Electronic Supplementary Information

pH responsive host-guest polymerization and blending

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Homopolymer Characterization

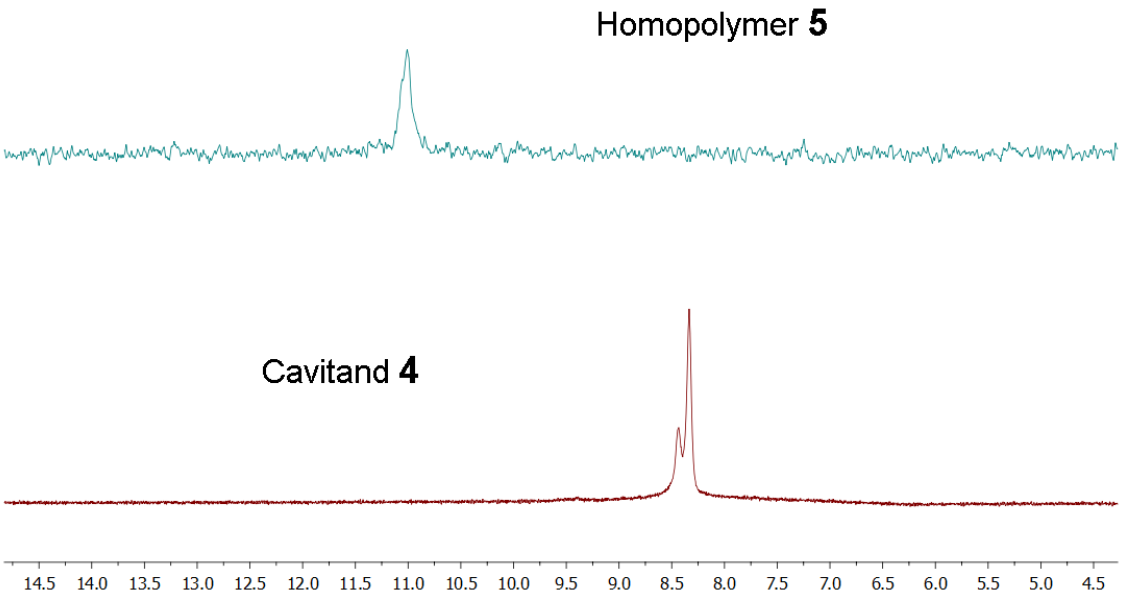


Figure S1 $^{31}P\{^{1}H\}$NMR spectra ($CDCl_3$, 400 MHz, 25 °C) of the cavitand **4** and the homopolymer **5**.

