Supplementary Material (ESI) for Soft Matter

Supporting Information

UCST-type Behavior of Poly[oligo(ethylene glycol) methylether methacrylate] (POEGMA) in Aliphatic Alcohols: Solvent, Co-Solvent, Molecular Weight, and End Group Dependences

Peter J. Roth[a] *Florian D. Jochum,*[a] *Patrick Theato*[a,b,c]

[a] Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

[b] World Class University (WCU) program of Chemical Convergence for Energy & Environment (C_2E_2), School of Chemical and Biological Engineering, College of Engineering, Seoul National University (SNU), Seoul, Korea

[c] Department of Materials Science and Engineering, University of Sheffield, Sheffield, UK

Email: rothpe@uni-mainz.de; theato@uni-mainz.de or P.Theato@sheffield.ac.uk

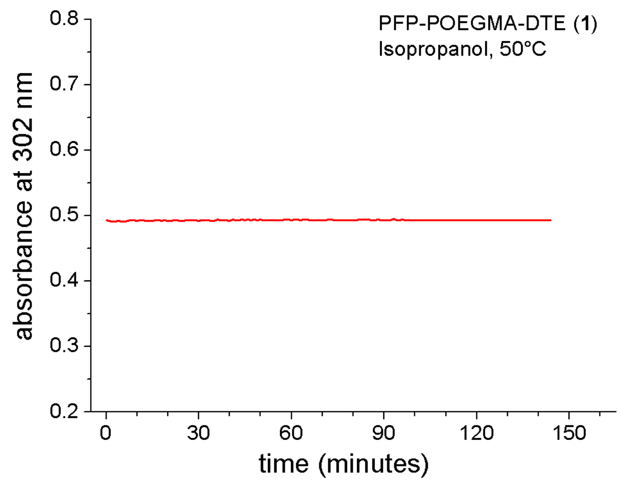

Figure S1. In order to show that the dithioester end group of polymer (1) did not decompose during heating in alcohols, a sample of (**1**) was heated in isopropanol to 50°C for 2.5 h while recording the dithioester absorbance at 302 nm. As the graph shows, no decrease in absorbance and thus no decomposition were observed within this time period. UCST measurements were performed in less than 1 h.

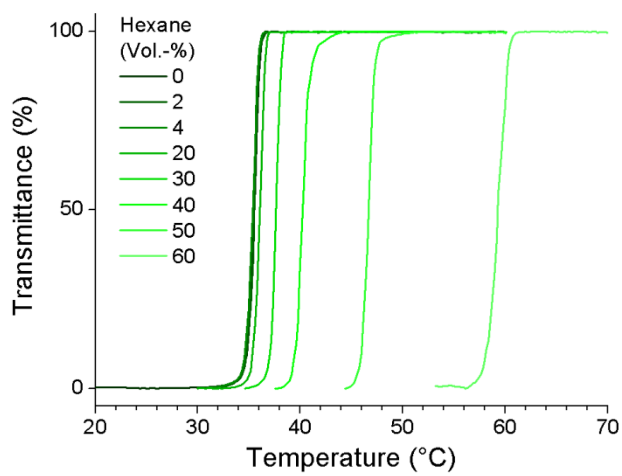

Figure S2. Transmittance versus temperature curves for 23.2 kg/mol POEGMA (1) in mixtures of isopropanol and hexane, depending on volume percentage of hexane. The temperatures of 50% transmittance are plotted in Figure 3 of the main article.

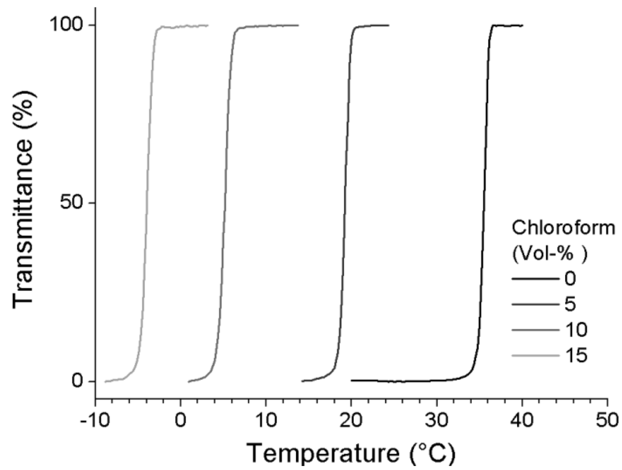

Figure S3. Transmittance versus temperature curves for 23.2 kg/mol POEGMA (**1**) in mixtures of isopropanol and chloroform, depending on volume percentage of chloroform. The temperatures of 50% transmittance are plotted in Figure 3 of the main article.

