Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Synthesis and solution behaviour of dual light- and temperature-responsive poly(triethylene glycol-*co*-spiropyran) copolymers and block copolymers

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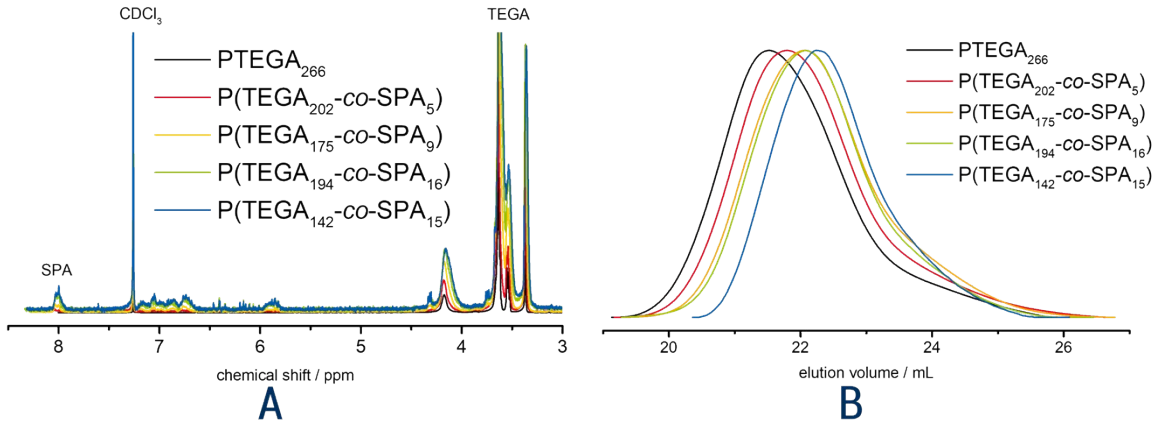

Figure S1: Characterisation of P(TEGA-co-SPA) copolymers: ^{1}H-NMR in $CDCl_3$ on a 300 MHz Bruker NMR spectrometer, chemical shift normalised to the solvent, and the intensity normalised to the TEGA signal at 3.3 ppm(A); SEC RI traces recorded on a triple detection SEC in THF (B).

Table S1: Summary of the prepared polymers, characterized by SEC, NMR and refractive index increment.

Composition	**x_{SPA} (Monomer)**	**M_n[b] / g mol^{-1}**	**$Đ$[b]**	**Polymer[a]**	**dn/dc / mL g^{-1}**
$PTEGA_{266}$	0 %	58,000	1.42	0 % SPA	0.0588±0.0019
$P(TEGA_{202}$-co-$SPA_5)$	5 %	46,000	1.34	4 % SPA	0.0704±0.0010
$P(TEGA_{175}$-co-$SPA_9)$	10 %	42,000	1.26	9 % SPA	0.0832±0.0028
$P(TEGA_{194}$-co-$SPA_{16})$	15 %	49,000	1.22	13.5 % SPA	0.0951±0.0015
$P(TEGA_{142}$-co-$SPA_{15})$	20 %	37,000	1.34	16 % SPA	0.1158±0.0037
a) 300 MHz ^{1}H-NMR in $CDCl_3$, b) THF-SEC, MALLS-Triple detection.					

