

Supplementary Information to

Surface-Initiated Kumada Catalyst-Transfer Polycondensation of
Poly(9,9-dioctylfluorene) from Organosilica Particles: Chain-
Confinement Promoted β -Phase Formation

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1. *Materials and Instrumentation.*

$\text{Et}_2\text{Ni}(\text{bipy})$ [ref. 16 of the main text], 2-bromo-7-iodo-9,9-dioctylfluorene, [ref. 12b of the main text], were prepared as previously described. All reagents and solvents were purchased from Aldrich. ^1H (500.13 MHz), ^{31}P (202.46 MHz), and ^{13}C (125.74 MHz) NMR spectra were recorded on a Bruker DRX 500 spectrometer using a 5 mm $^1\text{H}/^{13}\text{C}/^{19}\text{F}/^{31}\text{P}$ gradient probe. The ^1H spectra were referenced on the residual solvent peak (CDCl_3 : $\delta(^1\text{H}) = 7.26$ ppm; THF-d_8 : $\delta(^1\text{H}) = 3.57$ ppm, $\delta(^{13}\text{C}) = 67.2$ ppm). GPC measurements were carried out on an Agilent 1100 Series (Agilent, USA) normal-temperature size exclusion chromatograph, equipped with refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, UK), eluent – chloroform and flow rate 1 mL min^{-1} . Calibration was based on polystyrene standards obtained from Polymer Standards Service (PSS, Germany). UV-vis measurements were carried out using the Lambda 800 spectrophotometer (Perkin Elmer, Germany). Fluorescence measurements were recorded with a Fluorolog 3 (Horiba JobinYvon, USA).

2. *Synthesis of [2-(4-bromo-phenyl)-ethyl]-triethoxy-silane*

Hydrosilylation was carried out by adding triethoxysilane (100 g) to 4-bromostyrene (18.3 g, 0.1 mol) dropwise in the presence of 160 mg of chloroplatinic acid (2mL of 1:1 ethanol/diethyl ether solution) as a catalyst and stirring for 1 h. After the excess of triethoxysilane was removed by vacuum distillation, the oily residue was fractionized by vacuum distillation. The resulting product (16.6g, yield 48%) is a mixture of Markovnikov and anti-Markovnikov adducts.

3. Preparation of 880 nm organosilica particles.

The monodispersed spherical ~880 nm in the diameter, silica-core organosilica-shell particles were prepared by modified Stöber method via sequential sol-gel hydrolysis of tetramethyl orthosilicates (TMOS) and [2-(4-bromo-phenyl)-ethyl]-triethoxy-silane (**2**) under controlled conditions, according to the following procedure. Three solutions, I (containing 11.25 ml of TMOS in 67.5 ml of ethanol), II (containing 1.875 ml of TMOS, 2.92 g of silane **1** and 22.5 ml of ethanol), and III (containing 28.5 ml of 25% ammonia in water and 150 ml of ethanol), were prepared separately. The solution I and II were consecutively added to the solution III, with the rate 0.5 mL/min under an argon blanket into a round-bottom flask under stirring at 440 min⁻¹ and stirred overnight at room temperature. The dispersion was then transferred out of the reactor, and the powders were washed with ethanol and ultrapure water by repeated centrifugation (at 5000 rpm for 15 min) and further dried at 70 °C for 12 h.