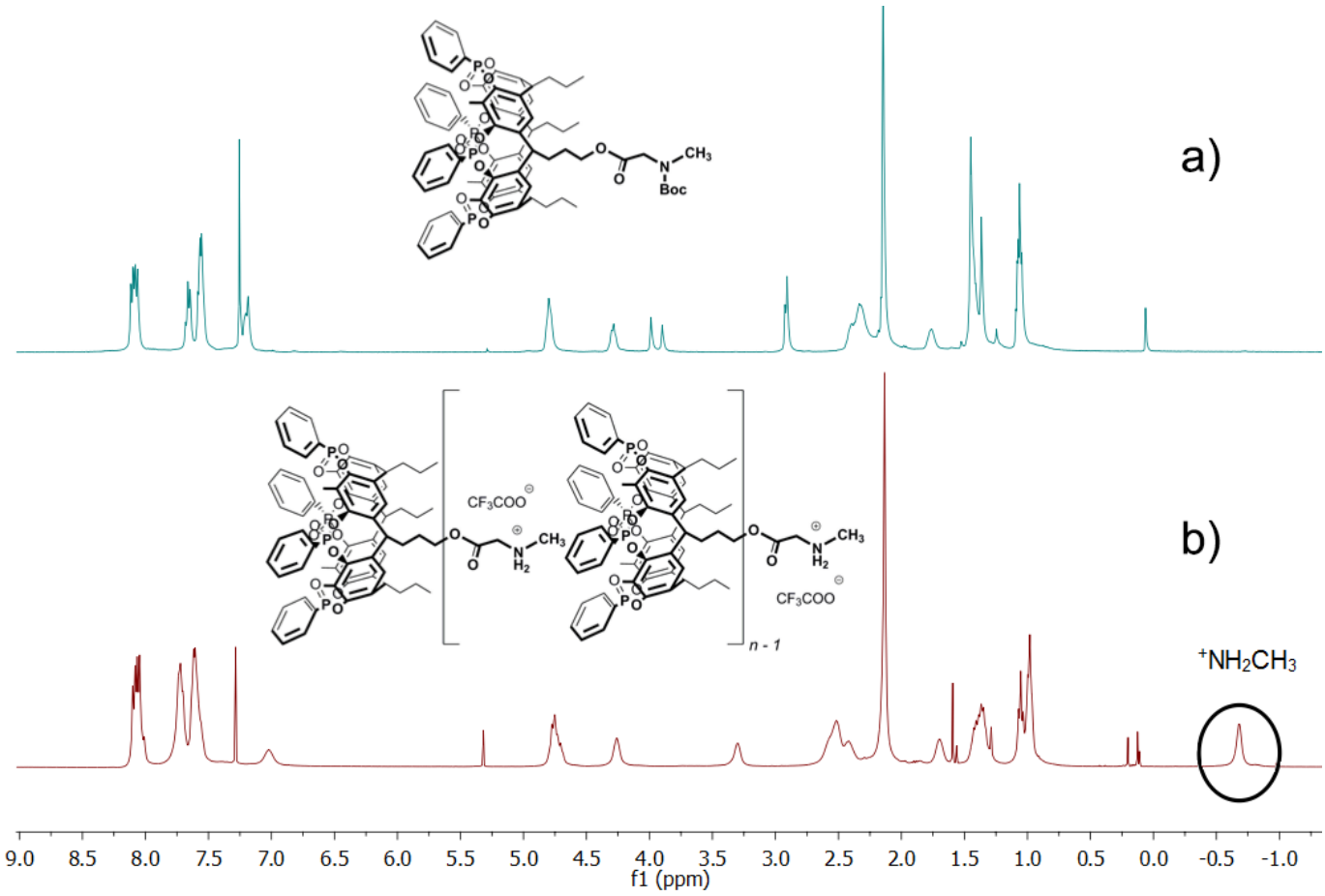
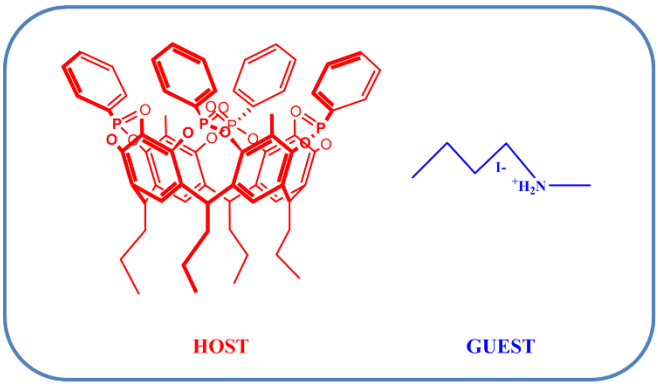


Figure S2 ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 10 mM, 25 °C) of: a) monomer BOC protected; b) homopolymer **5**.

