

Supporting information

Nanoparticles from Catalytic Step Growth Polymerization

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Materials and General Considerations. Unless noted otherwise, all manipulations of ruthenium complexes were carried out under an inert atmosphere using standard glovebox or Schlenk techniques. Toluene was distilled from sodium under argon. Demineralised water was distilled under nitrogen and degassed three times after distillation. Ruthenium alkylidenes **2** and **3** were supplied by Aldrich.

NMR spectra were recorded on a Varian Unity INOVA 400 or on a Bruker AC 250 spectrometer. ^1H and ^{13}C NMR chemical shifts were referred to the solvent signal. Dynamic light scattering was carried out on a Malvern Nano-ZS ZEN 3600 particle sizer (173° back scattering). The autocorrelation function was analyzed using the Malvern dispersion technology software 3.30 algorithm to obtain volume and number weighted particle size distributions. For the determination of particle size, a few drops of a latex sample were diluted with ca. 3 mL of water. TEM images were obtained on a Zeiss Libra 120 instrument (acceleration voltage 120 keV). Dispersions were dialyzed for TEM analysis to remove any free surfactant, and applied to a copper grid. Samples were not contrasted. Absorption spectra were recorded on a Varian Cary 50 spectrometer. Fluorescence spectra were obtained on a tailor-made setup consisting of a xenon flash lamp, a monochromator (Oriel 77250 1/8M), a spectrograph and a nitrogen-cooled CCD camera enabling photoluminescence detection from 310 nm to 940 nm.¹ Excitation wavelengths were chosen according to the respective absorption maxima.

Synthesis of Monomer 1.²⁻⁴ *1,4-Dipropoxybenzene*. KOH (81 g, 1.44 mol) was added to a solution of hydroquinone (64.2 g, 0.58 mol) in dry ethanol (550 mL), and refluxed for 20 minutes with mechanical stirring. 1-Bromopropane (200 mL, 2.2 mol) was added dropwise over the course of 1 hour, and the mixture was refluxed for another 3 hours. After solvent evaporation in vacuo, the residue was extracted with 500 mL CHCl_3 . The organic phase was filtered, extracted three times with 200 mL water, washed with 250 mL saturated NaHCO_3 solution, and dried over Na_2SO_4 . Solvent evaporation yielded the crude product, which was recrystallized three times from methanol (50 mL), to afford 85 g (75% yield) of white crystals.

^1H NMR (CDCl_3, δ): 6.81 (4H, s), 3.86 (4H, t), 1.76 (4H, sextet), 1.01 (6H, t)

1,4-Diiodo-2,5-dipropoxybenzene. ICl (175 g, 1.08 mol) was added dropwise to 300 mL of methanol, keeping the temperature below 10°C . After slow addition of 1,4-dipropoxybenzene (48.5 g, 0.25 mol) at 10°C , the mixture was refluxed for 4h. Cooling to room temperature and standing over night afforded needle-like crystals, which were collected by filtration. The crystals were rinsed three times with 100 mL of cold methanol, and recrystallized from methanol to afford 49.1 g (44% yield) of white product.

^1H NMR (CDCl_3, δ): 7.17 (2H, s), 3.89 (4H, t), 1.83 (4H, sextet), 1.06 (6H, t)

1,4-Dipropoxy-2,5-divinylbenzene (1). P(^tBu)₃HBF₄ (14.5 mg, 50 μmol), [Pd(dba)₂] (28.75 mg, 50 μmol), 2,6-di-*tert*-butyl-4-methylphenol (25 mg), and 1,4-diiodo-2,5-dipropoxybenzene (4.46 g, 10 mmol) were dissolved in 30 mL of dry degassed dioxane under inert conditions. Cy₂NMe (4.72 mL, 22 mmol) was added via syringe, and the mixture was further degassed by bubbling argon for 10 minutes. The reaction mixture was cannula-transferred into an autoclave. 30 bar static ethylene pressure were applied for 24 h under stirring at 80°C. After cooling to room temperature and release of the ethylene pressure, the mixture was poured into 100 mL of distilled water, and extracted three times with 20 mL ethyl acetate. The combined organic phases were washed with 20 mL water and brine, respectively, and dried over MgSO₄. Solvent evaporation in vacuo yielded a yellow crude product, which was flashed through a plug of silica (hexane/toluene = 9). TLC of the crude product solution showed only one spot, corresponding to the product. Solvent evaporation afforded 2.03 g (82% yield) of **1** as white crystals.

