Electronic Supplementary Information

Molecular Nanoribbon Gels

Marta Martínez-Abadía, Rajeev K. Dubey, Mercedes Fernández, Miguel Martín-Arroyo, Robert Aguirresarobe, Akinori Saeki, and Aurelio Mateo-Alonso

POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, 20018 Donostia-San Sebastián, Spain. E-Mail: amateo@polymat.eu

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan.

Ikerbasque, Basque Foundation for Science, Bilbao, Spain.
Figure S1. SEM images of the xerogel of NR-13 in 1-octanol (3% w/w).
Figure S2. SEM images of the xerogel of NR-33 in 1-octanol (1.3% w/w).
Figure S3. SEM images of the xerogel of NR-53 in 1-octanol (1.3% w/w).
Figure S4. Thixotropy loop by continuous flow test at T=20 °C for NR-53 (1.3% w/w).
Figure S5. Strain sweep test at $T = 20 ^\circ C$ performed at constant angular frequency of 10 rad/s ($G'$ are the filled symbols and $G''$ are the empty symbols).
Figure S6. Continuous-step strain measurements at $T = 20 \, ^\circ\text{C}$ for a) NR-53, b) NR-33 and c) NR-13. ($G'$ are the filled symbols and $G''$ are the empty symbols). The applied strain sequence is the following: 0.5% for 300 s + 100% for 100 s + 0.5% for 300 s + 100% for 300 s + 0.5% for 300 s.
Figure S7. Sol state of NR-13 (3.0% w/w), NR-33 (1.3% w/w) and NR-53 (1.3% w/w).
Figure S8. Excitation spectra of a) NR-13 (703 nm), b) NR-33 (721 nm) and c) NR-53 (679 nm), excitation wavelengths are given between brackets.
General Experimental Methods

Reagents for synthesis were, if not otherwise specified, purchased from Aldrich, Fluka, TCI or Acros. Commercial chemicals and solvents were used as received. Column chromatography was carried out using Silica gel 60 (40-60 μm) from Scharlab. Analytical thin layer chromatography (TLC) was done using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck. UV-active compounds were detected with a UV-lamp from CAMAG at wavelength \( \lambda = 254 \) or 366 nm. NR-13, NR-33 and NR-53 were synthesized according to reported methods.¹

The gelation test was performed using vial inversion method. The organogels were prepared by heating up the dispersion until all material was dissolved. Then the samples were allowed to cool down in air to room temperature.

Scanning Electron Microscopy was performed on a JEOL JSM-7000F operated at 5 kV. The samples were prepared by depositing drops of the sol state (3% w/w in 1-octanol for NR-13 and 1.3% w/w for NR-33 and NR-53) on a glass, and when the gel was formed on the surface the solvent was dried first with a piece of paper and finally under vacuum for 18 hours at room temperature. Finally, the samples were sputtered with chrome (10 nm).

Transmission Electron Microscopy was performed using a TECNAI G2 20 TWIN (FEI), operating at an accelerating voltage of 200 KeV in a bright-field image mode. The samples were prepared by forming the gel and then diluting with more solvent (0.07% w/w in 1-octanol for NR-13 and 0.1% w/w for NR-33 and NR-53). These dispersions were deposited on a carbon film copper grid, and the solvent was dried under vacuum for 18 hours at room temperature.

The X-ray powder diffraction patterns were collected by using a PHILIPS X’PERT PRO automatic diffractometer operating at 40 kV and 40 mA, in theta-theta configuration, secondary monochromator with Cu-Kα radiation (\( \lambda = 1.5418 \) Å) and a PIXcel solid state detector (active length in 2\( \theta \) 3.347º). Data were collected from 1 to 50° 2\( \theta \) (step size = 0.026 and time per step = 300 s, total time 40 min) at room temperature. A variable divergence slit was used, giving a constant 4.0 mm area of sample illumination.

Rheological characterization was carried out with both continuous and oscillatory tests, using an AR G2 Stress-Controlled Rheometer (TA instrument), equipped with a Peltier plate and a 20 mm diameter 2º cone-plate geometry. The Small Amplitude Oscillatory Shear test (SAOS) was the rheological method of choice to investigate the network
structure at equilibrium. The test is non-destructive as small stresses or small deformations were applied to protect the structures. For this purpose, preliminary strain sweep tests were performed to determine the linear viscoelastic regime. A dynamic sweep strain from 0.01 to 100 % strain at a frequency of 10 rad/s was applied. Then, oscillating frequency sweep tests were performed under linear viscoelastic conditions at two temperatures T=20°C and T=50°C to evaluate the gel-sol transition. Thixotropy, which is a time-dependent shear thinning property, was studied by continuous shear tests at T=20°C and Large Amplitude Oscillatory Shear test (LAOS) Continuous shear test allowed to obtain the viscosity values taken in a linear ramp from 0.1 to 100 s^{-1} (ramp up) within 180 s, held at 100 s^{-1} for 10 s, and then decreasing from 100 to 0.1 s^{-1} (ramp down) within 180 s. Oscillatory continuous-step strain measurement were performed at 10 rad/s using the following sequence: 0.5% for 300 s + 100% for 100s + 0.5% for 300 s + 100% for 300s.

The sol-gel transitions (T_{sol-gel}) of the different gels have been estimated by monitoring visually the changes in the fluidity with the temperature using a Stuart SMP30 melting point apparatus.

Absorption and, emission and excitation spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer, and a LS55 Perkin-Elmer Fluorescence spectrometer, respectively.

FP-TRMC experiments were conducted for the sample on a quartz plate using the third harmonic generator (THG; 355 nm) of a Nd:YAG laser (Continuum Inc., Surelite II, 5–8 ns pulse duration, 10 Hz) as the excitation source (9.1 \times 10^{15} photons cm^{-2} pulse^{-1}). The frequency and power of microwave were ~9.1 GHz and 3 mW, respectively. The photoconductivity transient \( \Delta \sigma \) was converted to the product of the quantum yield (\( \phi \)) and the sum of charge carrier mobilities \( \Sigma \mu \) (= \( \mu_+ + \mu_- \)) by the formula \( \phi \Sigma \mu = \Delta \sigma (e_0 F_{\text{light}})^{-1} \), where \( e \) and \( F_{\text{light}} \) are the unit charge of a single electron and a correction (or filling) factor, respectively.

References

1. R. K. Dubey, M. Melle-Franco and A. Mateo-Alonso, J. Am. Chem. Soc., 2021, 143, 6593-6600.