ITC measurements



Solvent CH_2Cl_2

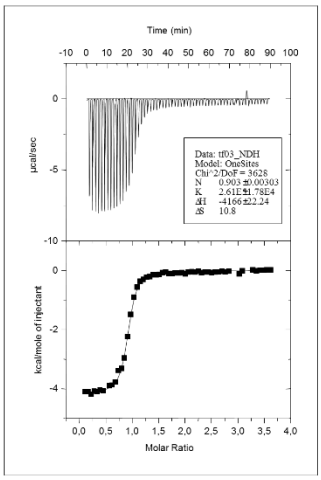
T = 298 K

HOST concentration = 0.405 mM

GUEST concentration = 5.93 mM

N° of experiments = 3

Typical obtained ITC trace:



K (M^{-1})	(2,6 ± 0,1)•10^6
ΔH (KJ mol^{-1})	-43,1 ± 0,1
TΔS (KJ mol^{-1})	-6,1 ± 0,7
ΔG (KJ mol^{-1})	-37,0 ± 0,1
N	0,844 ± 0,07

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Figure S3 Ka determination of **Tiiii[C_3H_7, CH_3, Ph]@*N*,*N*-methylbutyl ammonium iodide** complex in dichloromethane by ITC

Homopolymer Characterization

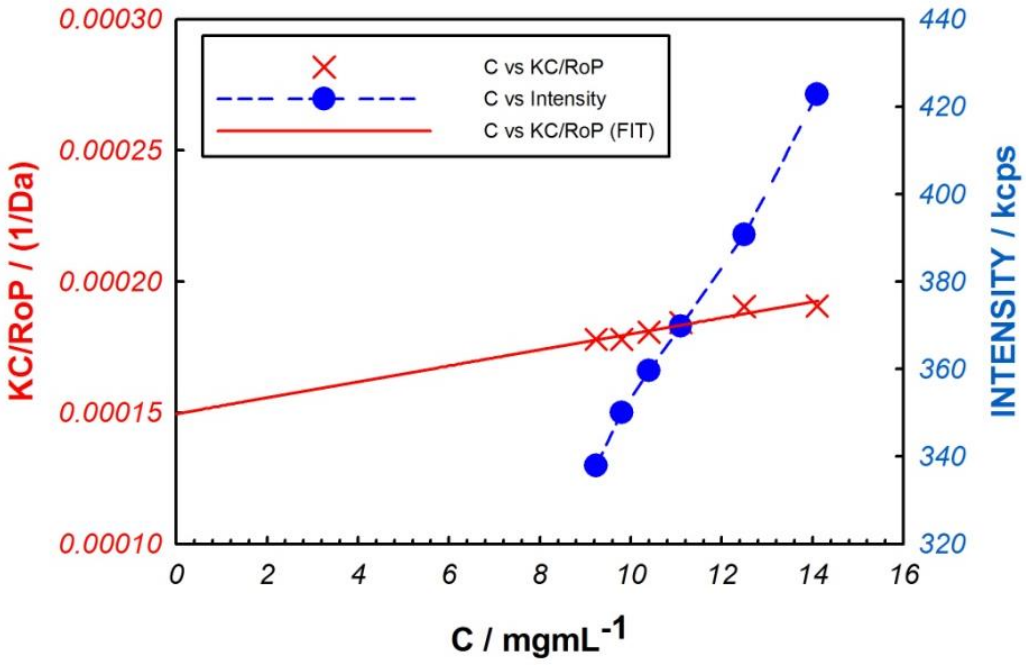


Figure S4 Debye plot for the SLS analysis ($CHCl_3$, 25 °C) of **Tiiii** homopolymer in the 9.2-14.1 mg mL^{-1} concentration range (M_w = 7 ± 1 KDa).