¹H NMR (CDCl₃, δ): 7.05 (2H, dd), 6.98 (2H, s), 5.72 (2H, dd), 5.23 (2H, dd), 3.92 (4H, t), 1.81 (4H, sextet), 1.05 (6H, t).

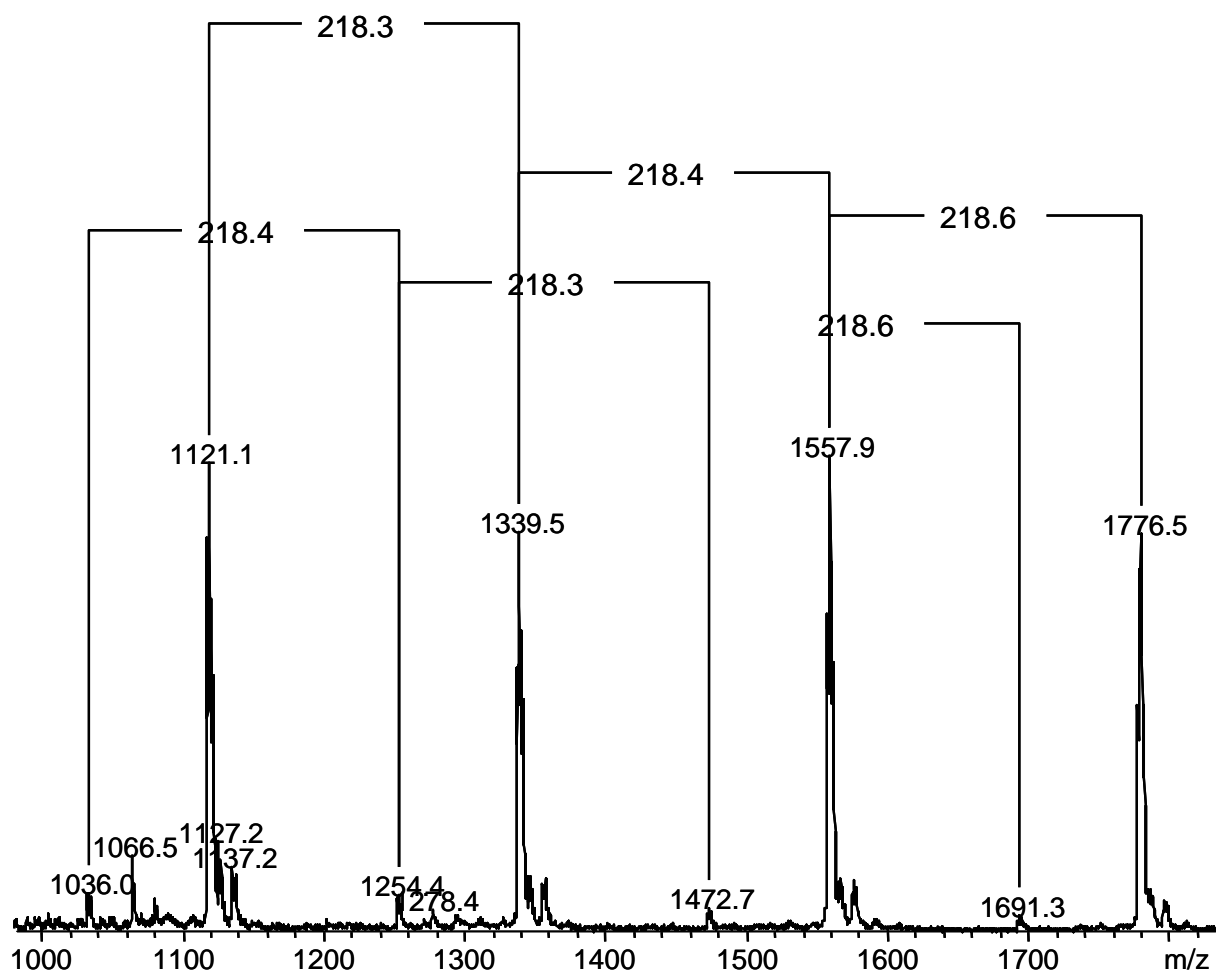


Figure S1. MALDI-TOF mass spectrum of poly-**1**. $M = 1121 + n \times 218$: $\text{H}_2\text{C}=\text{CH}-[p\text{-}(2,5\text{-}(\text{}^n\text{PrO})_2\text{C}_6\text{H}_2)\text{-CH}=\text{CH-}]_{n+5}\text{H}$; $M = 1036 + n \times 218$: $2\text{-}(i\text{PrO})\text{C}_6\text{H}_4\text{-HC}=\text{CH}-[p\text{-}(2,5\text{-}(\text{}^n\text{PrO})_2\text{C}_6\text{H}_2)\text{-CH}=\text{CH-}]_{n+4}\text{H}$.

Sample preparation for NMR studies of activation of catalyst precursor **3**: 10 mg (16 μmol) of Hoveyda-Grubbs 2nd generation ruthenium alkylidene (**3**), 19.6 mg (80 μmol) of 1,4-dipropoxy-2,5-divinylbenzene (**1**), and 2,6-di-*tert*-butyl-4-methylphenol (<1 mg) weighed into a Young-NMR tube. The tube was immersed in liquid nitrogen, and toluene- d_8 was vacuum-transferred into the tube. The tube was sealed, and the solids were dissolved just at the melting point of toluene. The tube was kept at -80°C until the transfer into the NMR spectrometer. In the NMR spectrometer, spectra were acquired while the sample was gradually warmed to 25°C (Figure S2).