4. Preparation of the initiating sites on the organosilica particle surfaces.

To develop $|\text{-Si-(CH}_2\text{)}_2\text{-C}_6\text{H}_4\text{-Ni(dppe)-Br}$ initiator sites on the particles surface we applied a two-step procedure that includes the reaction of the particles with Et₂Ni(bipy) followed by the addition of an excess of the *dppe* ligand. Et₂Ni(bipy) solution in THF (70mg in 7ml) was added at room temperature to the dispersion of the particles in THF (400 mg in 5 ml) in a several portion, adding the new portion after a clear indication of the consumption of a previous portion of Et₂Ni(bipy), i.e., after disappearance of the green color inherent to Et₂Ni(bipy). Normally, the reaction requires some induction period (0.5-2 hours), but afterwards, proceeds very rapidly. It is noteworthy that the induction period is longer for THF of higher purity, suggesting that some traces of water or oxygen catalyze the reaction. This “titration” procedure permits efficient conversion of all accessible $|\text{-Si-(CH}_2\text{)}_2\text{-C}_6\text{H}_4\text{-Br}$ surface groups, thus avoiding contamination of the particles by unreacted Et₂Ni(bipy). Afterwards, the particles were separated by centrifugation (at 5000 rpm for 15 min), redispersed in THF and the solution of *dppe* in THF was added (105.6 mg of *dppe* in 4 ml of THF to 400 mg of the particles in 4 ml of THF). Afterwards, the suspension was allowed to react one hour

at room temperature. Upon the ligand exchange, the particles change their color from reddish-brown to orange. Prior the SI-KCTP, the particles were carefully purified from physisorbed Ni compounds by several centrifugation/redispersion cycles (at 5000 rpm for 15 min) using anhydrous and degassed THF and CH₂Cl₂ in argon atmosphere. The washing with CH₂Cl₂ leads to removal of some unidentified Ni complexes, as follows from yellow color of supernatant solutions obtained upon first centrifugation/redispersion cycles. The purification cycles were repeated until the supernatant solution remained colorless.

5. KCTP of **1** from the 460 nm organosilica particles: grafting of PFO

The monomer **1** was prepared as follows: 2-bromo-7-iodo-9,9-dioctylfluorene (15 mmol) was placed in a round-bottomed flask equipped with a magnet stirrer bar, and the atmosphere was replaced with argon. Dry THF (200 mL) and iso-propylmagnesium chloride & LiCl (1 M solution, 16 mL, 16 mmol) were added via a syringe and the mixture was stirred at 0°C for 1h.

To perform SI-KCTP, the monomer **1** was injected to the dispersion of the activated particles and the polymerization was performed at room temperature for 40 minutes. After the polymerization the resulting composite particles were subjected onto careful purifications to separate them from any ungrafted polymers (referred here and in the main text as “unbound PFO”), catalyst and byproducts. A typical purification procedure included several centrifugation/redispersion cycles using the following solvents and additives in the following consequence: 5N HCl, water, methanol, chloroform, THF.

The hairy particles having PFO shell were extensively characterized. For analytical purposes, grafted PFO chains were detached from the silica core by dissolution of the later in an aqueous HF. The mass fraction of the released polymer relative to the sample before the HF-treatment was found to be of ~10 % that agrees well with the TGA data. The detached PFO exhibits a monomodal GPC trace with $M_n = 48\ 000$ g/mol and $M_w = 180\ 000$ g/mol.

For the density of PFO, $\rho_{PFO} \sim 1$ g/cm³, the dry-state thickness of the PFO shell, $h_{PFO} = 25$ nm and $M_{n,PFO} = 17\ 000$ g/mol, $\sigma = N_A \times \rho_{PFO} \times h_{PFO} / M_{n,PFO} = \sim 0.89$ chain/nm². Radius of gyration, R_g , for PFO of different molecular weight was previously measured (M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. P. Woo, M. Soliman, *Acta Polym.* 1998, 49, 439.) and for PFO sample with $M_n = 17\ 000$ g/mol is about 10 nm in THF. This value was used for estimation of a reduced tethered density (Σ) according to the following equation: $\Sigma = \sigma \pi R_g^2 = 0.89 \times 3.14 \times 10^2 = 280$.