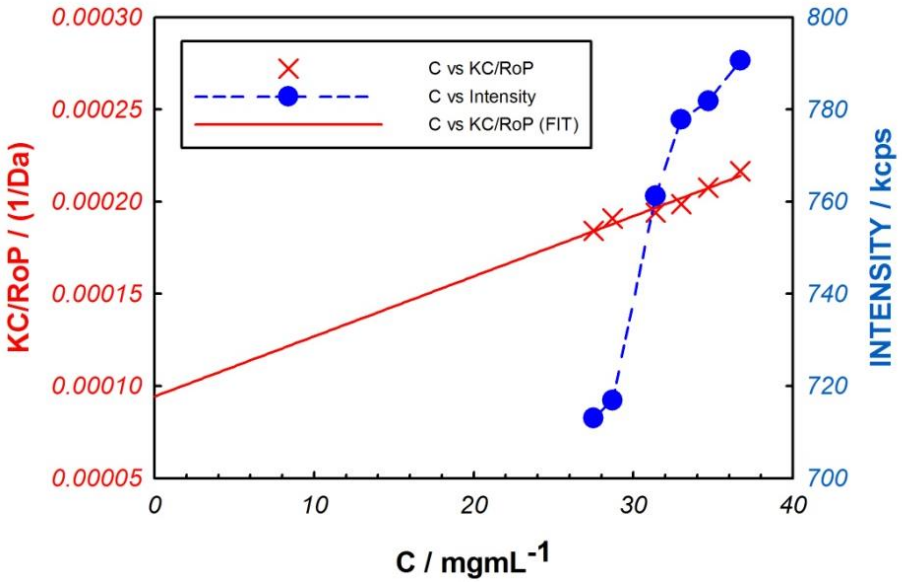


Figure S5 Debye plot for the SLS analysis ($CHCl_3$, 25 °C) of homopolymer **5** in the 25.5-36.7 mg mL^{-1} concentration range (M_w = 11 ± 1 KDa).

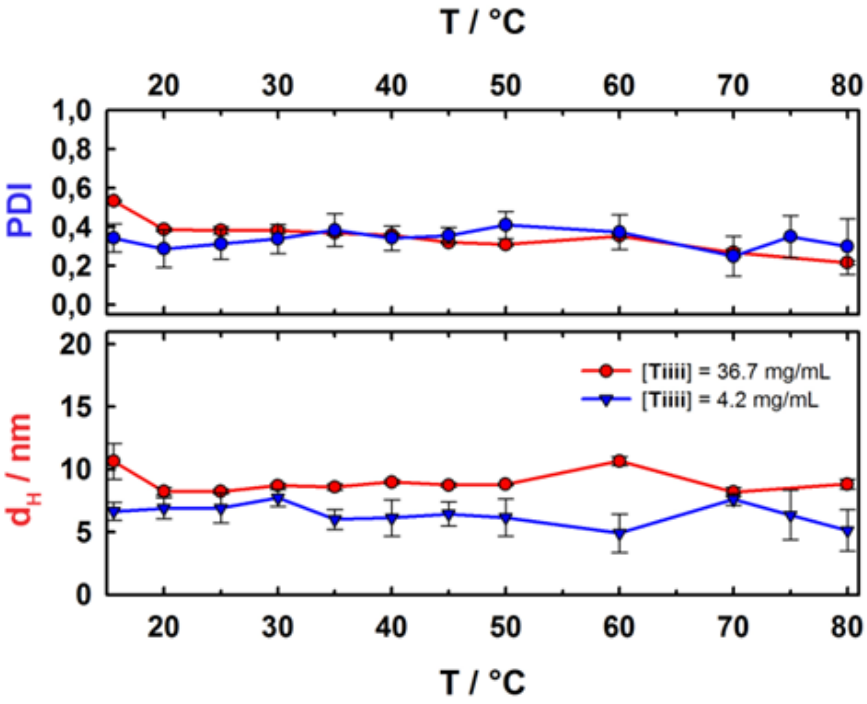


Figure S6. DLS experiment at various temperature for two different concentration: 36.7 and 4.2 mg mL^{-1}.