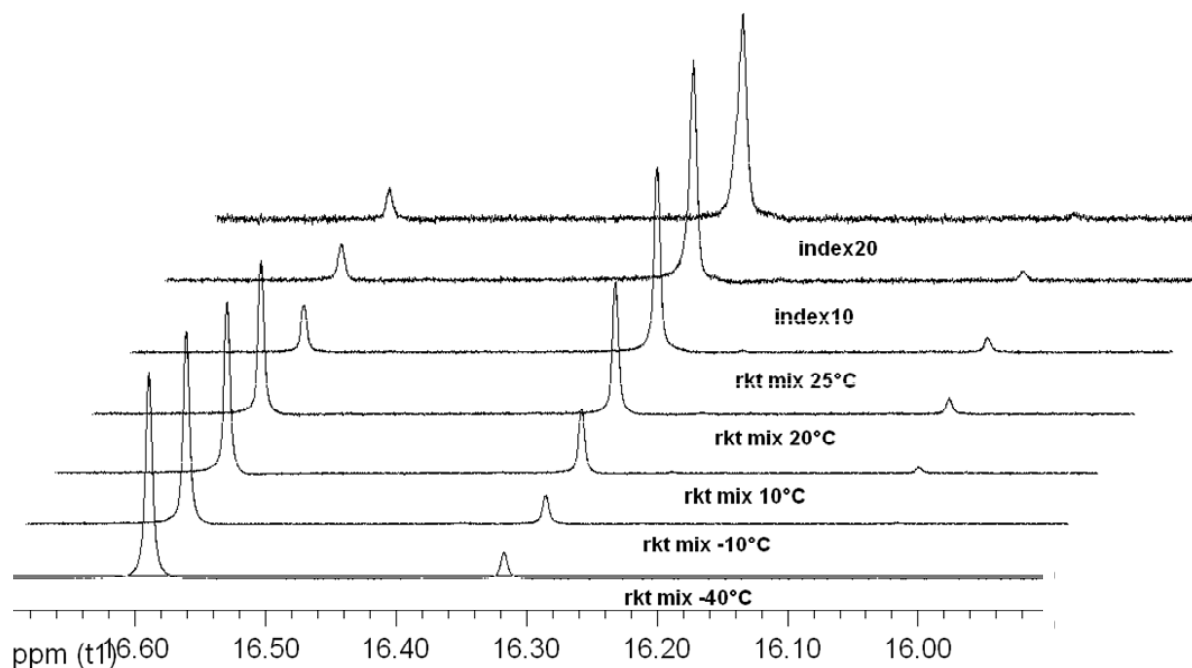


Figure S2. Alkydine signals during acquisition. ‘Index 10’ corresponds to 7 h reaction time, ‘index 20’ to 15h reaction time at 25°C .