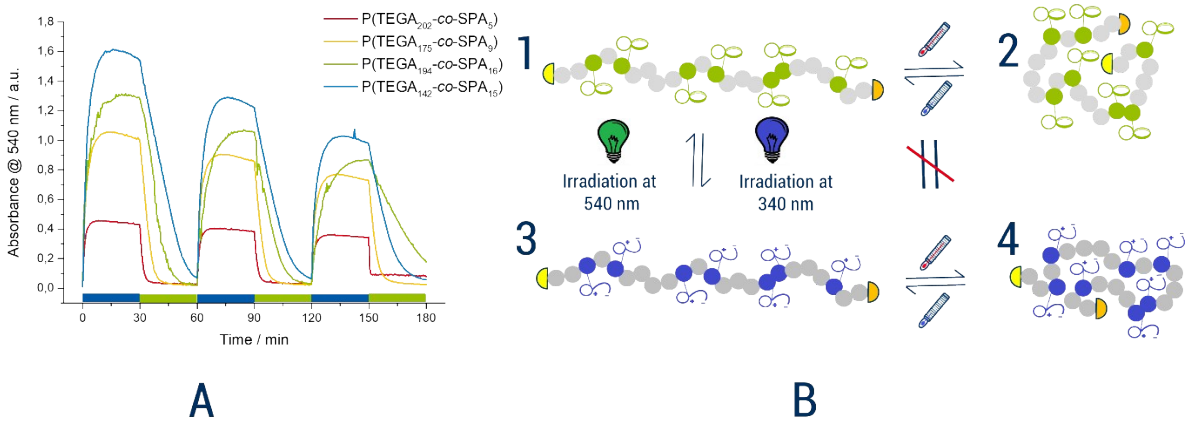

Figure S2: Three consecutive irradiation cycles consisting of 30 min of irradiation at 340 nm, followed by 30 min of irradiation at 540 nm. The respective amount of copolymer was dissolved in a pH 8 TRIS-buffer solution at 0.125 mg mL^{-1}. Coloured lines indicate the irradiation pattern (A). Schematic depiction of the behaviour of the P(TEGA-co-SPA) copolymers upon heating and irradiation. The copolymer is dissolved in the SP form (1), and upon heating becomes insoluble (2). In addition, the SPA-moiety can be switched by UV-light into the MC form (3); the MC form can also be switched from soluble to insoluble (4) upon heating (B).

Kinetics of the photo-response

The following formula was used to calculate the reaction kinetics:

$$[y] = [y_0] + Ae^{-kt}$$

All irradiation traces were fitted using this formula, and the required parameters are listed in Table S2, and shown graphically in Figure S3.

Table S2: Kinetics of the photo-response fitted by first order kinetics. Separated for irradiation with 340 nm (UV) and 540 nm (green) light.

Copolymer	$[y_0]_{(UV)}$	A(UV)	k(UV)	$[y_0]_{(green)}$	A(green)	k(green)
P(TEGA$_{202}$-*co*-SPA$_5$)	0.39786	-0.36512	-0.86288	0.05101	0.33641	-0.68377
P(TEGA$_{175}$-*co*-SPA$_9$)	0.89253	-0.8374	-0.51389	0.01824	0.89359	-0.28122
P(TEGA$_{194}$-*co*-SPA$_{16}$)	1.07936	-0.94828	-0.21033	-0.23604	1.36866	-0.07442
P(TEGA$_{142}$-*co*-SPA$_{15}$)	1.29076	-1.21699	-0.38624	-0.38272	1.66462	-0.06432

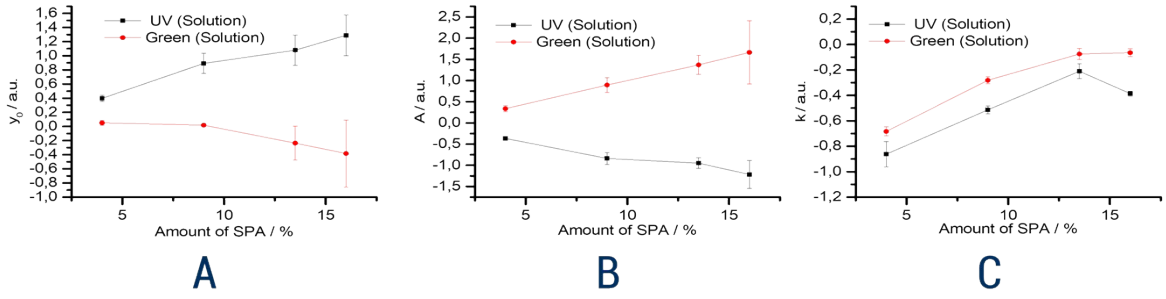

Figure S3: Plot of the first order kinetic parameters (A) y_0, (B) A, and (C) k, related to the plot equation.

