Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Modular Ambient Temperature Functionalization of Carbon Nanotubes with Stimuli-Responsive Polymer Strands

Nicolas Zydziak,[a,b] *Christof Hübner,*[b] *Michael Bruns,*[c] *Andrew P. Vogt,*[a]

*Christopher Barner-Kowollik**[a]

[a] *Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany. Email: christopher.barner-kowollik@kit.edu, http://www.macroarc.de*

[b] *Polymer Engineering, Fraunhofer Institut für Chemische Technologie, Josef-von-Fraunhoferstr. 7, 76327 Pfinztal (Berghausen), Germany.*

[c] *Institute for Applied Materials (IAM-ESS) and Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

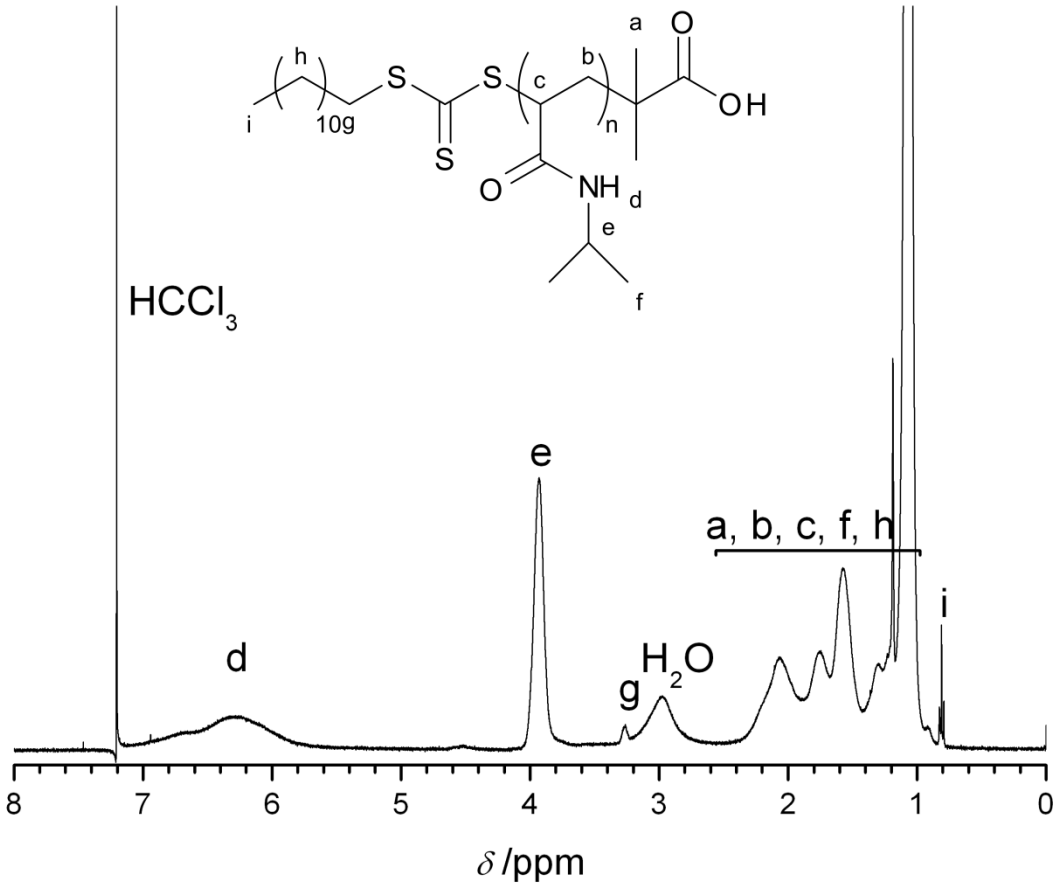

Figure ESI 1 ^{1}H-NMR overview spectrum of PNIPAM **P4**

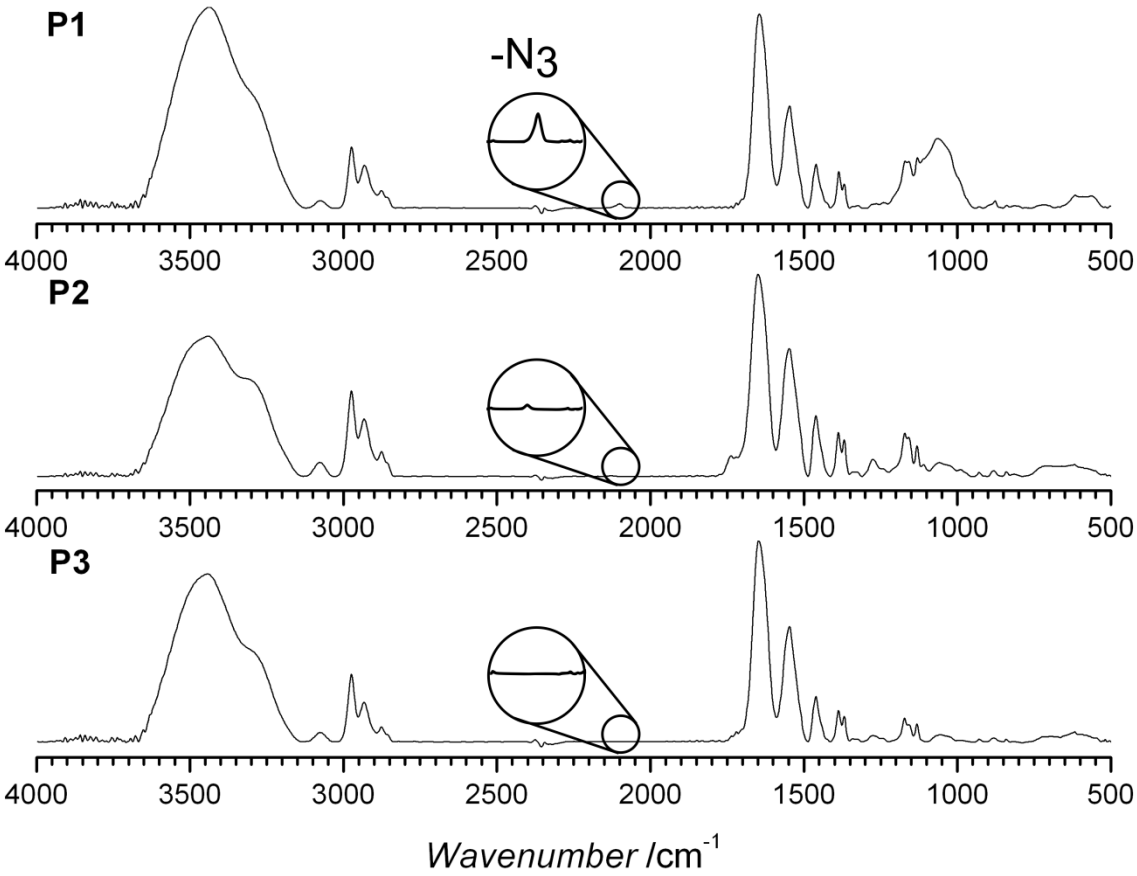

Figure ESI 2 FTIR spectra of PNIPAM with different end-group (azide, **P1**), (bromine, **P2**), and (Cp, **P3**) in KBr pellets with recognizable azide peak for **P1** at 2096 cm^{-1} (zoomed part of the spectra).