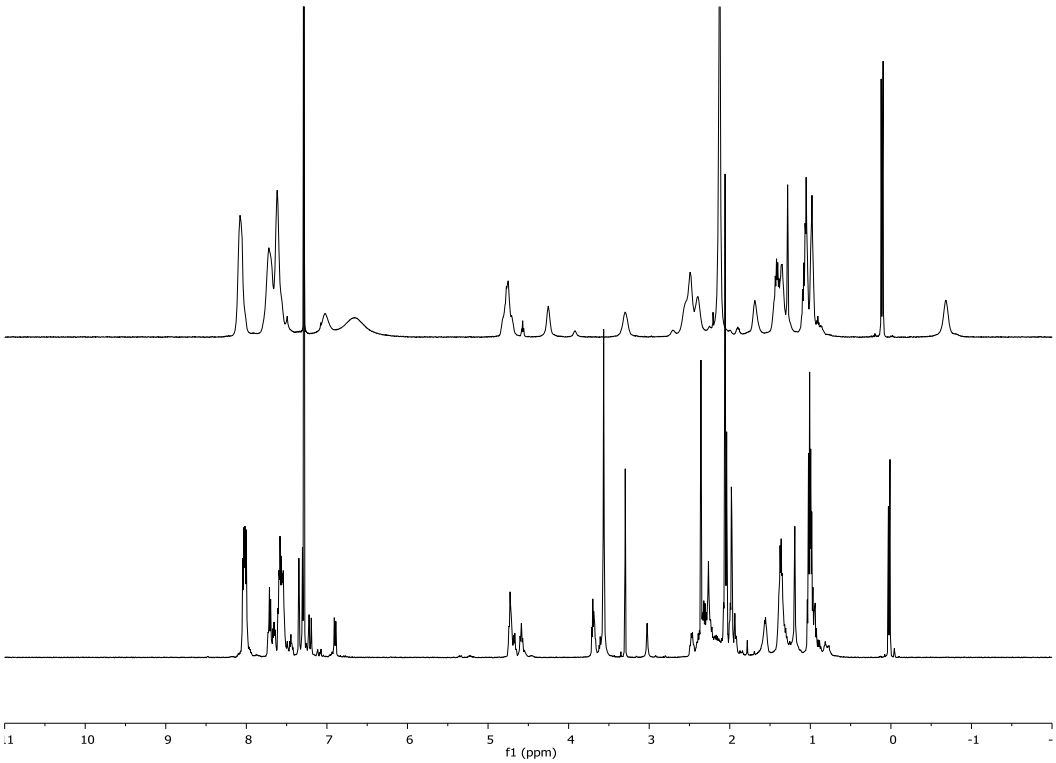


Figure S7 500 MHz ^{1}H NMR spectra of 5 mM **5** in $CDCl_3$. Top: before addition of aqueous NaOD in CD_3OD (see text), Bottom: after addition of aqueous NaOD in CD_3OD (see text).