Temperature-response of the copolymer

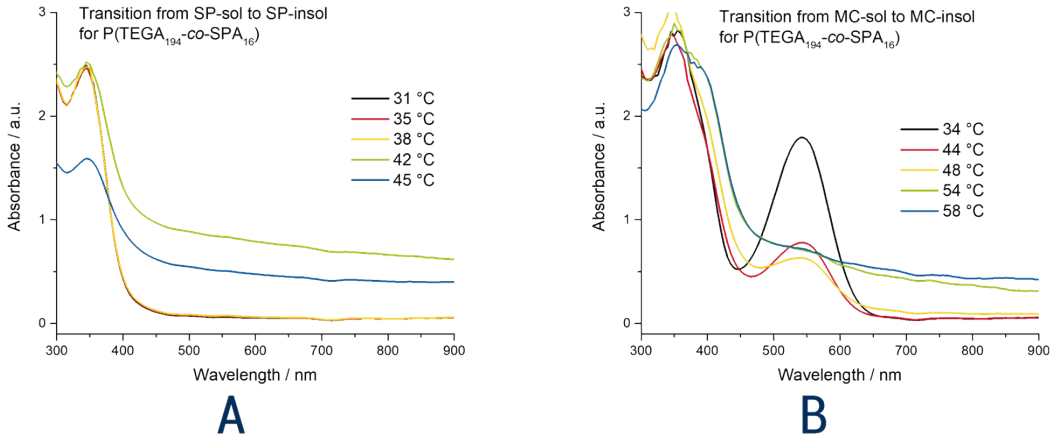

Figure S4: UV-Vis spectra of P(TEGA$_{194}$-co-SPA$_{15}$) upon heating above the transition temperature from a soluble to insoluble state. The SP form is obtained by irradiation with a 540 nm light (A), and the MC form is obtained upon irradiation at 340 nm (B).