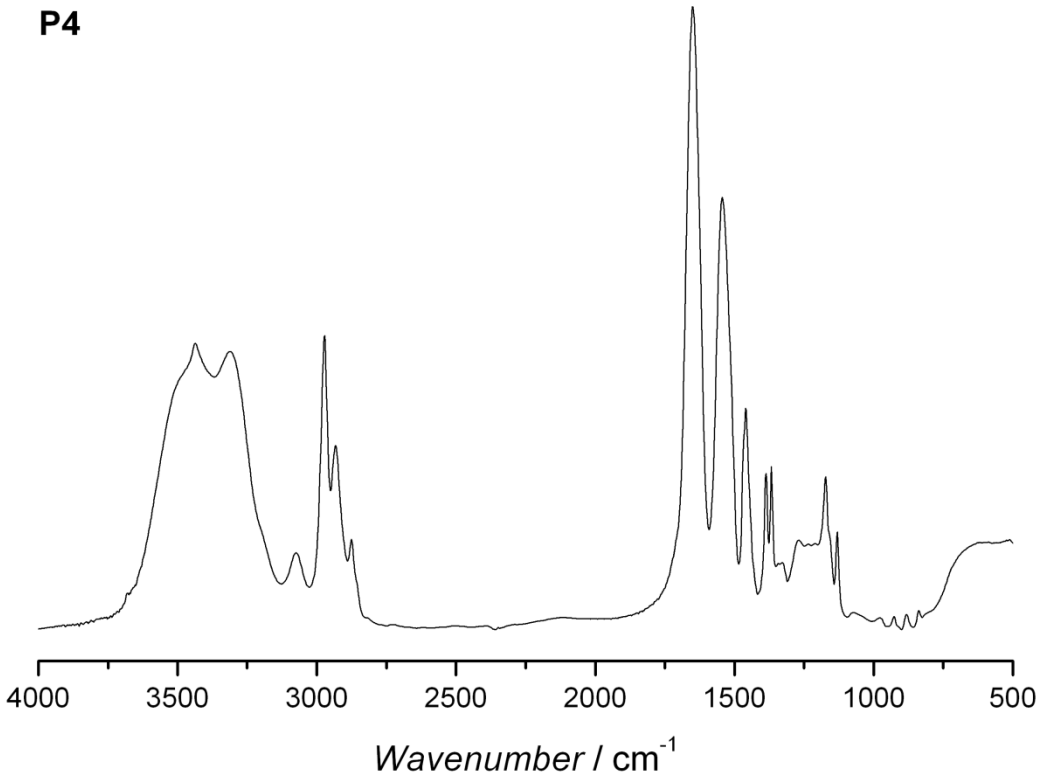

Figure ESI 3 FTIR spectra of PNIPAM with acidic end-group (**P4**) in KBr pellets.

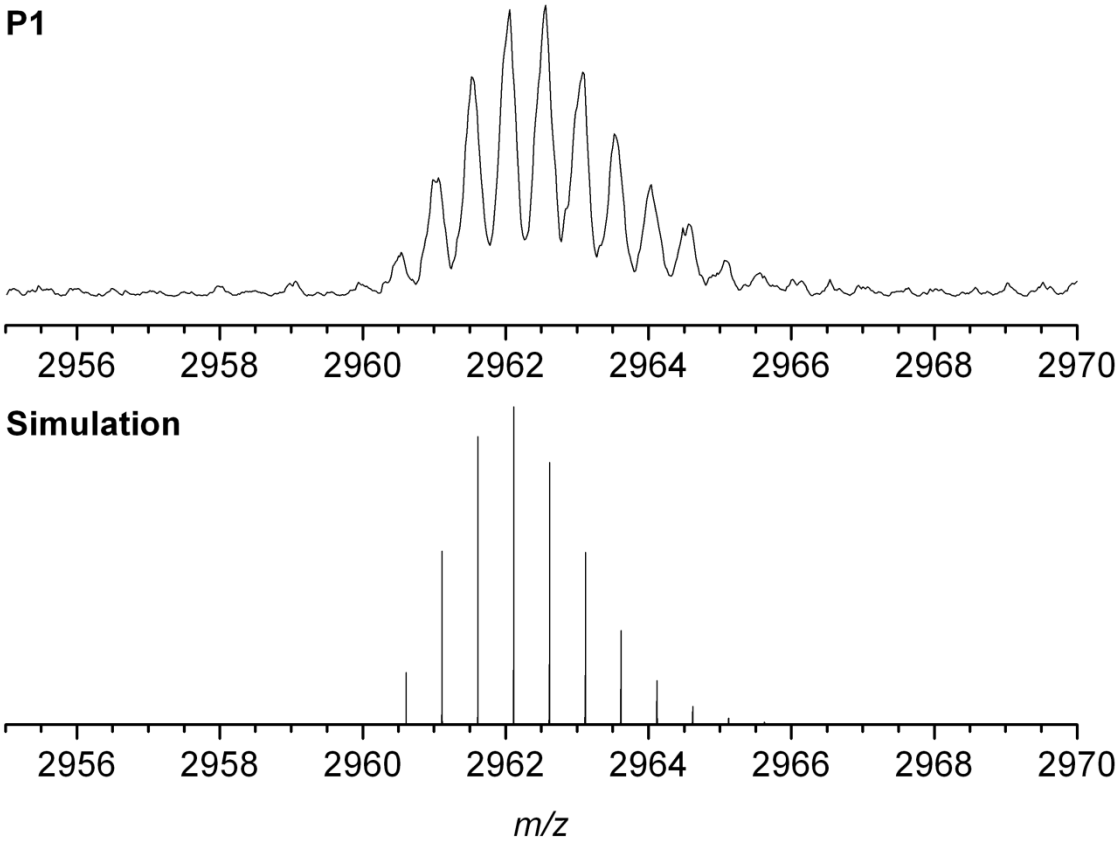

Figure ESI 4 ESI-MS isotopic pattern of doubly charged PNIPAM with an azide end-group (**P1**, top) and the respective simulated isotopic pattern (bottom). The spectrum is recorded via direct infusion.