6. Absorption and fluorescence spectra of the μ -PFO particles, degrafted and unbound PFO.

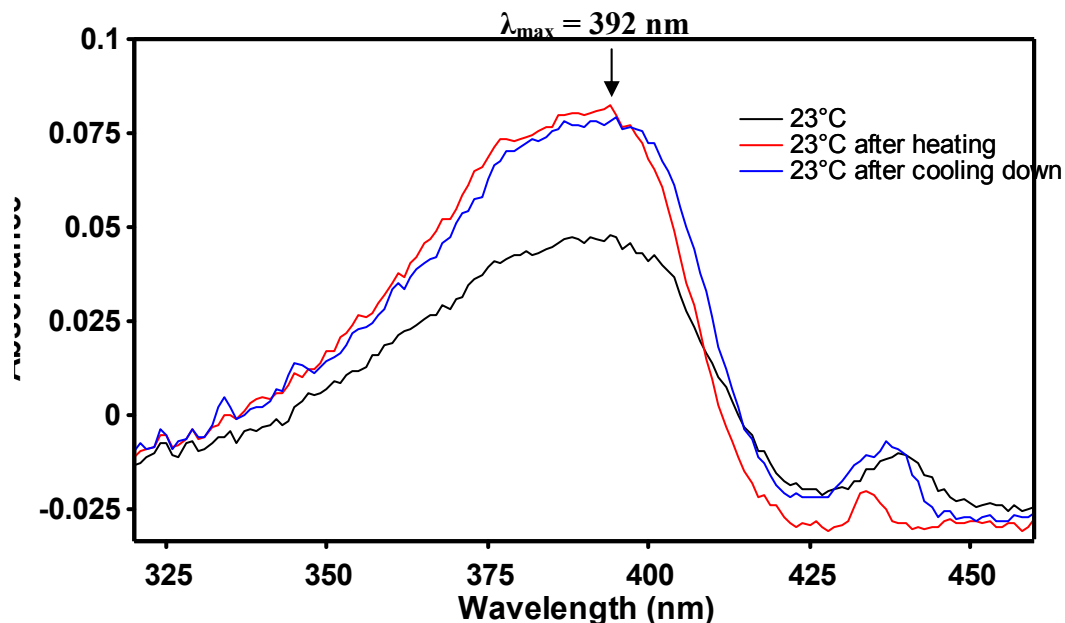


Figure S1. (a) UV-vis of the PFO degrafted from the μ -PFO particles ($M_w = 180\,000$ g/mol) in THF recorded at room temperature: as dissolved sample without heating (black); being heated for 2 hours at 50°C and then allowed to cool to RT (red); being heated at 50°C for 2 hours and then cooled down to -20°C (blue).