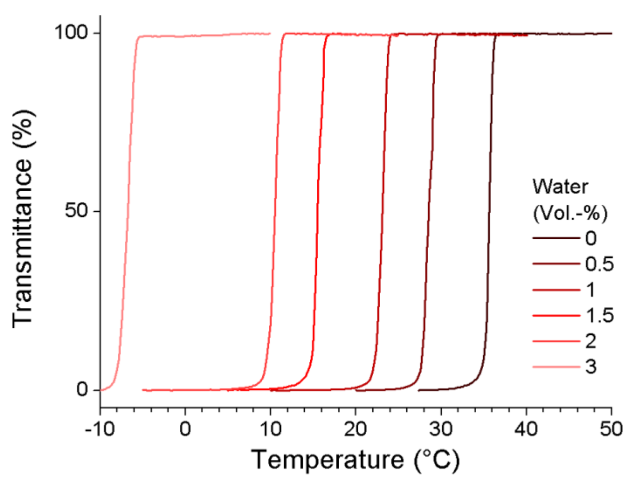

Figure S4. Transmittance versus temperature curves for 23.2 kg/mol POEGMA (**1**) in mixtures of isopropanol and water, depending on volume percentage of water. The temperatures of 50% transmittance are plotted in Figure 3 of the main article.

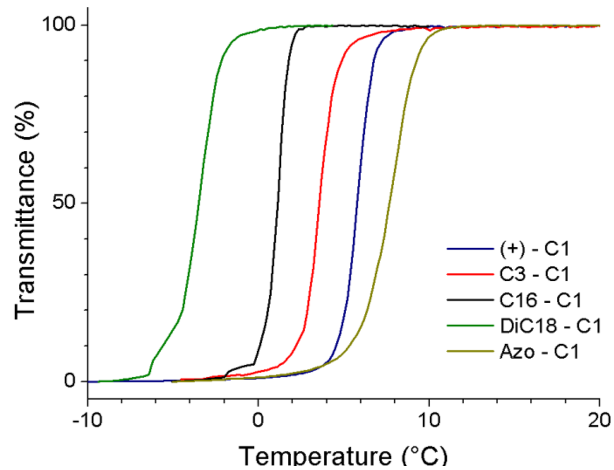

Figure S5. Transmittance versus Temperature curves for 5.4 kg/mol POEGMA (**2**) with one C1 end group and varying second end groups in 5 g/L isopropanol solutions. The temperatures of 50% transmittance are plotted in Figure 4a of the main article.

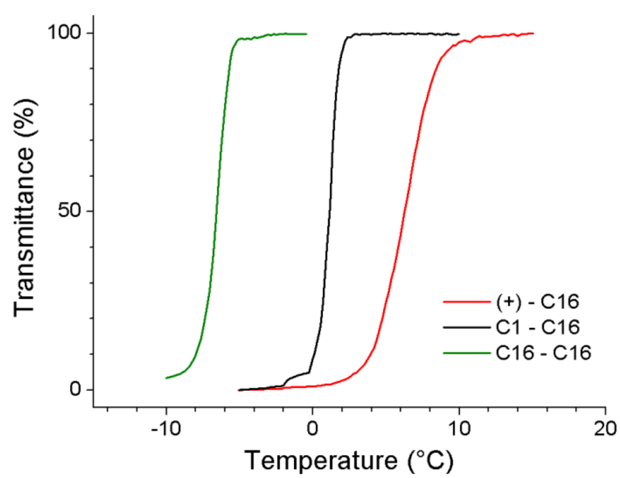

Figure S6. Transmittance versus Temperature curves for 5.4 kg/mol POEGMA (**2**) with one C16 end group and varying second end groups in 5 g/L isopropanol solutions. The temperatures of 50% transmittance are plotted in Figure 4b of the main article.

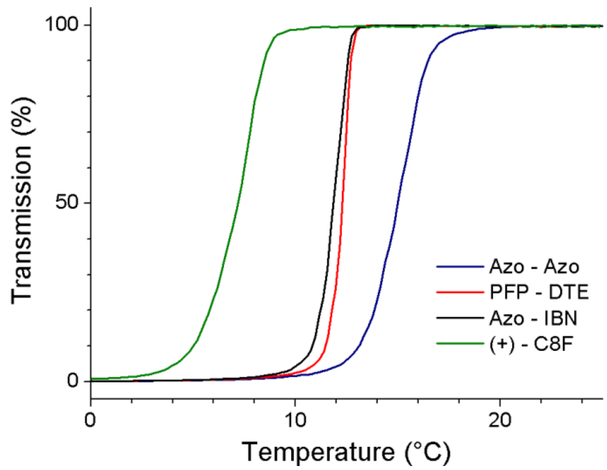

Figure S7. Transmittance versus Temperature curves for 5.4 kg/mol POEGMA (**2,3**) with remaining end group combinations.

