

Supporting Information for

Synthesis of Hetero-Telechelic α , ω Dye

Functionalized Polymer by the RAFT Process and

Energy Transfer between the End Groups

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S1. Dynamic and Static Light Scattering of Starting Polymer **1**

S1.1 Method. Static and dynamic light-scattering measurements were performed with an ALV-SP86 goniometer, a Uniphase HeNe laser (22 mW output power at 632.8 nm wavelength), an ALV/High QE APD avalanche diode fiber optic detection system, and an ALV-3000 correlator in linear mode.

The static scattering intensities were analyzed according to Zimm, yielding the mass average of the molecular weight M_w , the mean square radius of gyration (z-average) $R_g^2 = \langle R_g^2 \rangle_z$ and the second virial coefficient A_2 .

The correlation functions showed a narrow, monomodal decay and were fitted by a sum of two exponentials, from which the first cumulant Γ_1 was calculated. The z-average diffusion coefficient D_z usually obtained by extrapolation of Γ_1/q^2 to $q = 0$, was measured at a scattering angle of 20° only, because the size was well below 10nm. No angular and concentration dependency was observed. The inverse z-average hydrodynamic radius, $R_h = \langle 1/R_h \rangle_z^{-1}$ was evaluated by formal application of Stokes law. The polydispersity parameter μ_2 was obtained by normalization of the second cumulant.

The dilute polymer solutions in methanol (4 concentrations $1.0 \leq c \leq 5.0$ g/L) were measured from 30° to 150° in steps of 5° (SLS) or at 20° only (DLS). Prior to measurement, the solutions were filtered through $0.2 \mu\text{m}$ pore size Dimex filters (Millipore LG). The refractive index increment at $\lambda = 632.8\text{nm}$ was measured by a home-built Michelson interferometer as described elsewhere [1] and determined to be $(dn/dc) = 0.1492 \text{ cm}^3/\text{g}$ in methanol.

S1.2 Light Scattering Results.