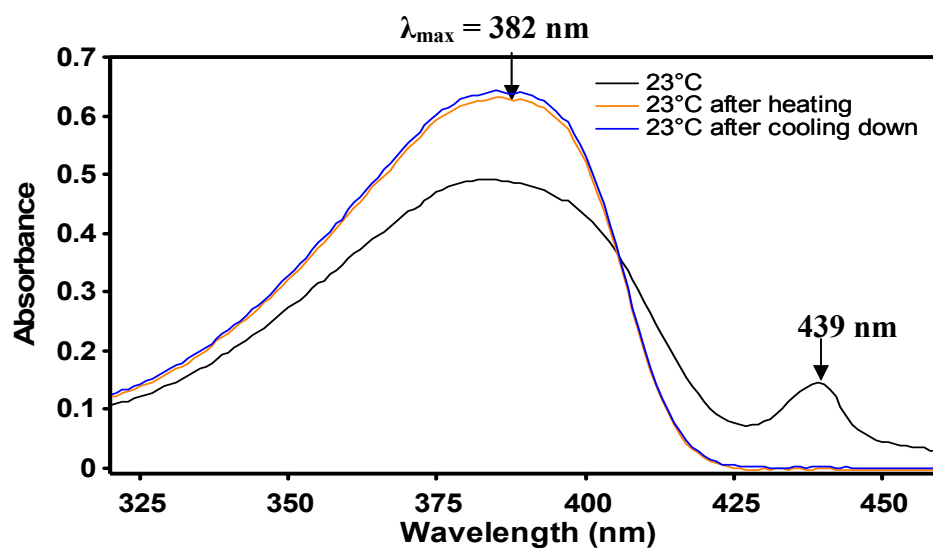


Figure S2. (a) UV-vis of the unbound PFO sample (one formed in the grafting experiment as a side product to the μ -PFO particles) ($M_w = 69\,900$ g/mol) in THF recorded at room temperature: as dissolved sample without heating (black); being heated for 2 hours at 50°C and then allowed to cool to RT (red); being heated at 50°C for 2 hours and then cooled down to -20°C (blue): after the cooling, the peak at 439 nm characteristic for the α -phase did not recover.

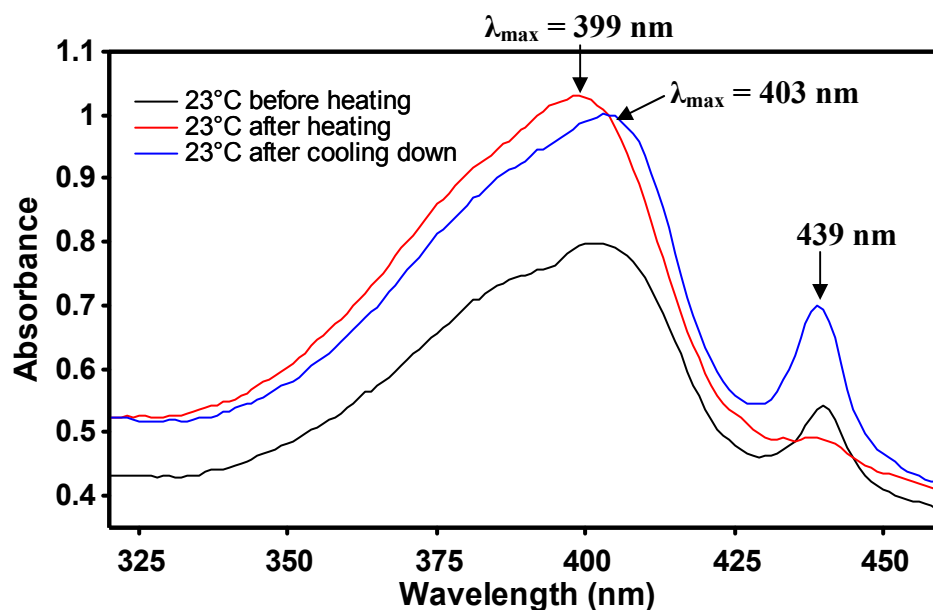


Figure S3. (a) UV-vis of the μ -PFO particles in THF recorded at room temperature: as dispersed without heating (black); being heated for 2 hours at 50°C and then allowed to cool to RT (red); the dispersion being heated at 50°C for 2 hours and then cooled down to -20°C (blue).

For further comparison, photophysical properties of the “unbound PFO” formed in the grafting process as the side product were also studied. The absorption maximum of the degrafted PFO (Fig. S1) is slightly red-shifted relative to the absorption maximum of the unbound PFO (Fig. S2, $\lambda_{\text{max}} = 392 \text{ nm}$ versus 382 nm), that might be due to a higher molecular weight and, hence, a larger conjugation length of the former PFO sample. If dissolved in THF without heating, both PFO samples exhibit a relatively weak absorption at 439 nm that reflects a small fraction of the planar conformation of PFO (β -phase). Emission spectra of the unbound (Fig. S7) and degrafted PFO samples (Fig. S6) at 382 nm excitation wavelength show substantial contributions from both amorphous α -phase (417 nm) and from the β -phase (441, 465, 500 nm). Upon heating above 50°C the signatures of the β -phase in the absorption and emission spectra disappear completely and they do not recover upon the cooling to RT; the cooling of the degrafted PFO sample down to -20 °C recovers the signatures of the β -phase in an accordance with earlier reported data. In contrast, the cooling of the unbound PFO down to -20 °C does not recover the β -phase (likely, its recovering requires lower temperatures).

