Electronic Supplementary Material (ESI) for Polymer Chemistry.

From nanospheres to micelles: simple control of PCL-*g*-PEG copolymers amphiphilicity through thiol-yne photografting.

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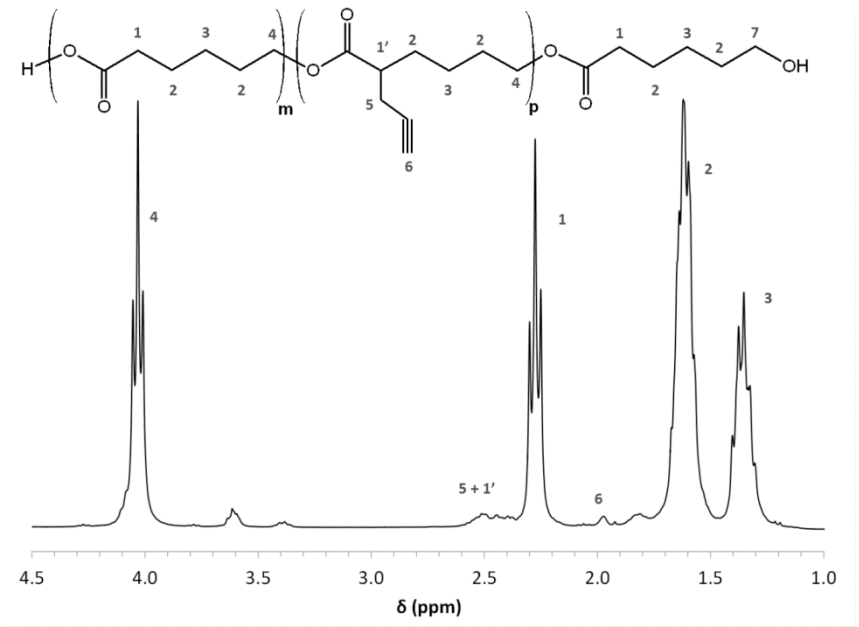

Figure S1. ^{1}H NMR (300MHz, $CDCl_3$) spectrum of propargylated PCL (PCL-yne).

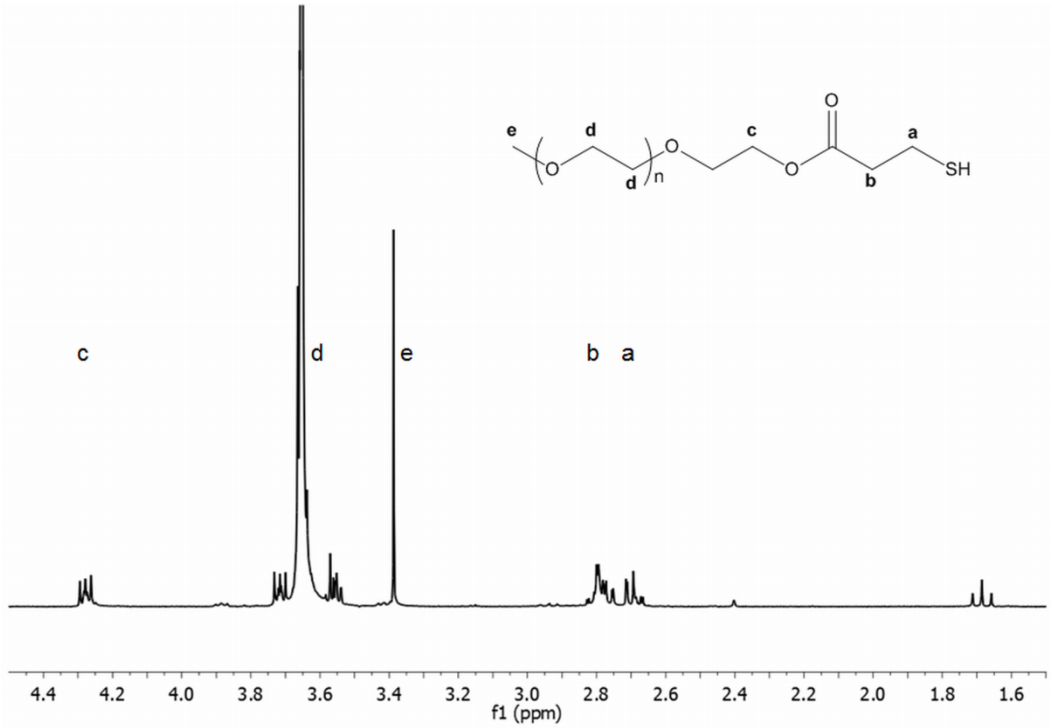

Figure S2. ^{1}H NMR (300MHz, $CDCl_3$) spectrum of thiolated-PEG (PEG-SH).