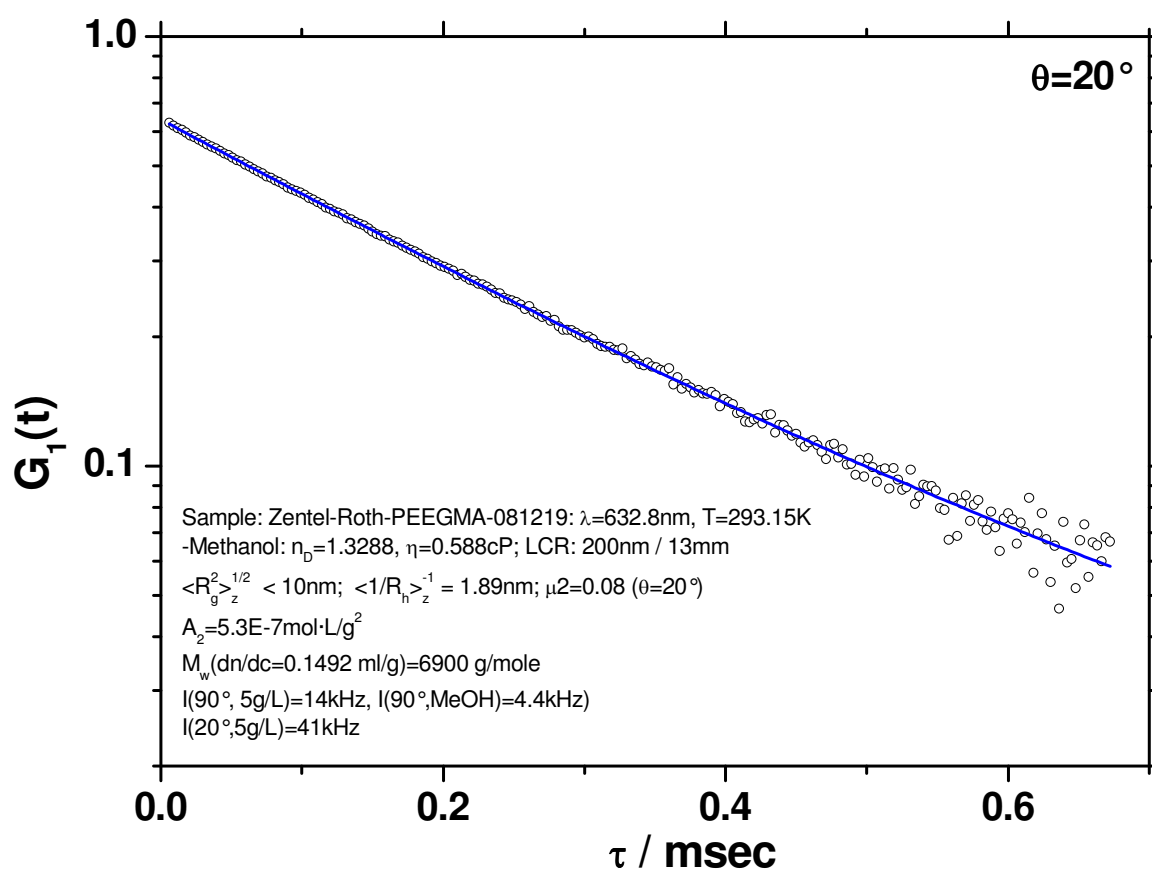


Fig. S1: Field autocorrelation function at $\theta = 20^\circ$: hydrodynamic radius 1.89nm , $\mu_2 = 0.08$.

PDEGMA (I) in MeOH at 293.15K, Filtration LG-200nm; Conc 5g/L:

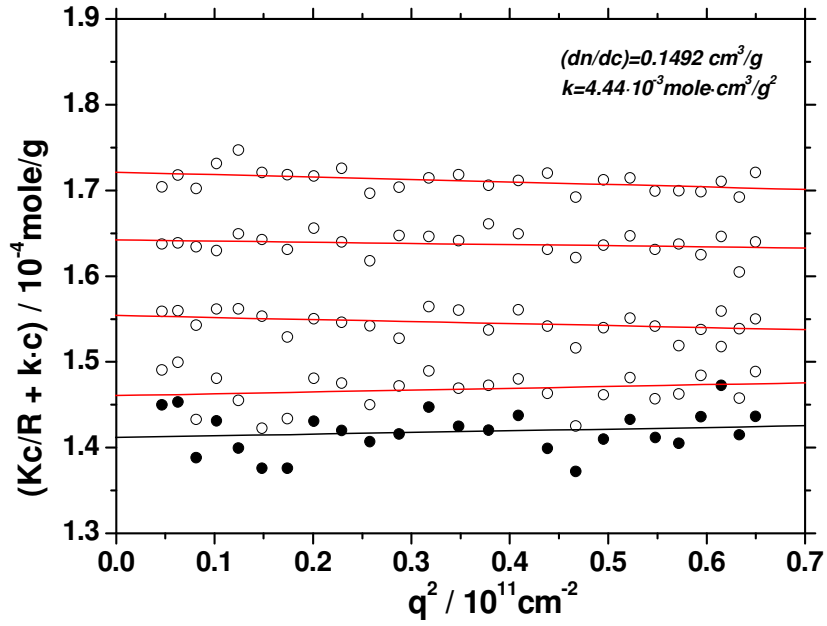


Fig. S2: Modified Zimm-plot with extrapolation to zero concentration: within error: no angular dependency ($R_g < 10\text{nm}$), no concentration dependency; ($A_2=0$, see Fig. 3); extrapolated molar mass $M_w=6900 (\pm 5\%) \text{ g/mole}$

