Electronic Supporting Information

Use of 4-piperidones in one-pot syntheses of novel, high-molecular-weight linear and virtually 100%-hyperbranched polymers

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1. Experimental

1.1 Materials

Trifluoromethanesulfonic acid (TFSA) and trifluoroacetic acid (TFA) were distilled under dry nitrogen before use. N-(1-phenethyl)piperidone (**1g**) was purified by recrystallization with charcoal from a hexanes/methylene chloride (99/1 (v/v)) mixture. Hydrochloride-4-piperidone (**1a**) was used as received. Piperidones (**1b-f**) were distilled prior to use. All compounds were obtained from Aldrich.

1.2 Characterization

NMR spectra were recorded on Bruker Avance 400 Spectrometer, operating at 400.13 and 100 MHz for ^{1}H and ^{13}C respectively. Dimethylsulfoxide-d_6 was used as a solvent. Infrared (IR) spectra were measured on a Perkin-Elmer FT-IR-ATR spectrometer. The inherent viscosities of 0.2% polymer solutions in 1-methyl-2-pyrrolidinone (NMP) were measured at 25 °C using an Ubbelohde viscometer. Molecular weights were determined by gel permeation chromatography (GPC). The chromatography system was equipped with three Waters styragel columns and measurements were made at 40 °C with THF as the solvent at

a flow rate of 1.0 ml/min. The SEC-MALS measurements were performed at 25 °C using a separation system comprising two size-exclusion columns, a Waters HSPgel HR MB-L and a HR MB-B with a range from 5×10^2 to 7×10^5 and from 1×10^3 to 4×10^6 respectively, connected in series. The chromatography system was a Water Alliance 2695, equipped with a 100 μL sample loop and flow rate of the mobile phase was 0.5 ml· min^{-1}; the polymer concentration in tetrahydrofuran solution was 2.5 ml min^{-1}, the light scattering photometer was a Dawn Eos multiangle light scattering (MALS) instrument (Wyatt Technology, Santa Barbara, CA). Simultaneous concentration detection was performed using an Optilab REX interferometric refractometer (Wyatt Technology, Santa Barbara, CA). Both detectors used a wavelength of 690 nm. The angular dependence of the scattered light was extrapolated to zero angle using the linear Berry fit method. The dn/dc of polymers was determined using a solution with a concentration that ranged from 0.1×10^{-3} to 1.0 × 10-^{3}. The data acquisition was carried out with ASTRA software version 5.1.7.3 (Wyatt Technologies Corp.). The *T*g was evaluated by differential scanning calorimetry (DSC) measured at 10 °C/min on DuPont 910.

1.3 Polymer Synthesis

1.3.1 Preparation of 2aB

In a typical synthesis hydrochloride-4-piperidone (**1a**) (0.2 g, 1.3 mmol), biphenyl (**B**) (2 g, 1.3 mmol), methylene chloride (1.1 ml), TFA (0.4 ml) and TFSA (5 ml) were stirred in a single-necked flask (10 ml) for 5 hours. The resulting clear, viscous, orange solution was then poured slowly into an aqueous solution of $NaHCO_3$. The yellow fibrous solid was filtered off, washed with water and dried in convection oven under nitrogen flow for 24 hours. The polymer thus obtained (1.45 g, 97% yield) had an inherent viscosity η_{inh} of 1.11 dL g^{-1} (NMP).

1.3.2 Preparation of 2bB

1-Methyl-4-piperidone (**1b**) (0.8 ml, 0.789 g, 6.97 mmol), biphenyl (**B**) (1.075 g, 6.97 mmol), methylene chloride (2.8 ml), TFA (0.4 ml) and TFSA (5 ml) were stirred in a single-necke flask (10 ml) for 6 hours. The resulting viscous, red solution was then poured slowly into an aqueous solution of $NaHCO_3$. The yellow fibrous solid was filtered off, washed with water and dried in convection oven under nitrogen flow for 24 hours. The polymer thus obtained (1.69 g, 98% yield) had an inherent viscosity η_{inh} of 0.65 dL g^{-1} (NMP). The polymer had molecular weights, *Mw* and *Mn*, of 22630 and 15850, respectively. The ^{1}H NMR spectrum of polymer **2bB** is given in Figure S3.