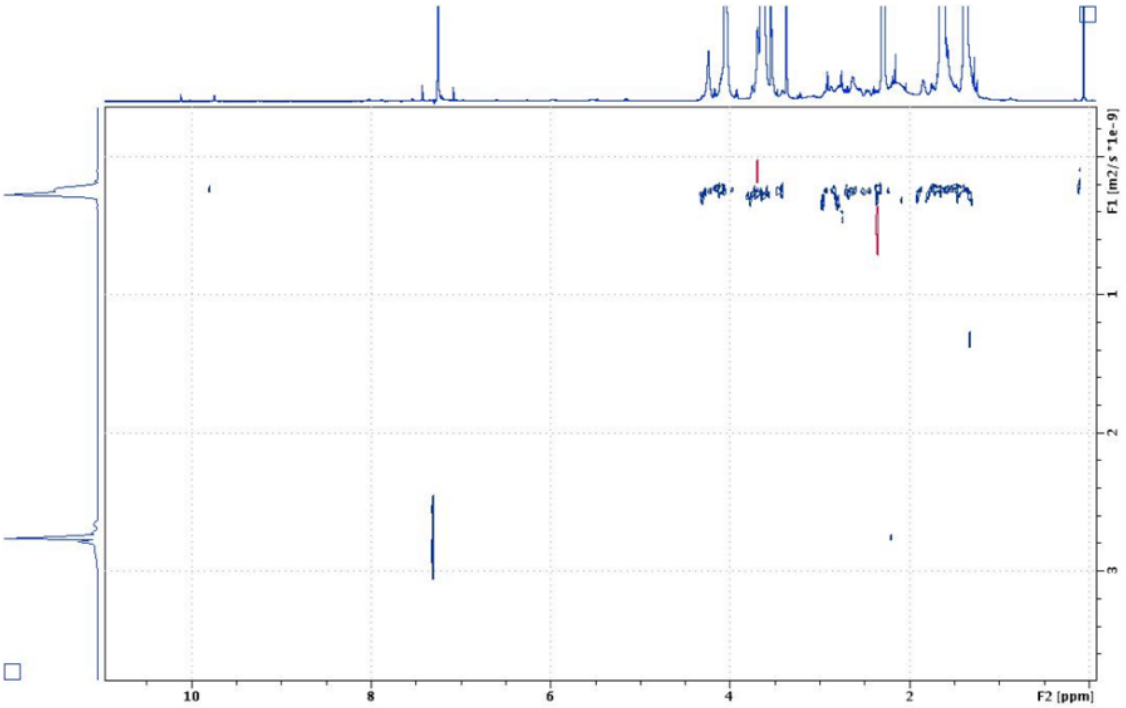

Figure S3. DOSY NMR spectrum of PCL-*g*-$PEG_{1.15}$ in DMSO-d6.

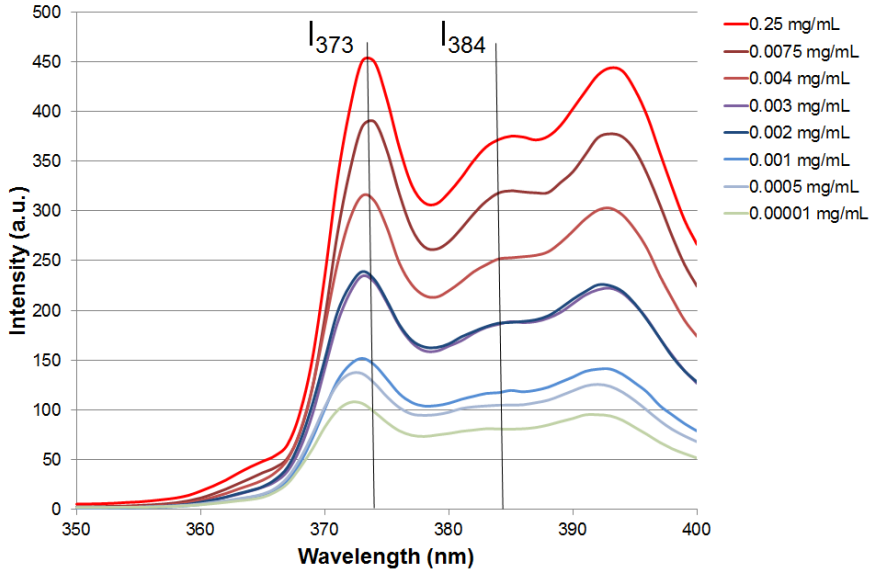

Figure S4. Emission spectra at λex = 340 nm of pyrene in aqueous solutions of various concentrations of PCL-*g*-$PEG_{1.15}$.

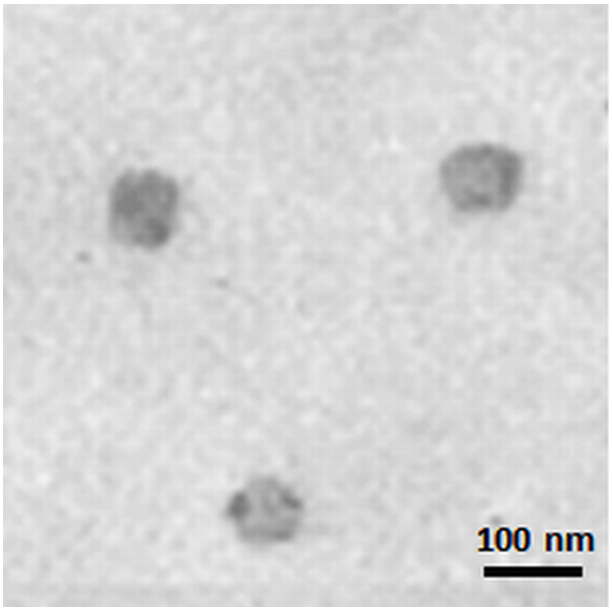

Figure S5. TEM picture of curcumin loaded PCL-g-$PEG_{1.15}$ micelles.