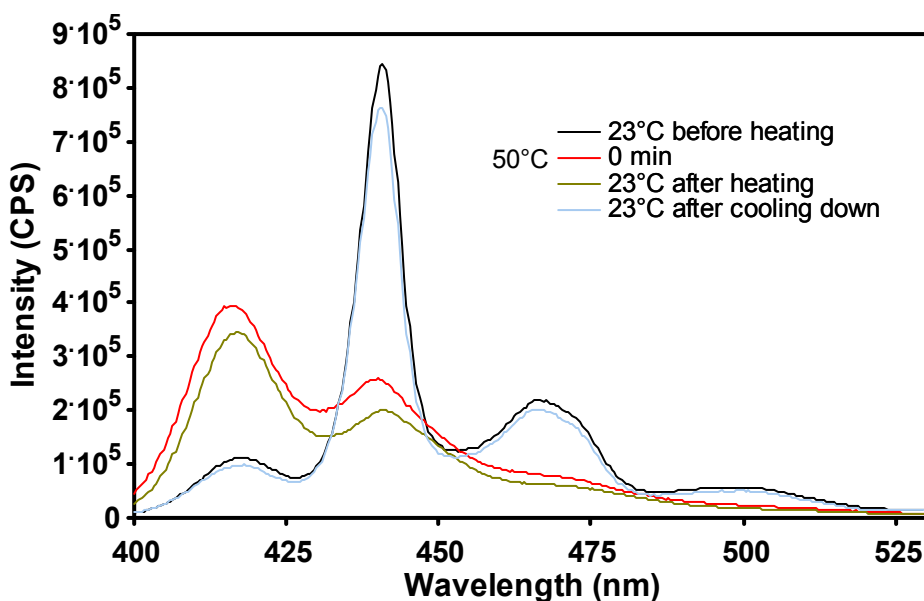


Figure S4. Emission spectra of the μ -PFO particles in THF at 382 nm excitation wavelength: as dispersed without heating (black); being heated for 2 hours at 50°C (red); and then allowed to cool to RT (light-brown); and then cooled down to -20°C (light-blue).

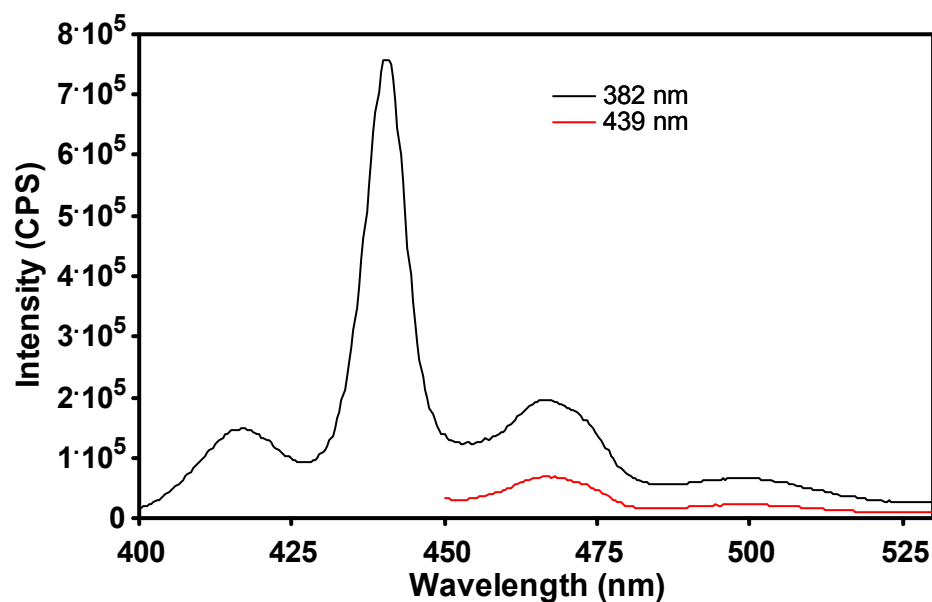


Figure S5. Emission spectra of the μ -PFO particles being dispersed in THF without heating at recorded at room temperature at two different excitation wavelengths: 382 nm (black line) and 439 nm (red).