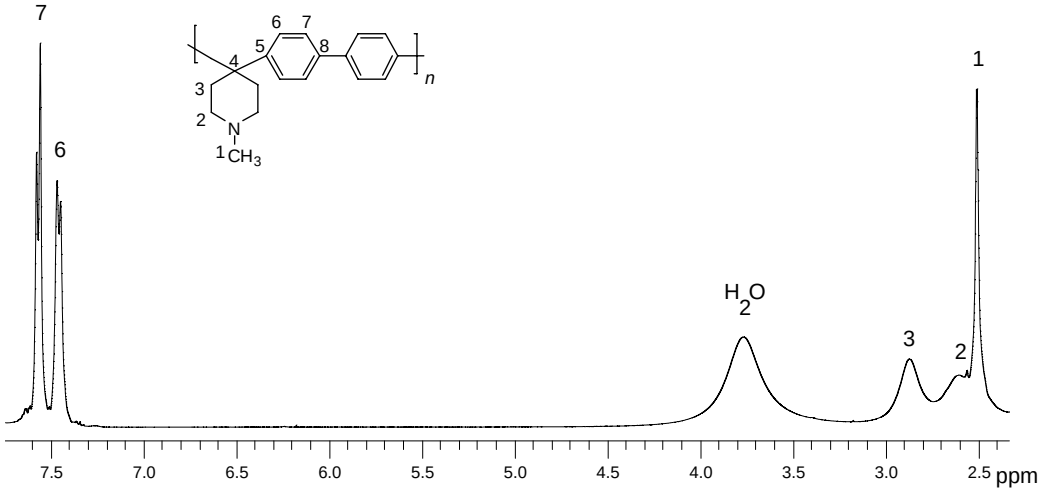

Fig.S3. ^{1}H NMR spectrum of polymer **2bB** (solution in DMSO-d_6).

1.3.3 Preparation of 2dA

1-Acetyl-4-piperidone (**1d**) (0.42 g, 2.97 mmol), 4,4′-diphenoxybenzophenone (**A**) (1.08 g, 2.97 mmol), TFA (0.2 ml) and TFSA (2.5 ml) were stirred in a 10 ml single-necked flask for 7 hours. The resulting viscous, orange solution was then poured slowly into an aqueous solution of $NaHCO_3$. The white fibrous solid was filtered off, washed with water, and dried. The resulting white powder (1.25 g, 86% yield) had an inherent viscosity η_{inh} of 0.08 dL g^{-1} (NMP). The polymer had molecular weights, *Mn* and *Mw,* of 4719 and 6490, respectively.

1.3.4 Preparation of 2g

In a typical synthesis N-(1-phenethyl)piperidone (**1g**) (0.275 g, 0.00135 mol), TFSA (1.8 ml) and TFA (0.2 ml) were stirred in a 5 mL single-neck flask at room temperature for 41 h, and the resulting viscous yellow solution was poured slowly into water (100 ml). The white precipitate was filtered off and dried. The resulting white fiber-like powder (**2g**) (0.244g, 93% yield) had molecular weights of *Mn* and *Mw* of 54490 and 67714, respectively. The ^{1}H NMR spectrum of polymer **2g** is given in Figure S4.