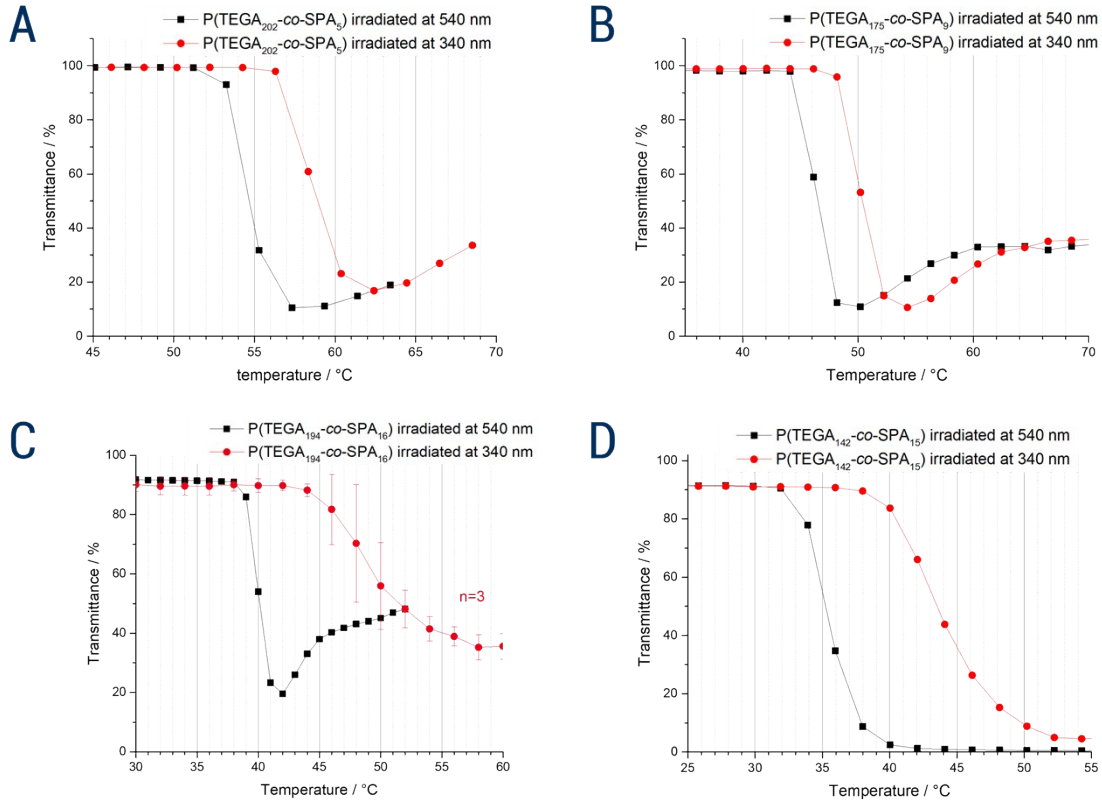

Figure S5: Transmittance of the dissolved copolymers in a pH 8 TRIS buffer at 700 nm at different temperatures while irradiating with a 200 W Hg(Xe)-lamp using different wavelength filters.

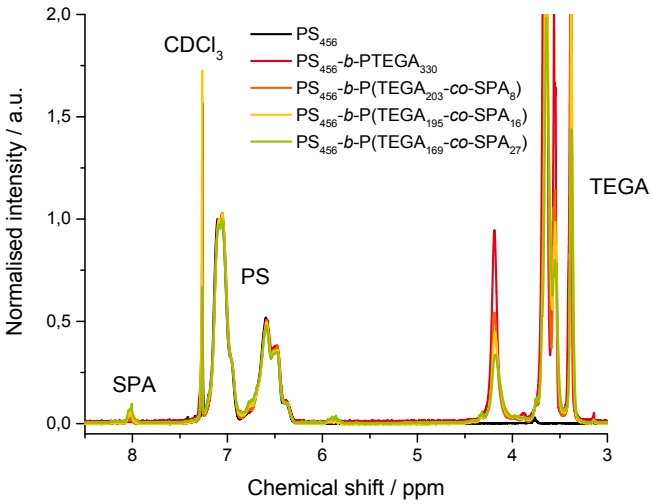

Figure S6: ^{1}H-NMR spectra of the diblock terpolymers in $CDCl_3$; the signal at 8 ppm indicates the presence of SPA, the signal from 7.3 to 6 ppm indicates the presence of polystyrene, and the signal at 3.3 ppm indicates the presence of TEGA moieties.

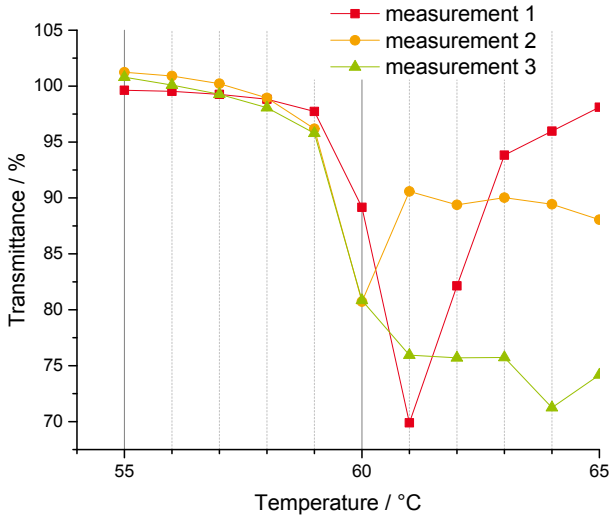

Figure S7: Transmittance at 700 nm of PS_{456}-b-$PTEGA_{330}$ micelles in a pH 8 TRIS buffer measured three times to determine the cloud point.

*Table S3: The transition temperature plotted over the amount of SPA in the copolymer, as well as for the terpolymer using the equation y = m * x + b.*

	Irradiation Wavelength / nm	b	m	R^2
Copolymer	540	64.16 ± 0.96	-1.22 ± 0.09	0.9771
	340	63.32 ± 1.30	-1.78 ± 0.13	0.9802
Diblock Terpolymer	540	60.33	-1.36	-
	340	60.33	-2.02	-