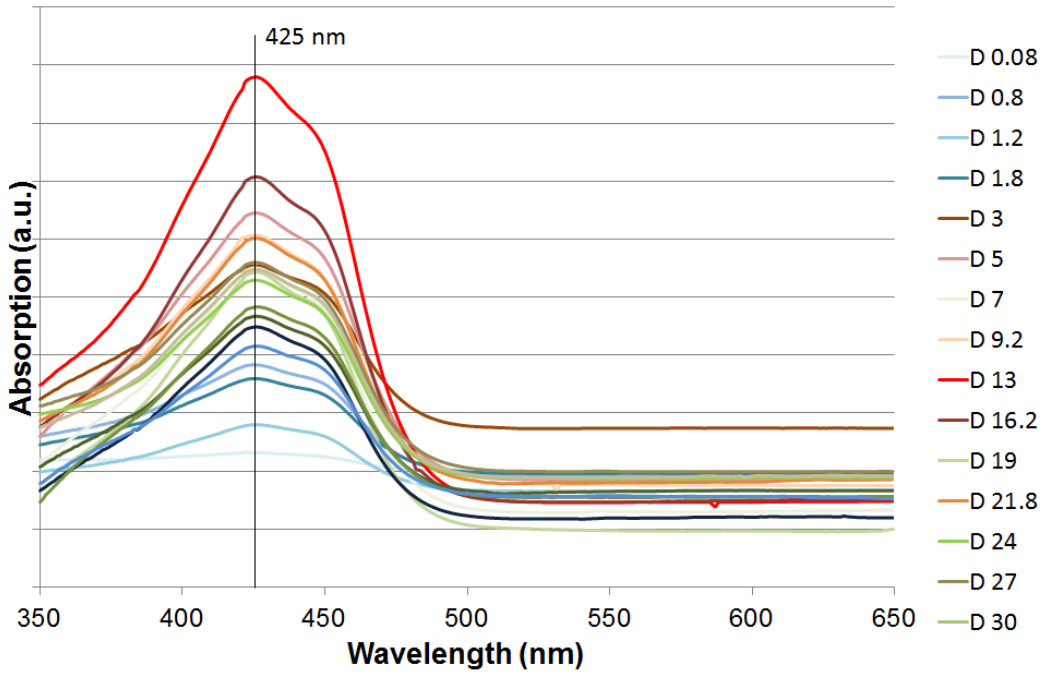

Figure S6. Typical UV-visible spectra of curcumin in the release medium as a function of the time (D corresponds to days)

Table S1. Thiol-yne coupling of benzyl mercaptan on PCL-yne (7% alkyne groups) in THF, UV activation, 2h, RT, photoinitiator DMPA (0.5 eq).

Entry	Benzyl mercaptan	number of BM groups grafted per alkyne	Special conditions	Mn	(Đ)
1	20 eq.	1.5	/	18000	2.6
2	10 eq.	1.5	/	24000	3.5
3	5 eq.	1.3	/	29000	3.8
4	10 eq.	1.5	Quartz cuvette	19000	5.1
5	10 eq.	1.5	successive addition of DMPA & SH	15000	2.0
6	10 eq.	1.5	successive addition of PCL & DMPA	22000	2.8

Table S2. Comparison of encapsulation efficiencies and drug loadings for various PCL/PEG macromolecular architectures

Entry	Type of copolymer	MW PCL (kg/mol)	MW PEG (kg/mol)	Curcumin/ polymer (wt:wt)	EE (wt%)	DL (wt%)	Ref
1	PCL-*g*-$PEG_{1.15}$	22	0.75	1 : 7	92	12.1	this work
2	PCL-*b*-$PEG_{1.3}$*	4.8	2.4	1 : 7	53	6.6	[1]
3	PCL-*b*-PEG-*b*-$PCL_{1.2}$	5	6	1 : 7	77	9.6	[2]

* PCL-b-$PEG_{1.3}$ with linolenic PEG chain-end moeity.

[1] Z. Song, W. Zhu, N. Liu, F. Yang, R. Feng, Linolenic acid-modified PEG-PCL micelles for curcumin delivery, Int J Pharm, 471 (2014) 312–321

[2] R.L. Feng, Z.M. Song, G.X. Zhai, Preparation and in vivo pharmacokinetics of curcumin-loaded PCL-PEG-PCL triblock copolymeric nanoparticles, Int J Nanomed, 7 (2012) 4089-4098.