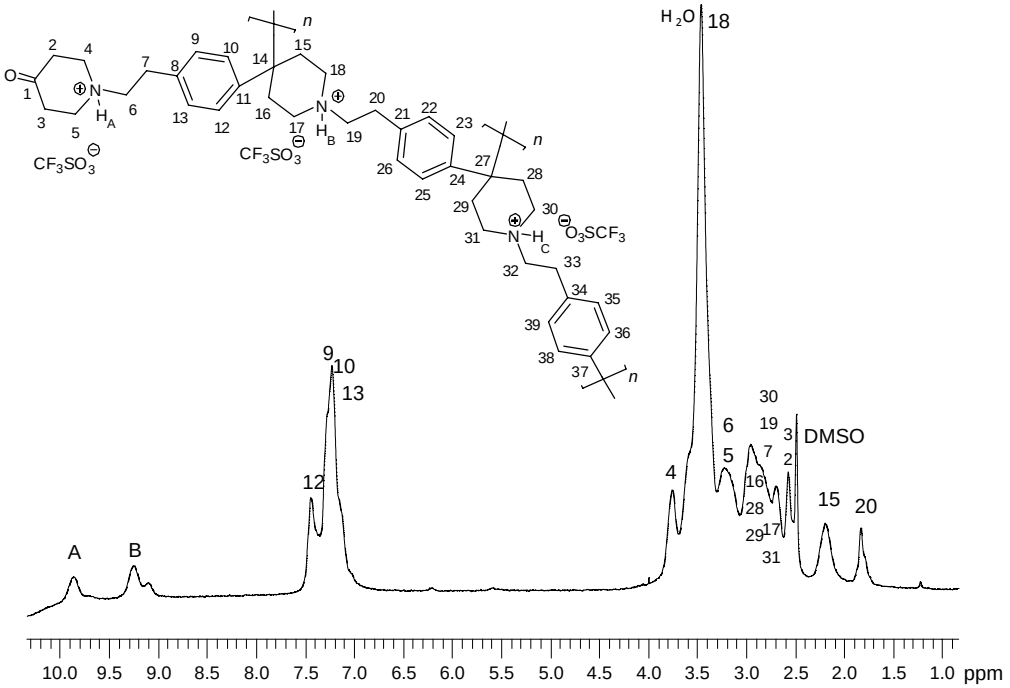

Fig.S4.^{1}H NMR spectrum of polymer **2g (**amine-triflate complex, solution in DMSO-d_6).

1.3.5 Preparation of 2g- NOH

Polymer **2g** (0.042g, 0.123 mmol) was dissolved in 5 ml of ethanol and added to the solution of hydroxylamine hydrochloride (0.061 g, 0.877 mmol) in 3 ml of water. The solution was stirred in a single-necked flask (10 ml) at reflux for 2 hours. The resulting white solution was poured in a Petri dish; the precipitate was washed with water and dried.

The yield of the polymers was 0.063 g (74%). The IR spectra of the polymer **2g** and **2g-NOH** are presented in Figure S5.

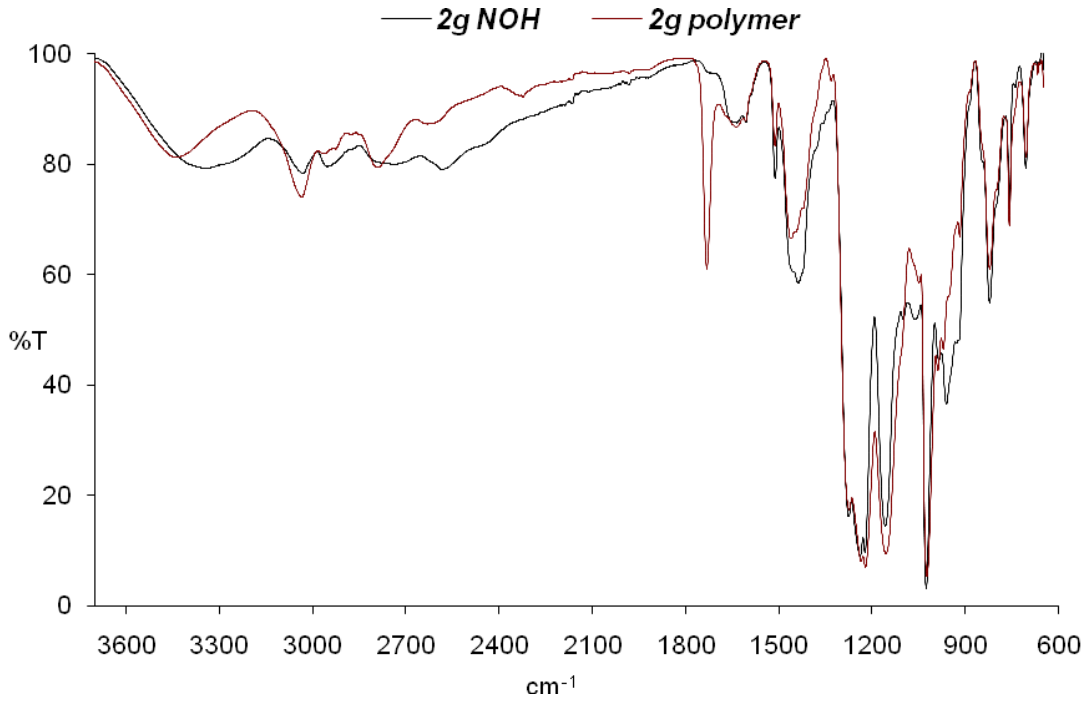

Fig.S5.FT-IR spectra of polymers **2g** and **2g-NOH**.