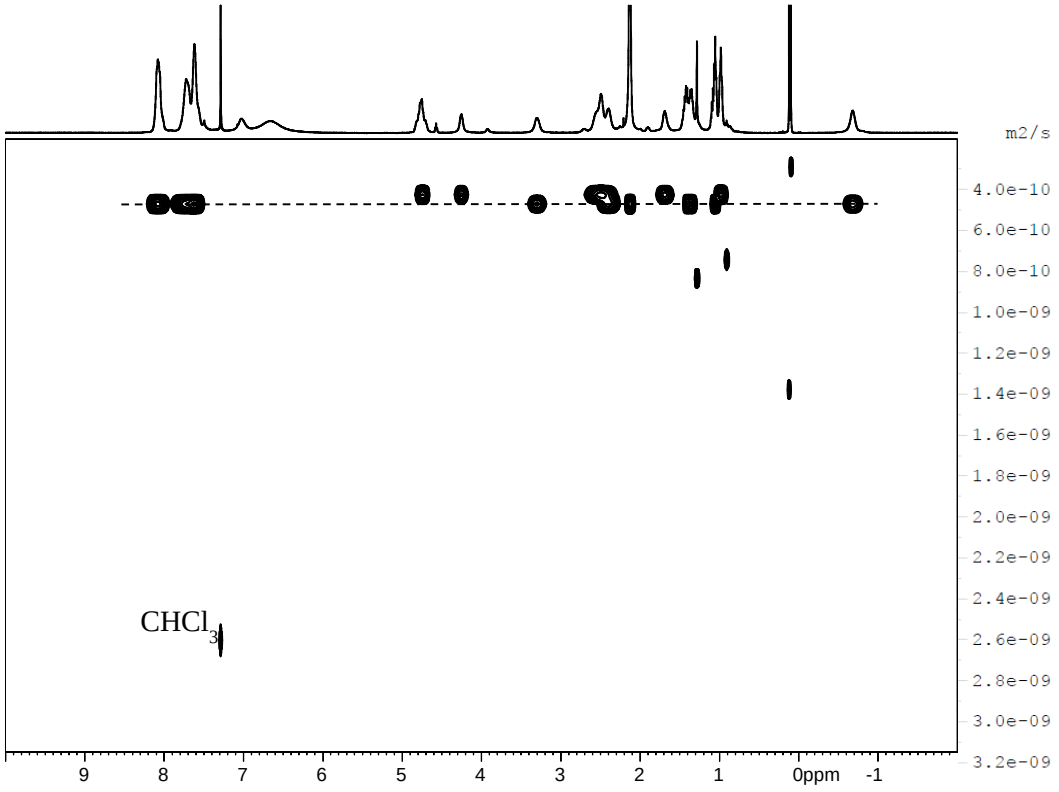


Figure S8 ^{1}H DOSY map of 5 mM **5** in $CDCl_3$ before addition of aqueous NaOD in CD_3OD (see text). The line is drawn at the average value of the diffusion coefficient estimated for the homopolymer.

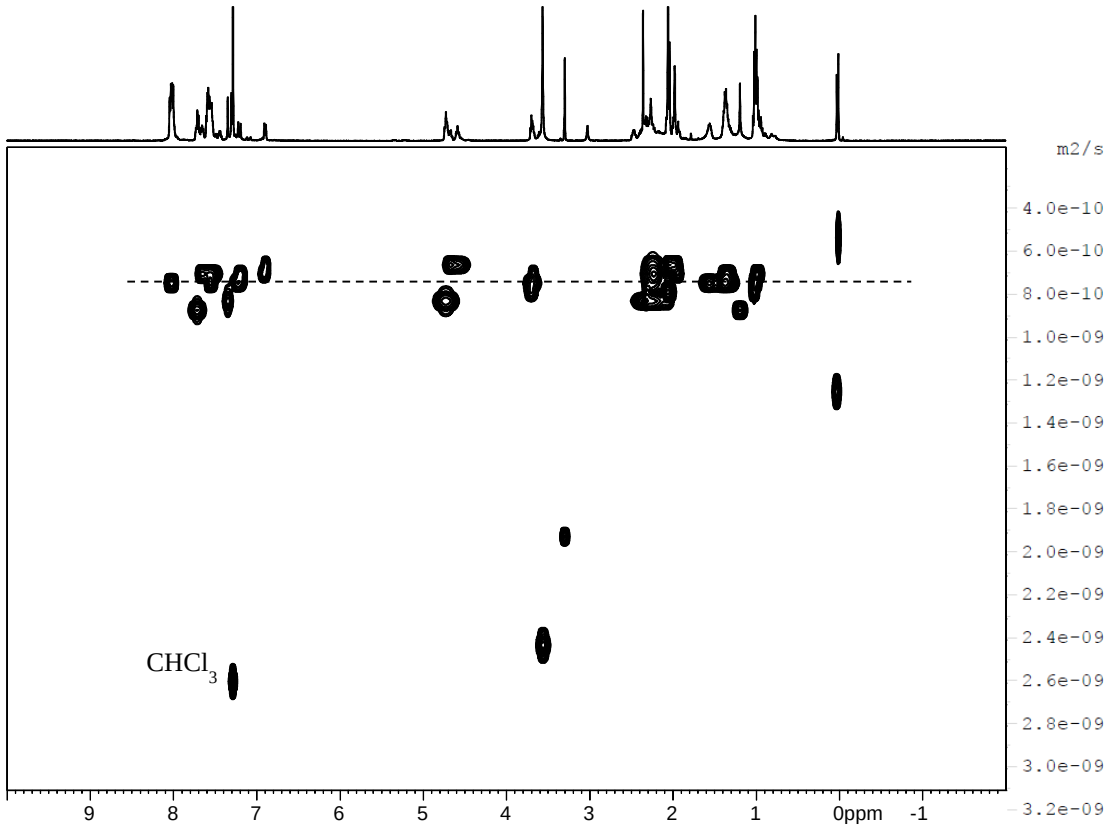
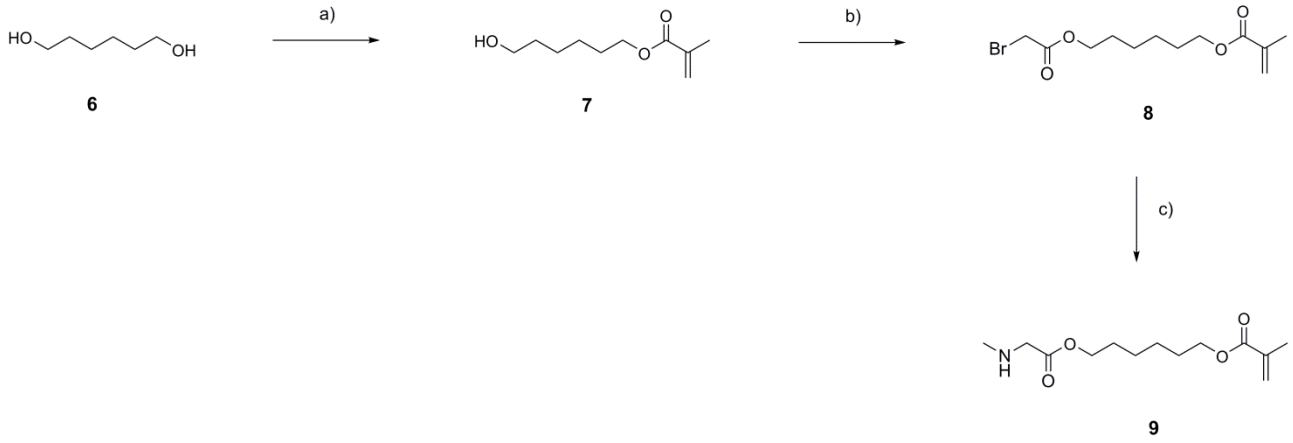