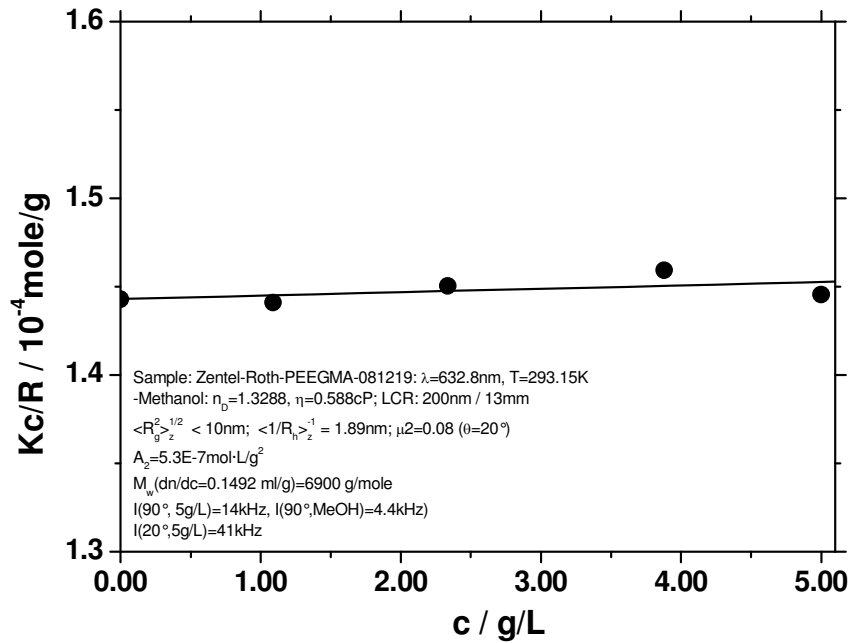
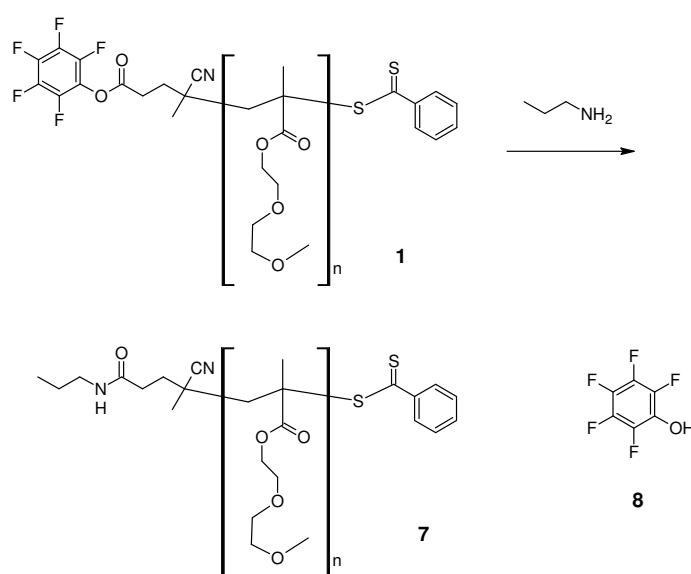


Fig. S3: Separated concentration dependency: $A_2=0$ (within error) and $R_g < 10\text{nm}$

$M_w=6900 (\pm 5\%) \text{ g/mole}$ (experimental $dn/dc = 0.1492 \text{ cm}^3/\text{g}$)

S2. Reactivity Difference of Pentafluorophenyl versus Dithioesters

The success of the orthogonal α/ω functionalization relied on the different reactivities of the two ester end groups. Prior to dye functionalization, polymer **1** was reacted with small amounts of propyl amine. The presence / conversion of the pentafluorophenyl (PFP) ester were monitored with ^{19}F NMR, while the presence of the dithioester (DTE) could be confirmed with UV-spectroscopy.



Scheme S1. Reaction of α -PFP, ω -DTE PDEGMA (**1**) with propyl amine.

With less than 1 equivalent of amine, the PFP ester was only partially aminolyzed as could be seen from a ^{19}F NMR measurement showing about 20% of fluorine remaining as PFP ester, and about 80% of free pentafluorophenol (**8**) (See figure S4, curve B). If 1 or more equivalents of propyl amine are added, the PFP ester was completely aminolyzed and no fluorine remains in the polymer (Figure 4, curve C). As base to scavenge the free phenol, the non-nucleophilic 1,8-bis(dimethylamino)naphthalene (proton sponge) was used.