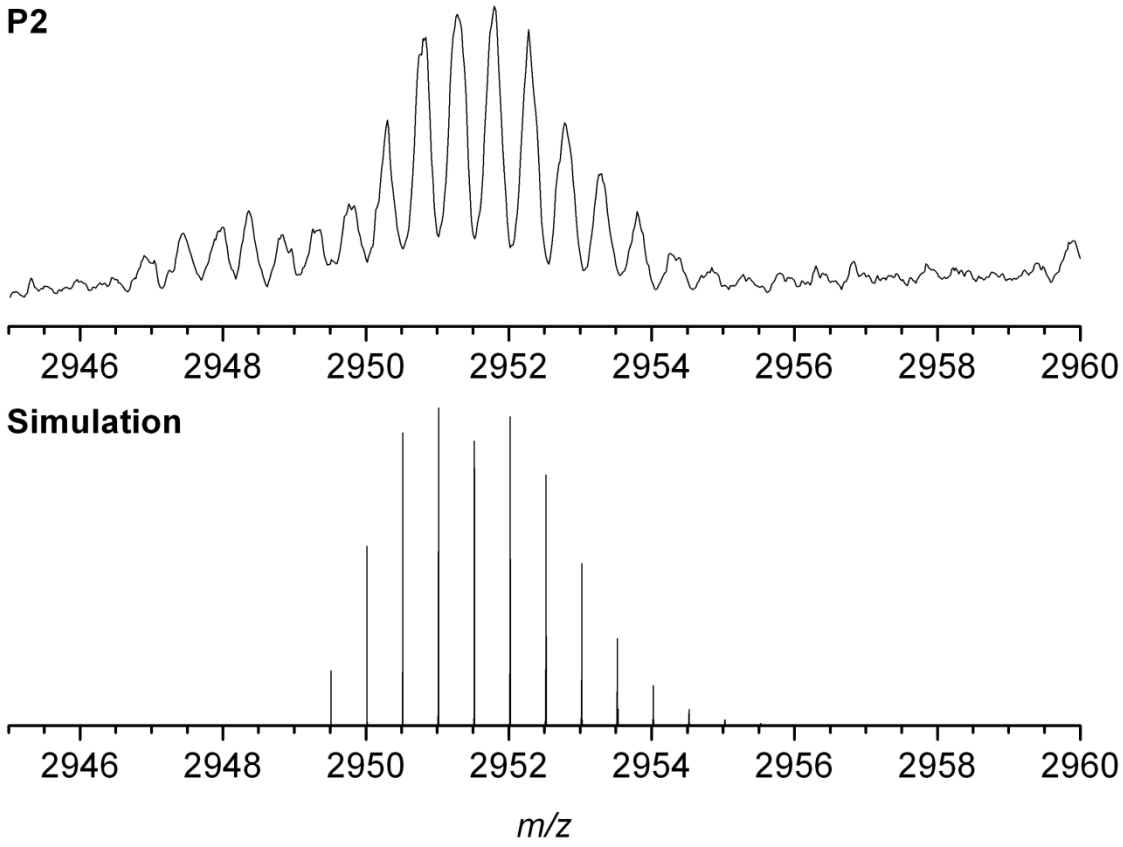

Figure ESI 5 ESI-MS MS isotopic pattern of doubly charged PNIPAM with bromine end-group (**P2**, top) and the respective simulated isotopic pattern (bottom). The spectrum is recorded via direct infusion.