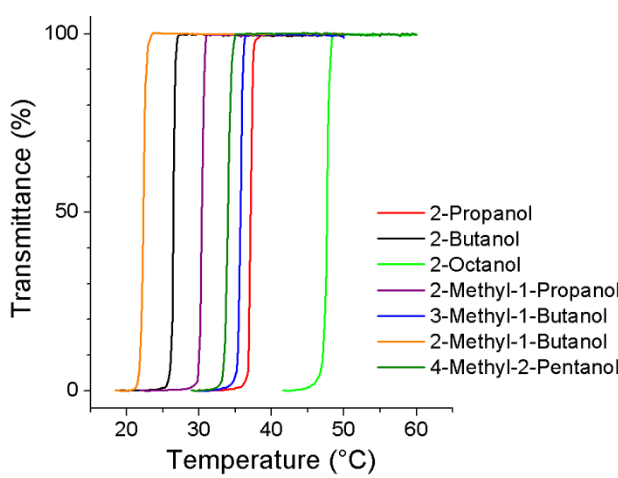

Figure S8. Transmittance versus Temperature curves for 23.2 kg/mol POEGMA (**1**) in various alcohols (other than 1-alkanols) at 16 g/L.

Table S1. List of Solvents and UCST of 23.2 kg/mol POEGMA (**1**) therein at 16 g/L.

Experiment No.	Solvent	UCST °C
45	Methanol	Soluble > -10°C
46	Ethanol	21.9
47	1-Propanol	29.1
48	1-Butanol	36.6
49	1-Pentanol	40.9
50	1-Hexanol	46.2
51	1-Heptanol	53.3
52	1-Dodecanol	75.4
53	2-Propanol	37.2
54	2-Butanol	26.4
55	2-Octanol	47.7
56	2-Methyl-1-propanol	30.4
57	3-Methyl-1-butanol	35.7
58	2-Methyl-1-butanol	22.2
59	4-Methyl-2-pentanol	34.0
60	2-Propen-1-ol	Soluble > -10°C
61	2-Propyn-1-ol	Soluble > -10°C
62	3-Butyn-1-ol	Soluble > -10°C
63	*tert*.-Butanol	Soluble > 25°C[1]
64	Trifluoroethanol	Soluble > -10°C
65	Benzyl alcohol	Soluble > -10°C
66	Acetone	Soluble > -10°C
67	Water	LCST at 62.9°C

[1] Melting point of *tert.*-butanol

The reversibility of the UCST-type transitions is demonstrated on two examples.

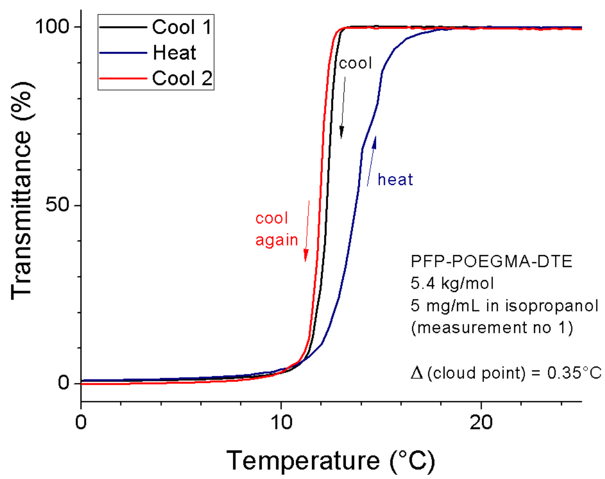

Figure S9. PFP-POEGMA-DTE (**1**) was cooled, heated and cooled again (rate 1°C/min) while the optical transmittance was recorded. A clear hysteresis upon heating can be seen. This is due to polymer aggregating and precipitating below the critical temperature. A re-dissolution by heating thus requires some additional time to completely dissolve the precipitate. Upon cooling the sample again, the first cloud point was reproduced.

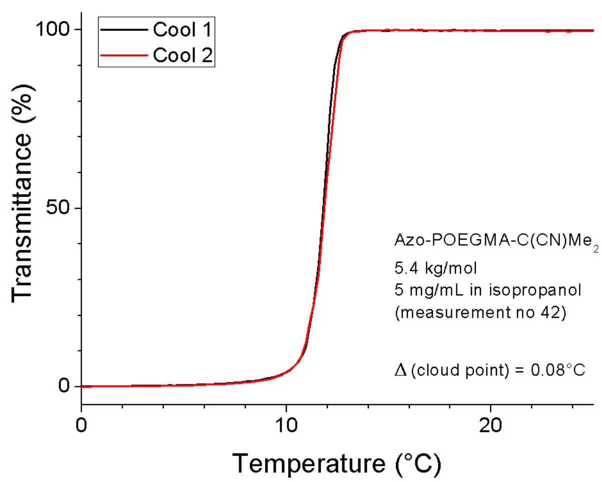

Figure S10. Cooling curves of polymer **3** (R^1 = azo) for two consecutive measurements. The cloud point was reproduced, showing the reversibility