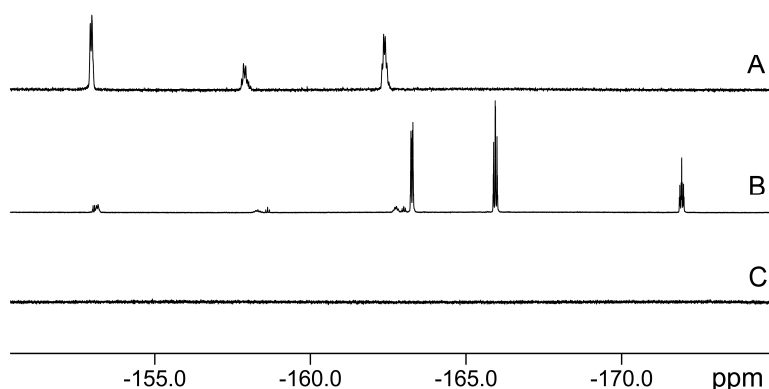


Figure S4. ^{19}F NMR spectra of (A) α -PFP, ω -DTE PDEGMA **1**, (B) after conversion with 0.8 equiv. of propyl amine before purification and (C) polymer **7** after purification. The signals at -153, -158, and -163 ppm originate from the polymer PFP ester, while the three signals at -163, -166 and -172 come from free pentafluorophenol **8**.

The DTE in these model reactions could be monitored with UV-vis spectroscopy due to the strong absorbance band at 302 nm. Figure S5 shows the absorbencies of solutions with the same concentration of polymer **1** before and polymer **7** after complete α end group conversion. The data showed that at least 98% of DTE were still present at the ω end group after the amidation of the PFP ester. This was in agreement with results published by other authors; they synthesized a chain transfer agent containing a DTE and *N*-hydroxysuccinimide (NHS) ester and were able to react this activated ester with various amines without any harm being done to the DTE.[2] As PFP esters are slightly more reactive than NHS esters,[3] the results found from these preliminary studies were as expected.

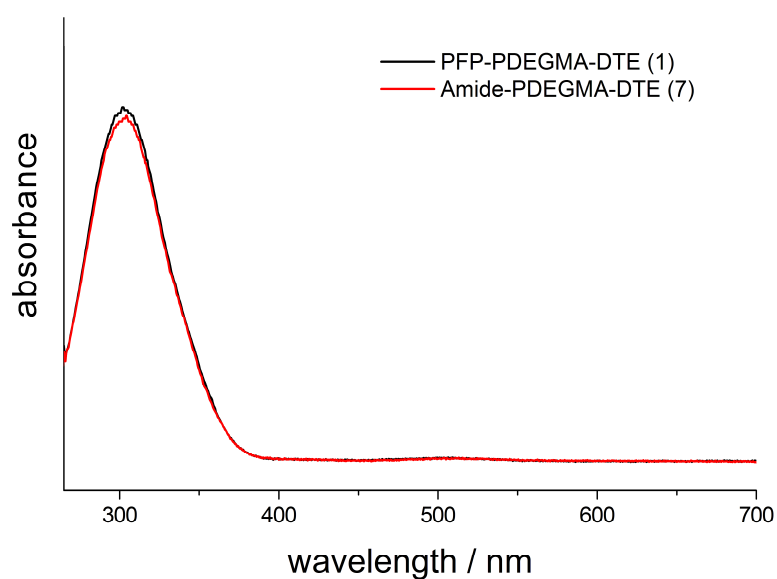


Figure S5. UV-vis spectra of polymer **1** (black curve) and polymer **7** (red curve).

S3. HSQC and UV-vis Data of Polymer **3**

Polymer **3** was analyzed by UV-vis and HSQC NMR to confirm the presence of both the α -Oregon Green dye and the ω -DTE end groups.