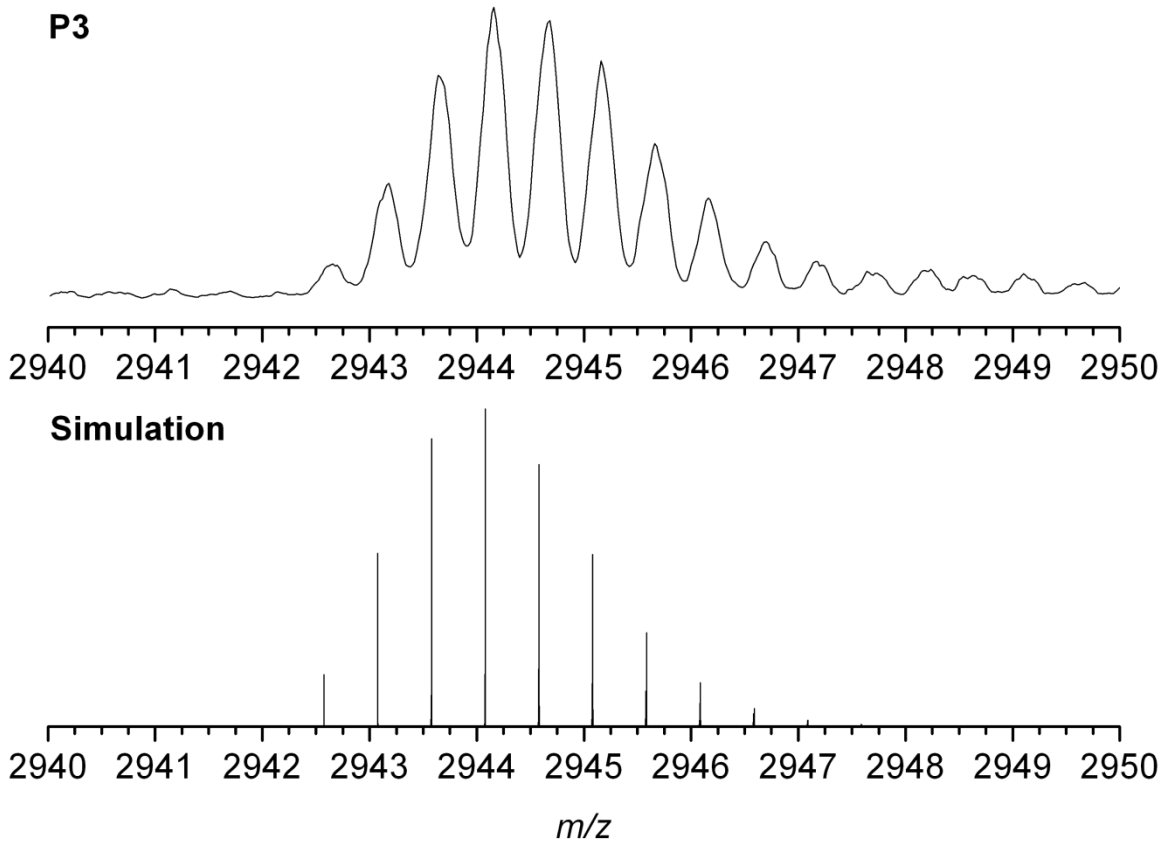

Figure ESI 6 ESI-MS isotopic pattern of doubly charged PNIPAM with bromine end-group (**P3**, top) and the respective simulated isotopic pattern (bottom). The spectrum is recorded via direct infusion.

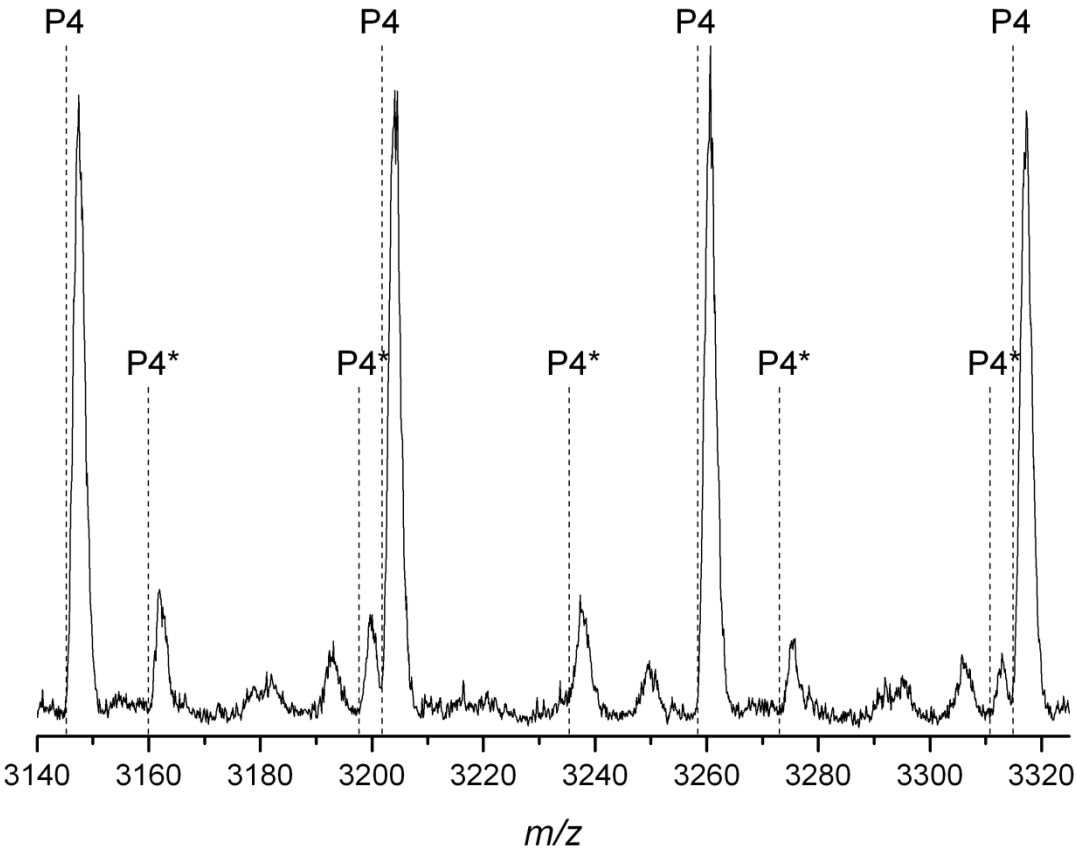

Figure ESI 7 ESI-MS spectra of doubly (denoted **P4**) and triple (denoted **P4***) charged PNIPAM with acidic end-group (**P4**). The spectrum is recorded via direct infusion.

Table 1 Summary of ESI-MS data for PNIPAM with acidic end-group (**P4**). The spectra were recorded via direct infusion.

Species	n [a]	Fomula	*m/z*		
			theoretical	experimental	*Δ*
P4	52	$[C_{329}H_{604}N_{52}O_{54}S_3Na_2]^{2+}$	3145.25	3144.82	0.43
	53	$[C_{335}H_{615}N_{53}O_{55}S_3Na_2]^{2+}$	3201.80	3201.73	0.07
	54	$[C_{341}H_{626}N_{54}O_{56}S_3Na_2]^{2+}$	3258.34	3258.18	0.16
	55	$[C_{347}H_{637}N_{55}O_{57}S_3Na_2]^{2+}$	3314.88	3314.45	0.43
P4*	80	$[C_{497}H_{912}N_{80}O_{82}S_3Na_3]^{3+}$	3159.95	3160.45	0.50
	81	$[C_{503}H_{923}N_{81}O_{83}S_3Na_3]^{3+}$	3197.64	3197.81	0.17
	82	$[C_{509}H_{934}N_{82}O_{84}S_3Na_3]^{3+}$	3235.34	3235.73	0.39
	83	$[C_{515}H_{945}N_{83}O_{85}S_3Na_3]^{3+}$	3273.03	3273.45	0.42
	84	$[C_{521}H_{956}N_{84}O_{86}S_3Na_3]^{3+}$	3310.73	3310.36	0.37