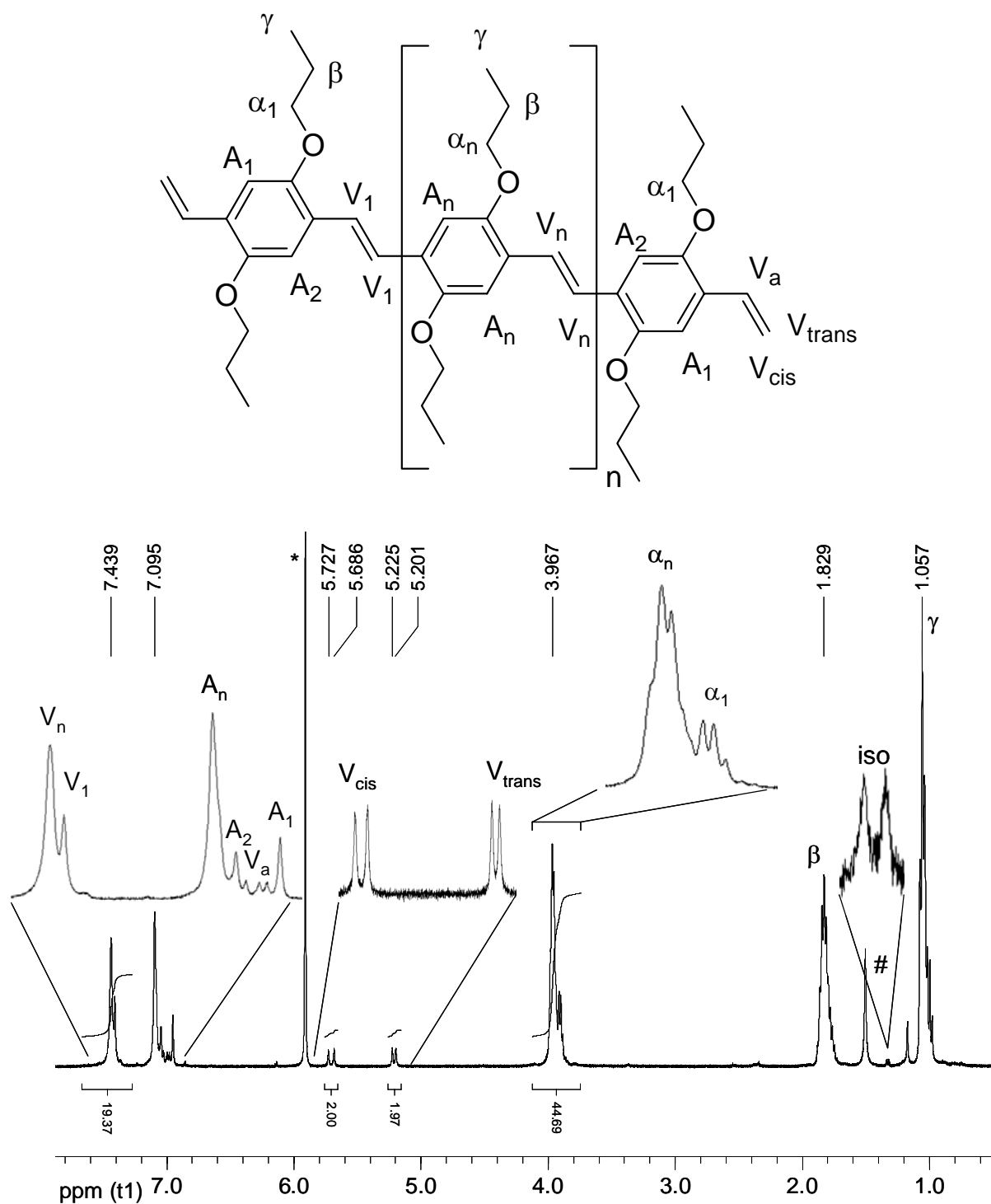


Figure S3. ¹H NMR spectrum (400 MHz, C₂D₂Cl₄) of poly-1 with assignments. The “iso” signal corresponds to the isopropoxy group of the benzylidene moiety of **3**, which represents an end group in a minor portion of chains (#: H₂O; *: deuterated solvent).

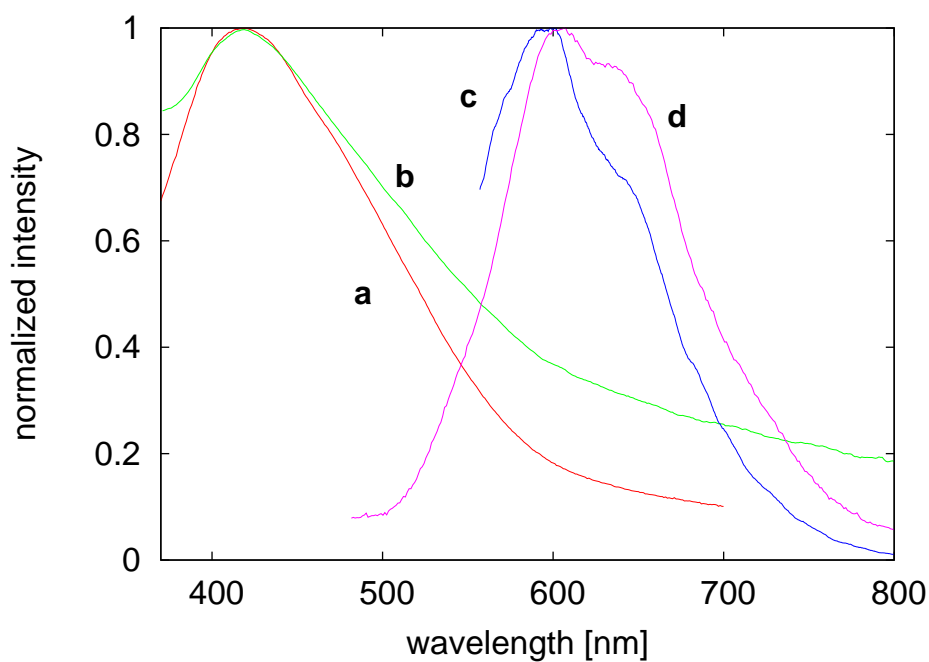


Figure S4. Normalized absorption spectra and photoluminescence spectra of an aqueous dispersion of poly-1 particles (a, d), and of a thin film cast from the particle dispersion (b, c).



Figure S5. Poly-1 dispersion (left), and image obtained by ink-jet printing (right).

References

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