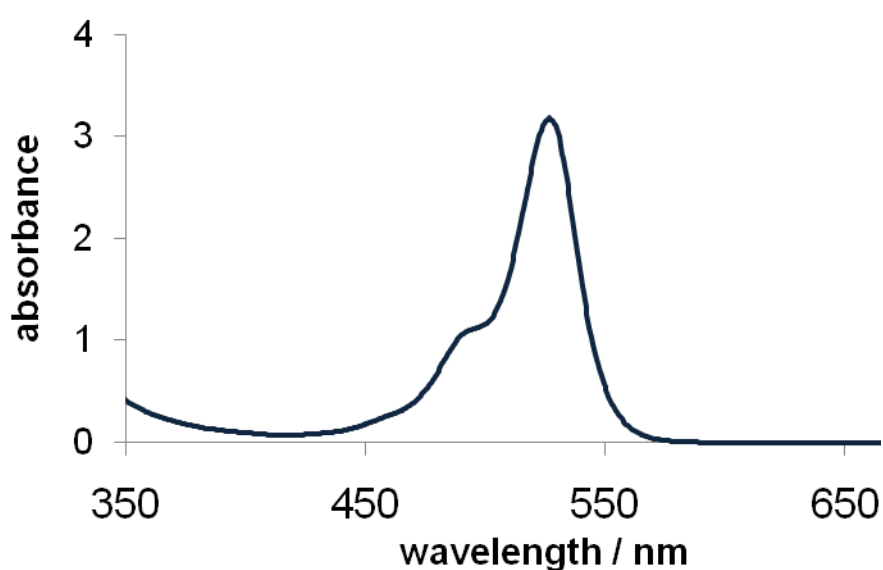


Figure S6. UV-vis absorbance of polymer **3** showing the characteristic peak of the Oregon Green end group.

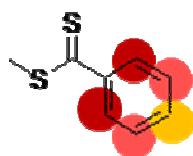
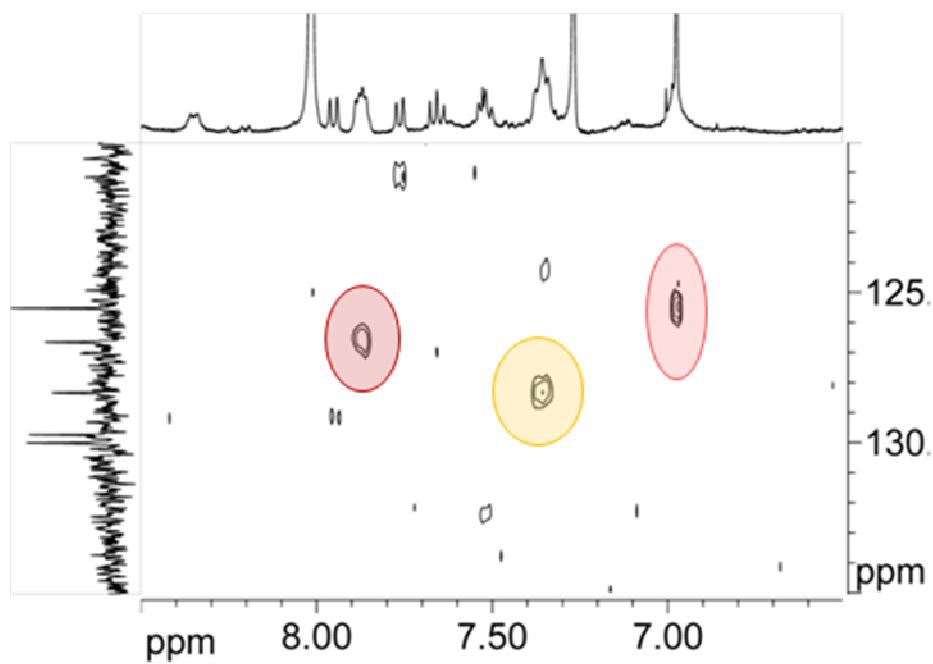


Figure S7. Section of a $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum showing the presence of the ω -DTE of polymer **3**. The signals are assigned in the structure; from left to right in the spectrum: ortho (2H), para (1H) and meta (2H).