[a] **n**: number of monomer units

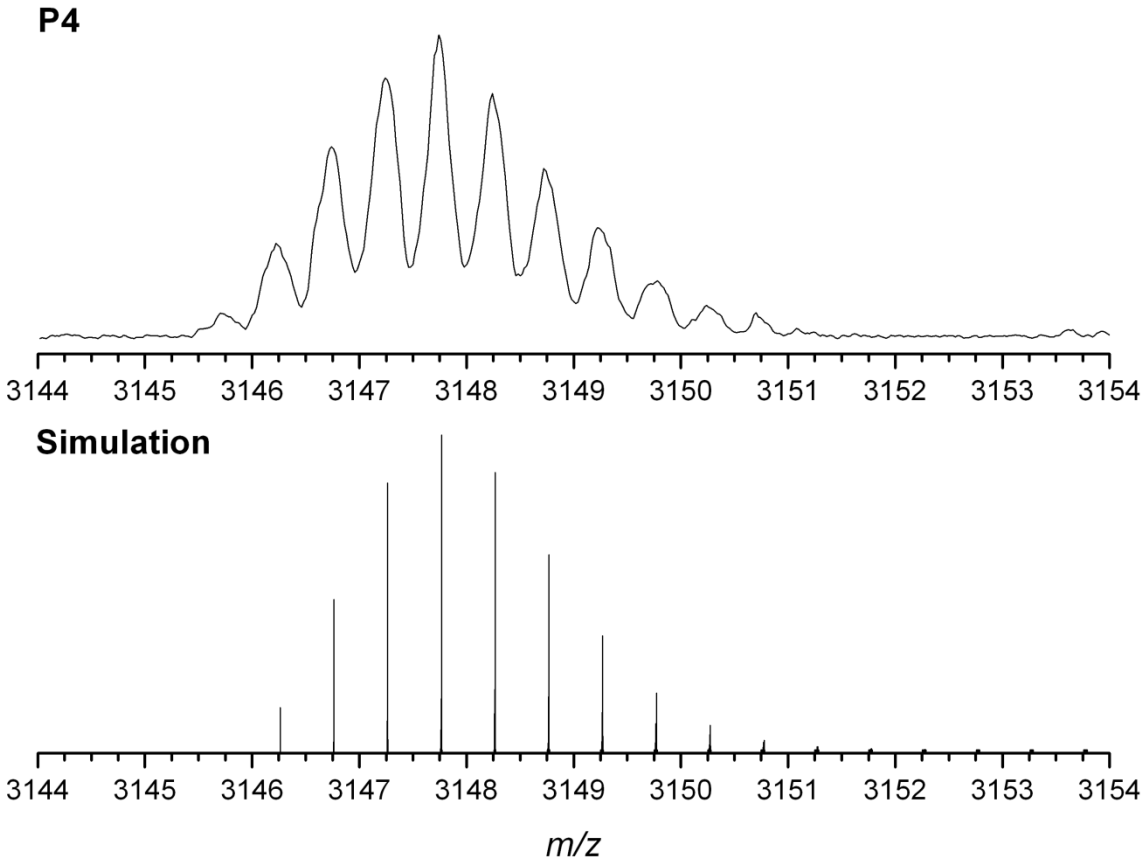

Figure ESI 8 ESI-MS isotopic pattern of doubly charged PNIPAM with acidic end-group (**P4**, top), and the respective simulated isotopic pattern (bottom). The spectrum is recorded via direct infusion.

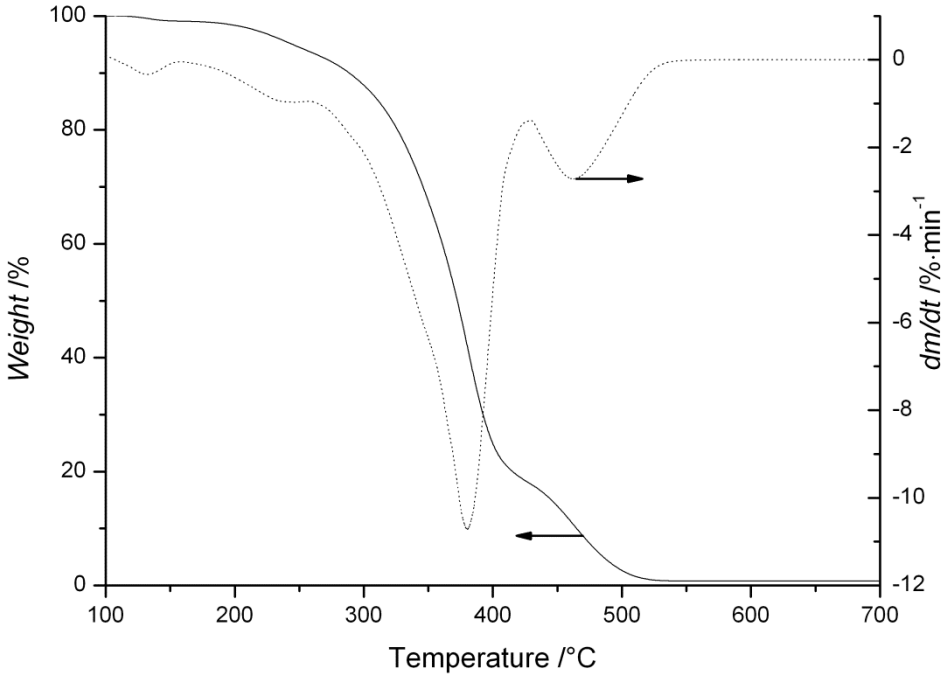

Figure ESI 9 Thermogravimetric profile and its derivative of PNIPAM with bromine endgroup (**P2**) with recognizable subsidiary degradation at 130 °C due to bromine elimination. Sample measured under ambient atmosphere with a heat flow of 10 °C·min^{-1}, with a preliminary isothermal step at 100 °C for 30 minutes.

