylhexane) (T-DAP9):** A solution of DAP9 (0.5 g, 0.92 mmol), T₂SH (0.334 g, 1.38 mmol), and DMPA (12 mg, 0.046 mmol) were dissolved in 0.5 mL of THF, followed by irradiation (365 nm) for 1 h. The solvent was removed under reduced pressure, followed by chromatography (SiO₂, Hex/EtOAc (2:1)) provided 0.36 g (83%) of the title compound as a high viscosity liquid.

**Characterization:**

**NMR concentration dependent experiments**

NMR concentration dependent experiments were carried at four different temperatures. At each temperature eight samples of different concentration were tested. The concentrations were 0.004 mol/L, 0.008 mol/L, 0.012 mol/L, 0.016 mol/L, 0.020 mol/L, 0.025 mol/L, 0.030 mol/L, 0.035 mol/L from dilute to concentrated, respectively. The experimental data for determination of the associate constant Kₐ of T-DAP9 at different temperatures is shown below. Kₐ is determined by using following equation (S2):

\[
\delta - \delta_H = \frac{\delta_C - \delta_H}{2} \left[ \frac{G}{H} + 1 + \frac{1}{K_a[H]} - \sqrt{\left( \frac{G}{H} + 1 + \frac{1}{K_a[H]} \right)^2 - 4 \frac{G}{H}} \right]^{-1}
\]
Where, H, G, C represent the host, guest and the complex; \([H]_t\) and \([G]_t\) are the total concentration of host and guest molecule at initial state, respectively; \(\delta_H\), \(\delta_C\), \(\delta\) are chemical shift of host and complex, and observed chemical shift. In our case, \([H]_t = [G]_t\).

![Figure S1](image1.png)  
**Figure S1.** Determination of associate constant of T-DAP9 at temperature of 31 °C.

![Figure S2](image2.png)  
**Figure S2.** Determination of associate constant of T-DAP9 at temperature of 38 °C.
Figure S3. Determination of associate constant of T-DAP9 at temperature of 45 °C.

Figure S4. DSC curve of T-DAP9 melt during cooling at 10 °C/min.
Figure S5. An example of the fit of the dielectric spectra with Eq. 1 (see the main text). Open symbols are experimental data and solids lines are the fits.

Figure S6. Shifted dielectric spectra at various temperatures with respect to the Debye mode at 297 K.
Figure S7. Creep compliance at various temperatures.

Reference:

(S1) Lou, N.; Wang, Y. Y.; Li, H. X.; Sokolov, A. P.; Xiong, H. M. *Polymer* 2012, 53, 4455.
(S2) Ilhan, F.; Gray, M.; Rotello, V. M. *Macromolecules* 2001, 34, 2597.