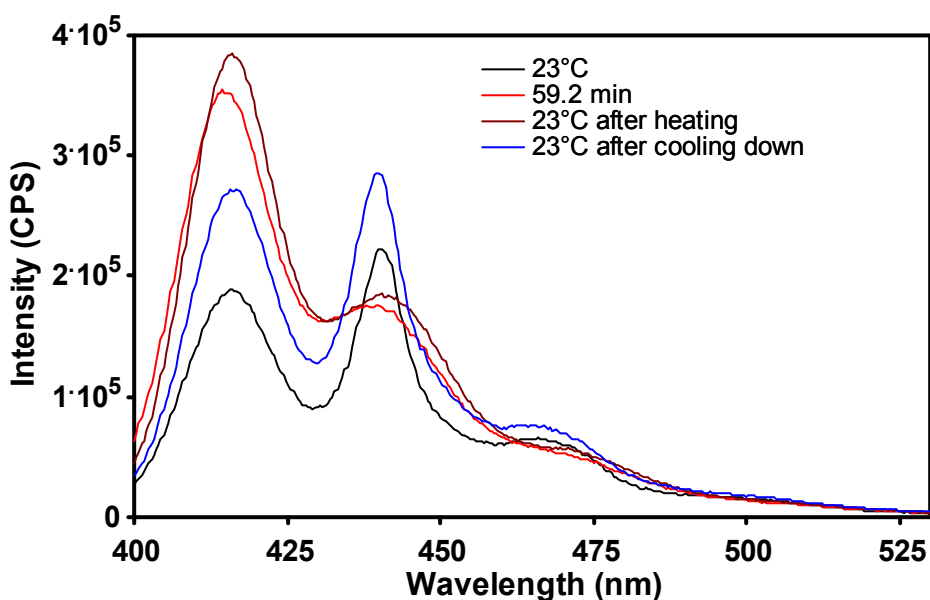


Figure S6. Emission spectra of the PFO degraded from the μ -PFO particles ($M_w = 180\,000$ g/mol) in THF at 382 nm excitation wavelength: as dispersed without heating (black); being heated for 2 hours at 50°C (red); and then allowed to cool to RT (brown); and then cooled down to -20°C (blue).