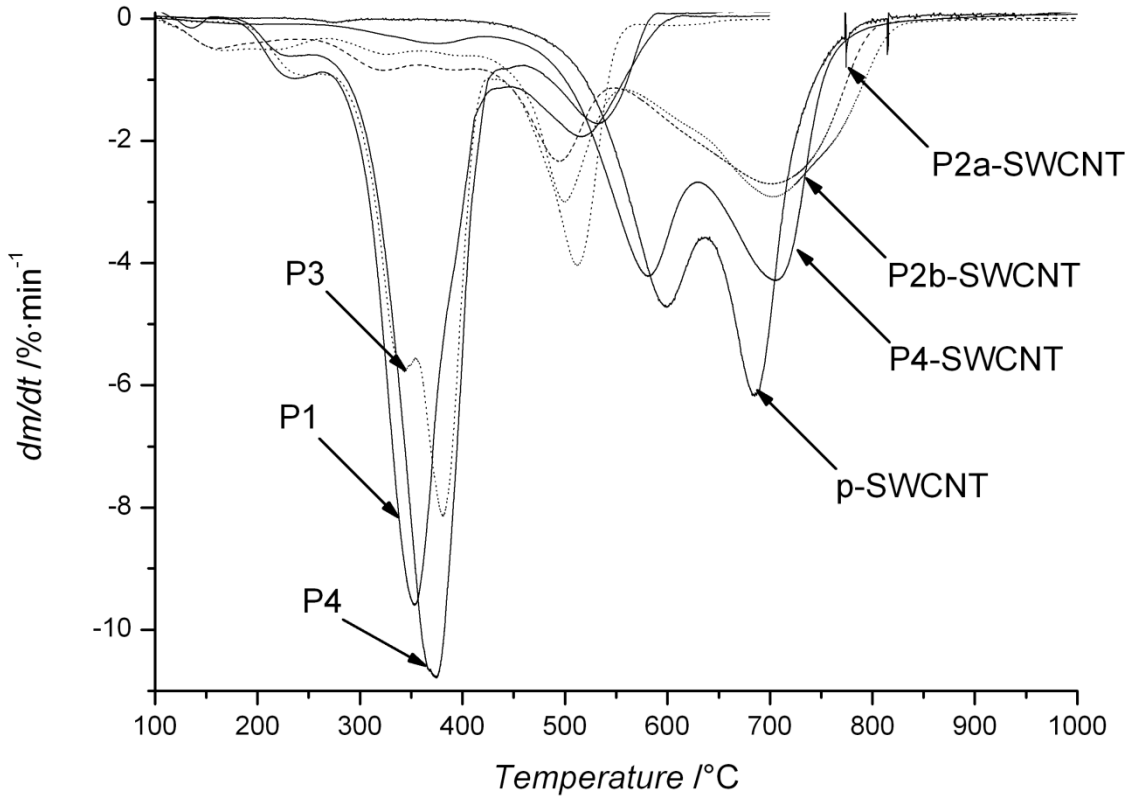

Figure ESI 10 Derivatives of thermogravimetric profiles of PNIPAM with different end-group (azide, **P1**), (Cp, **P3**) and (acid, **P4**), and pristine SWCNTs (**p-SWCNT**), functionalized with **P3** at ambient temperature (**P3a-SWCNT**), at 80 °C (**P3b-SWCNT**), and mixed with PNIPAM with acidic end-group (**P4-SWCNT**). All samples measured under ambient atmosphere with a heat flow of 10 °C·min^{-1}, with a preliminary isothermal step at 100 °C for 30 minutes.

Table ESI 2 Summary of thermogravimetric analysis of PNIPAM with different end-group (azide, **P1**), (bromine, **P2**), (Cp, **P3**) and with acidic end-group (**P4**).

Sample	T_i [a] /°C	T_f [b] /°C	T_m [c] /°C	*wt. %* at T_f	Sample	T_i [a] /°C	T_f [b] /°C	T_m [c] /°C	*wt. %* at T_f
P1	150	265	235	94.7	P3	170	270	245	94.3
	265	440	350	22.2		270	355	345	67.2
	440	620	520	2.7		355	425	380	31.6
P2	100	160	130	99.1		425	580	510	4.1
	160	260	240	93.5	P4	170	270	235	95.9
	260	430	380	17.8		270	435	375	17.3
	430	550	460	0.8		435	590	540	1.3

[a] $\boldsymbol{T_i}$: Initial temperature for degradation. [b] $\boldsymbol{T_f}$: Final temperature for degradation. [c] $\boldsymbol{T_m}$: Temperature of maximal weight loss (from first derivative). All samples measured under air atmosphere with a heat flow of 10 °C·min^{-1}, with a preliminary isothermal step at 100 °C for 30 minutes.

Table ESI 3 Summary of thermogravimetric analysis for pristine SWCNTs (**p-SWCNT**), SWCNTs functionalized with **P3** at ambient temperature (**P3a-SWCNT**), at 80 °C (**P3b-SWCNT**), and SWCNTs mixed with PNIPAM with acidic end-group (**P4-SWCNT**).

Sample	T_i [a] /°C	T_f [b] /°C	T_m [c] /°C	*wt. %* at T_f
p-SWCNT	430	640	600	57.2
	640	810	685	13.8
P3a-SWCNT	100	240	160	95.4
	240	355	320	88.3
	355	410	390	83.9
	410	545	495	63.6
	545	815	700	13.8
P3b-SWCNT	100	190	170	97.0
	190	270	220	93.5
	270	360	325	89.1
	360	410	395	86.2
	410	560	500	62.6
	560	850	700	12.6
P4-SWCNT	100	240	200	99.2
	240	420	375	94.6
	420	635	580	51.6
	635	810	705	10.7

[a] T_i: Initial temperature for degradation. [b] T_f: Final temperature for degradation. [c] T_m: Temperature of maximal weight loss (from first derivative). All samples measured under air atmosphere with a heat flow of 10 °C·min^{-1}, with a preliminary isothermal step at 100 °C for 30 minutes.