S4. Calculation of End Group Conversions of Polymers **5** and **6**

The end group conversions were calculated by measuring the absorbance of a solution with a known polymer concentration. The dye concentration was calculated from the absorbance of the solutions and the molar extinction coefficients. The cuvette thickness was 0.5 cm.

Polymer 5.

Molecular weight:	7450(*)	g/mol
Polymer concentration of sample:	0.398	g/L
	53.42	μmol/L
Oregon Green absorbance:	1.5955	
Oregon Green extinction coefficient:	84000	L/mol cm
Oregon Green concentration:	37.988	μmol/L
Oregon Green conversion:	71.1 %	
Texas Red absorbance:	1.3577	
Texas Red extinction coefficient:	109000(**)	L/mol cm
Texas Red concentration:	24.912	μmol/L
Texas Red conversion:	46.6%	

Polymer 6.

Polymer concentration of sample:	9.214	μmol/L
Texas Red absorbance:	0.2420	
Texas Red extinction coefficient:	109000(**)	L/mol cm
Texas Red concentration:	4.440	μmol/L
Texas Red conversion:	48.2%	

(*) from light scattering data including the weight of the new (partially) installed end groups

(**) measured in DMF.

S5. Absorption and Emission Spectra of Polymers **3**, **5** and **6**

Samples of polymers **3**, **5** and **6** having the same concentration of donors and the same concentration of acceptors, respectively, and thus additive absorbance curves (Figure S6), were prepared. If the dyes in polymer **5** would exist without any interaction between them, their emission spectrum should resemble a superimposition of the emission of the single-dye polymers **3** and **6** in a first approximation. However, a decreased donor emission and an increased acceptor emission were found, suggesting the transfer of energy (Figure S7).

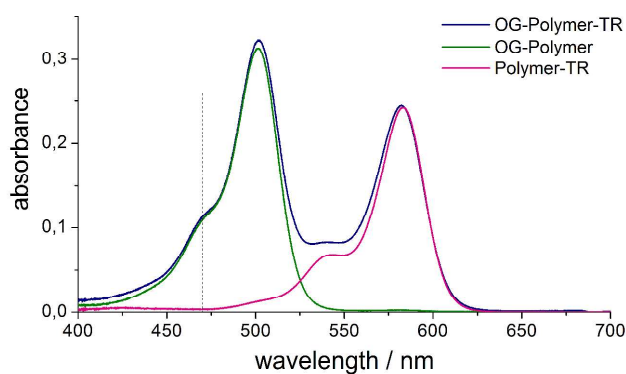


Figure S8. Absorption spectra of polymers **3** (green curve), **6** (red curve) and **5** (blue curve)

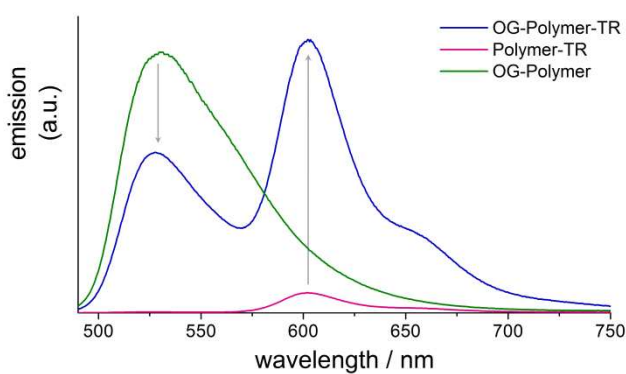


Figure S9. Emission spectra of polymers **3** (green curve), **6** (red curve) and **5** (blue curve)

Supporting Information References

- [1] Becker, A.; Köhler, W.; Müller, B. *Ber. Bunsenges.* **1995**, 89, 600-605.
- [2] Bathfied, M.; D'Agosto, F.; Spitz, R.; Charreye, M.-T.; Delair, T. *J. Am. Chem. Soc.* **2006**, 128, 2546–2547
- [3] Eberhardt, M.; Mruk, R.; Zentel, R.; Theato, P. *Eur. Polym. J.* **2005**, 41, 1569–1575