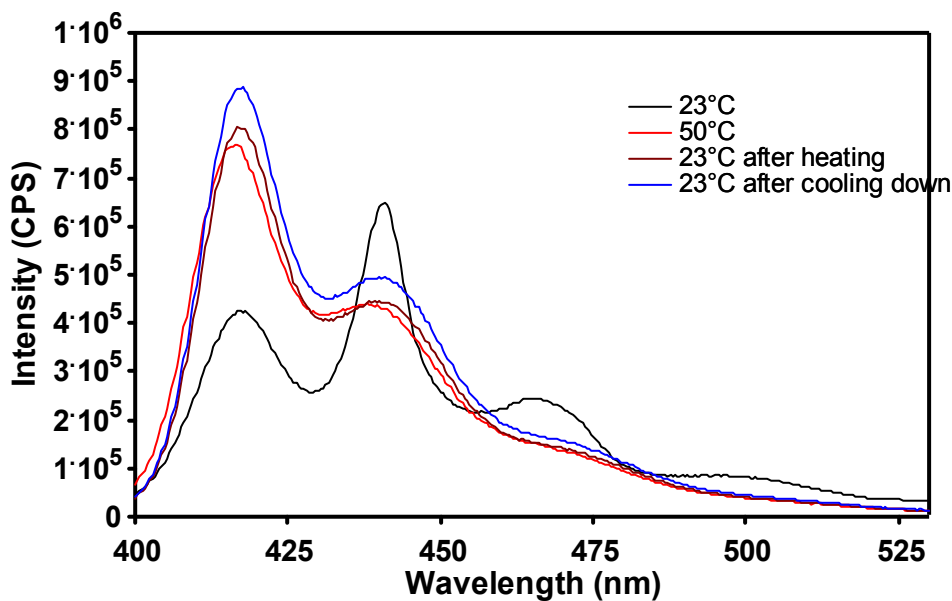


Figure S7. Emission spectra of the unbound PFO sample (one formed in the grafting experiment as a side product to the μ -PFO particles) ($M_w = 69\,900$ g/mol) in THF at 382 nm excitation wavelength: as dispersed without heating (black); being heated for 2 hours at 50°C (red); and then allowed to cool to RT (brown); and then cooled down to -20°C (blue).

7. KCTP of **1** using externally added initiator **Ph-Ni(dppe)Br**.

As a model process for SIP we firstly explored possibility to polymerize monomer **1** with externally added initiator Ph-Ni(dppe)Br. The presence of Ph-moiety as a starting group would be a sign of the chain-growth polycondensation of **1**. We found that the polymerization of **1** indeed involves the chain-growth mechanism. The reaction allows only moderate control over the molecular weight (MW) and MW distribution resulting into PFO with polydispersity index (PDI) in a 1.35-1.65 range, close to previously reported results with the polymerization of **1** induced by Ni(dppe)₂ and Ni(dppp)Cl₂ initiators¹. Ph- starting group is seen better in the ¹H NMR spectrum of PFO with smaller MW, however, the spectrum does not provide the information about a degree of the end-functionalization because of impossibility to separate the polymer that was initiated by Ph-containing initiator from the one, (re)initiated with the Ni without Ph group. To address this question, we performed the polymerization from the particles that allows an easy separation of grafted and non-grafted polymer by simple centrifugation procedures. Details of these experiments are given in the main text.

Experimental details. Synthesis of Ph-Ni(dppe)Br was described previously.² A solution of the Ph-Ni(dppe)Br initiator (either 10.7 mg, 0.02 mmol, 2 mol % or 5.4 mg, 0.01 mmol, 1 mol % in 1 ml of THF) was added to the solution of monomer **1** in THF (1 mmol in 20 ml of THF) via a syringe at room temperature and stirred for 30 minutes. The reaction mixture was quenched by 5 M hydrochloric acid and the products were extracted with chloroform. The organic layer was washed with water, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The resulting polymer was then subjected to extraction with methanol and acetone in a Soxhlet apparatus. The residue readily soluble in chloroform, THF and CH₂Cl₂ of PFO was analyzed by ¹H NMR and GPC. The first PFO sample obtained at the feed ratio of 50 had M_n=10300 g/mol, M_w = 13900 g/mol and PDI=1.35. The second PFO sample obtained at the feed ratio of 100 had M_n=22200 g/mol, M_w = 36400 g/mol and PDI=1.64. These results agree well with ones obtained by Huang et al (L. Huang, S. Wu, Y. Qu, Y. Geng, and F. Wang, *Macromolecules* 2008, **41**, 8944).

¹ (a) L. Huang, S. Wu, Y. Qu, Y. Geng, and F. Wang, *Macromolecules* 2008, **41**, 8944. (b) M. C. Stefan, A. E. Javier, I. Osaka and R. D. McCullough, *Macromolecules*, 2009, **42**, 30.

² V. Senkovskyy, R. Tkachov, T. Beryozkina, H. Komber, U. Oertel, M. Horecha, V. Bocharova, M. Stamm, S. A. Gevorgyan, F. C. Krebs, and A. Kiriy, *J. Am. Chem. Soc.*, 2009, **131**, 16445

Figure S8. ^1H NMR spectrum of PFO obtained at polycondensation of 1 initiated by Ph-Ni(dppe)-Br.