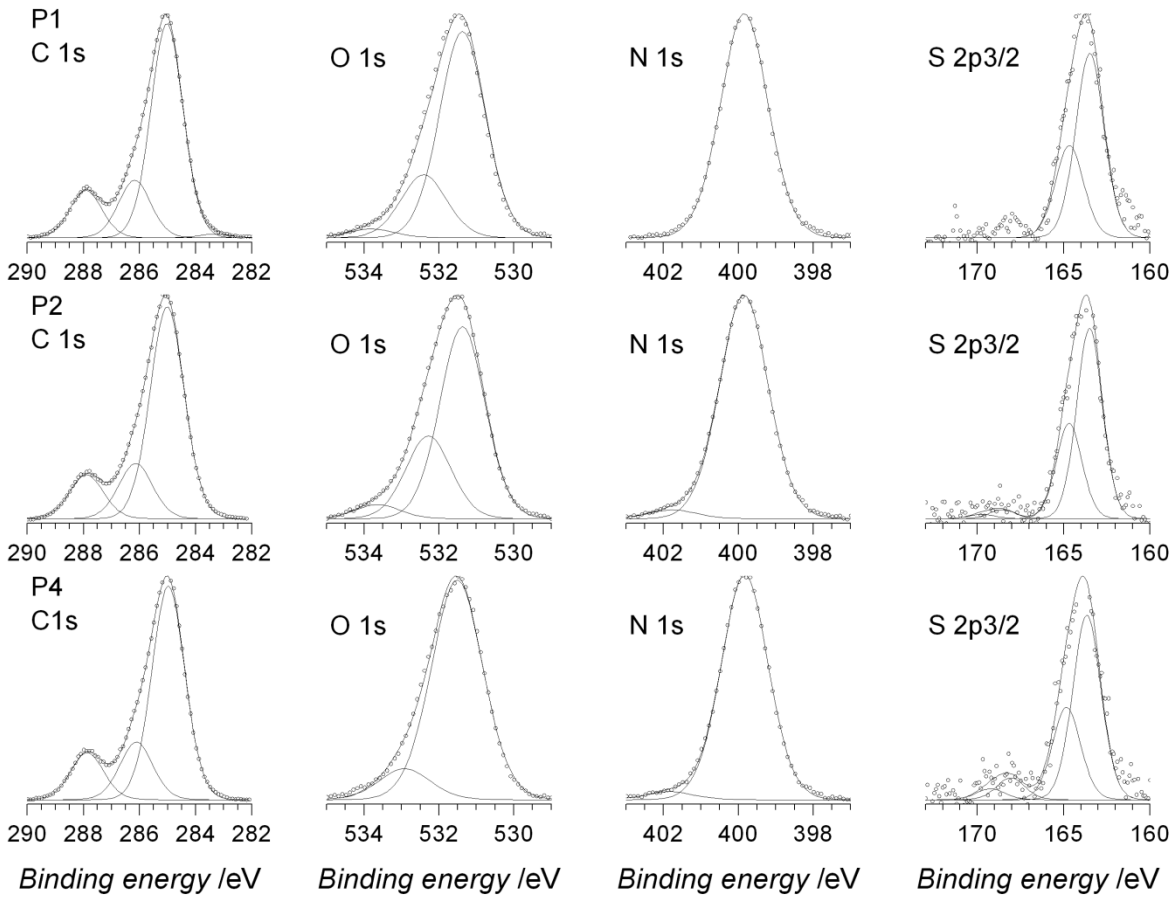

Figure ESI 11 XPS spectra of PNIPAM with different end-groups (azide, **P1**, top), (bromine, **P2**, middle) and with acidic end-group (**P4**, bottom) for each characteristic atom (carbon, oxygen, nitrogen and sulfur). All spectra referenced at 285.0 eV for C-C sp^2.

Table ESI 4 Assignment of binding energy and comparison of the bond contribution after the deconvolution of the XPS spectra of PNIPAM with different end-groups (azide, **P1**), (bromine, **P2**) and with acidic end-group (**P4**) for each characteristic atom (carbon, oxygen, nitrogen and sulfur). All spectra are referenced at 285.0 eV.

Atom	Binding energy /eV	*at.-%*			Entity
		P1	P2	P4	
S 2p3	163.5	0.51	0.45	0.38	S-C
	168.5	-	0.02	0.1	S=C
C 1s	285.0	49.3	51.9	49.7	CH_2, CH_3 sp^3
	286.1	13.3	13.5	14.0	C-N, C-O
	287.9	10.9	10.8	11.7	C=O
N 1s	399.8	10.2	10.1	10.9	N-C
	401.9	-	0.4	0.3	N^+-H
O 1s	531.4	12.9	12.1	11.3	O-C
	533.3	0.4	0.6	0.9	O=C

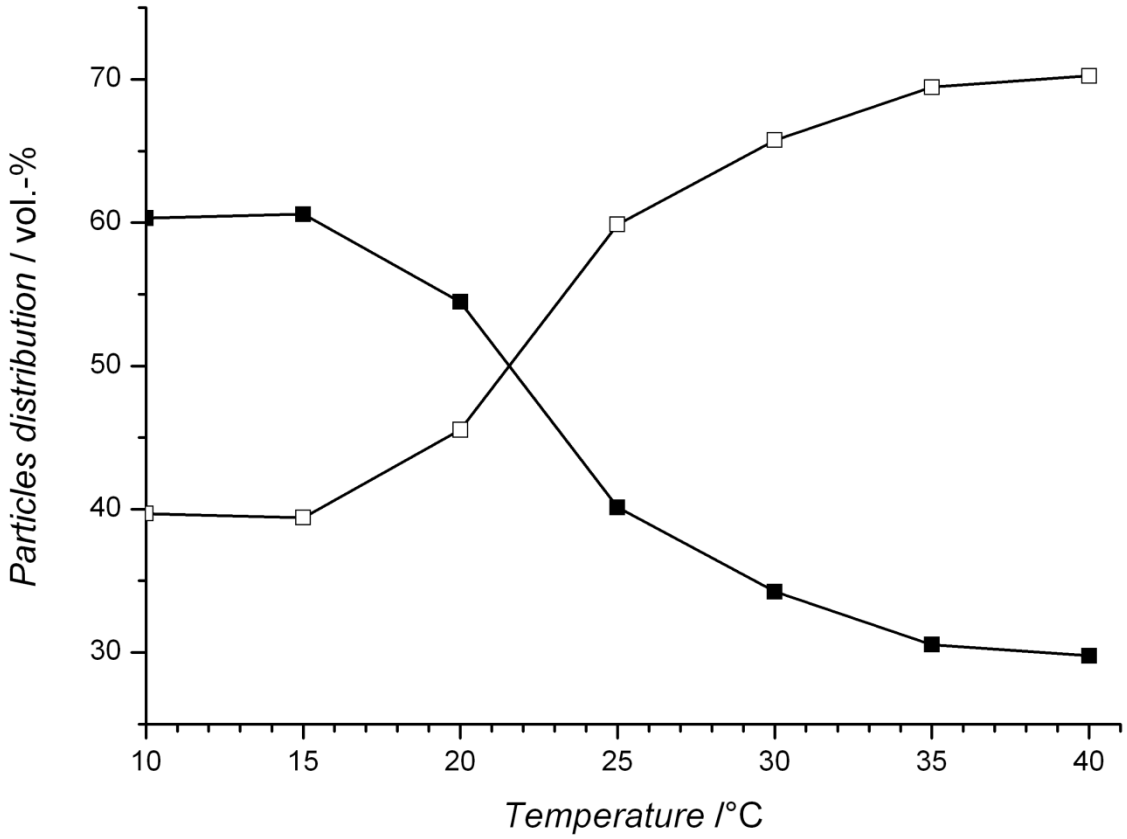

Figure ESI 12 Evolution of population in volume percent of individual SWCNTs (filled squares) and aggregates (white squares) with temperature from the 0.01 mg·mL^{-1} water dispersion of PNIPAM functionalized SWCNTs (**P3a-SWCNT** sample).

The following supporting information provides the results of already referenced molecules. The obtained results via NMR, EA and FTIR are reported.

Additional materials

1-Dodecanethiol (≥99%, Acros), Aliquot 336 (Sigma Aldrich), carbon disulfide (≥99%, VWR), 3-bromo-1-propanol (≥97%, Acros), sodium azide (≥99.5%, Sigma Aldrich), oxalyl chloride (≥98%, Acros), triethylamine (≥99%, Acros), 2-bromo-2-methylpropionyl bromide (≥98%, Acros), propargyl alcohol (≥99%, Alfa Aesar) were used as received.

Synthesis of DMP, DMP-N_3 and 2-propynyl 2-bromo-2-methylpropanoate

2-Dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (**DMP**) was synthesized according to literature.[1] ^{1}H NMR: 0.81 (t, 3H), 1.11-1.37 (m, 18H), 1.56-1.68 (m, 8H), 3.21 (t, 2H), 13.05 (s, 1H). ^{13}C NMR (δ, ppm): 220.8 (S-C=S); 178.8 (C=O); 55.6 (-S-*C*$(CH_3)_2$-CO); 37.1 (-CH_2-*C*H_2-S-C=S); 31.9 (-*C*(10)H_2-CH_2-S); 29.6 (-*C*(3)H_2-CH_2-S); 29.6 (-*C*(4)H_2-CH_2-S); 29.5 (-*C*(5)H_2-CH_2-S); 29.4 (-*C*(6)H_2-CH_2-S); 29.1 (-*C*(7)H_2-CH_2-S); 29.0 (-*C*(8)H_2-CH_2-S); 28.0(-*C*(9)H_2-CH_2-S); 27.9 (-*C*(2)H_2-CH_2-S); 25.1 (-S-*C*$(CH_3)_2$-CO); 22.7 (-*C*(11)H_2-CH_2-S); 14.1 (*C*H_3-$C_{11}H_{22}$-S-C=S). IR (KBr) (wavenumber, cm^{-1}) for DMP: 2917 and 2856 (C-C*s*), 1718 (C=O), 1070 (C=S), 1172 and 816 (C-C*b*).Elemental analysis, calculated: C = 56.00, H = 8.85, O = 8.78, S = 26.38; experimental: C = 55.18, H = 8.80, O = 8.80, S = 26.52.

The synthetic route described by Gondi *et al.*[2] was used for the synthesis of 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid 3-azidopropyl ester (**DMP-N_3**) and of the intermediate 3-azidopropanol. ^{1}H NMR (δ, ppm) for DMP-N_3: 4.15-4.21 (t, J=6.10 Hz, 2 H), 3.31-3.41 (t, J=6.69 Hz, 2 H), 3.23-3.30 (t, J=7.60 Hz, 2 H), 1.85-1.94 (quin, J=6.10 Hz, 2 H), 1.57-1.68 (m, 2 H), 1.19-1.42 (m, 18 H), 0.84-0.93 (td, J=6.80, 1.30 Hz, 3 H). ^{13}C NMR (δ, ppm) for DMP-N_3: 220.8 (S-C=S); 172.9 (C=O).; 62.8 (-CH_2-*C*H_2-O-C=O); 55.9 (-S-*C*$(CH_3)_2$-CO); 48.2 (-CH_2-*C*H_2-N_3); 37.0 (-CH_2-*C*H_2-S-C=S); 31.9 (-*C*(10)H_2-CH_2-S); 31.6 (-*C*H_2-CH_2-N_3); 29.6 (-*C*(3)H_2-CH_2-S); 29.5 (-*C*(4)H_2-CH_2-S); 29.4 (-*C*(5)H_2-CH_2-S); 29.3 (-*C*(6)H_2-CH_2-S); 29.1 (-*C*(7)H_2-CH_2-S); 28.9 (-*C*(8)H_2-CH_2-S); 28.0 (-*C*(9)H_2-CH_2-S); 27.9 (-*C*(2)H_2-CH_2-S); 25.3 (-S-*C*$(CH_3)_2$-CO); 22.7 (-*C*(11)H_2-CH_2-S); 14.1 (*C*H_3-$C_{11}H_{22}$-S-C=S). IR (KBr) (wavenumber, cm^{-1}) for DMP-N_3: 2923 and 2854 (C-C*s*), 2096 (C-N=N=N), 1735 (C=O), 1064 (C=S), 1155 and 814 (C-C*b*). Elemental analysis for DMP-N_3, calculated: C = 53.65, H = 8.33, N = 9.39, O = 7.15, S = 21.41; experimental: C = 51.00, H = 7.10, N = 8.93, O = 7.71, S = 23.61. ^{1}H NMR (δ, ppm) for 3-azidopranol: 3.71-3.61 (t, J = 6.00 Hz, 2H, -CH_2-C*H*$_2$-OH), 3.42-3.23 (t, *J* = 6.56 Hz, 2H, -CH_2- C*H*$_2$-N_3), 2.38 (br-s, 1H, OH), 1.82-1.69 (quin, 2H, HO-CH_2-C*H*$_2$-CH_2-N_3).

The same procedure as Luetdke *et al.* was followed for the synthesis of 2-propynyl 2-bromo-2-methylpropanoate.[3] ^{1}H NMR (δ, ppm): 4.76-4.8 (d, *J*=2.53 Hz, 2 H), 2.51-2.56 (t,

J = 3.00 Hz, 1 H), 1.93-1.99 (s, 6 H). ^{13}C NMR (δ, ppm): 170.9 (C=O), 76.9 (-*C*≡C-H), 75.5 (H-*C*≡C-), 54.9 (*C*-O), 53.5 (Br-*C*-$(CH_3)_2$), 30.7 (*C*H_3-C). IR (ATR) (wavenumber, cm^{-1}): 3296 (alkyn C-H*s*), 2975 (C-C*s*), 1732 (C=O), 1153 (C-C*b*).

1 J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754.
2 S. R. Gondi, A. P. Vogt and B. S. Sumerlin, *Macromolecules*, 2007, **40**, 474.
3 A. E. Luetdke and J. W. Timberlake, *J. Org. Chem.*, 1985, **50**, 270.