Figure S9 ^{1}H DOSY map of 5 mM homopolymer **5** in $CDCl_3$ after addition of aqueous NaOD in CD_3OD (see text). The line is drawn at the average value of the diffusion coefficient estimated for the monomer (only signals with the lowest fitting errors have been retained in the average). Scattering in the diffusion dimension is possibly due to equilibria between monomeric and residual oligomeric forms.

Synthesis of PBMA-Sarc

Synthesis of 6-((methylglycyl)oxy)hexyl methacrylate



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Scheme S1 Synthesis of monomer **9**: a) methacryloyl chloride, DMAP, Et_3N, DCM, r.t., 12 h, 48%; b) bromoacetyl chloride, Et_3N, DCM, r.t., 2 h, 66%; c) methylamine, NaI, ACN, r.t., 1 h, 87%.

6-hydroxyhexyl methacrylate (7)

To a solution of 1,6-hexanediol **6** (5.6 g, 48 mmol) in dichloromethane, DMAP (0.46 g, 4 mmol) and triethylamine (3.96 ml, 29 mmol) were added. The mixture was cooled at 0 °C and methacryloyl chloride (1.85 ml, 20 mmol) was added dropwise. The solution was warmed at room temperature and stirred overnight. The reaction was quenched with water, the organic phase was separated and evaporated under reduced pressure. The crude was purified by silica gel column chromatography (hexane:dichloromethane 7:3) to give **7** as colorless oil (1.86 g, 9.7 mmol, 48 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 6.05 (s, 1H, **H$_{TRANS}$**HC=C), 5.51 (s, 1H, **H$_{CIS}$**HC=C), 4.10 (t, 2H, ^{3}J= 6.6 Hz, (C=O)OC**H$_2$**CH_2), 3.58 (t, 2H, ^{3}J= 6.6 Hz, CH_2C**H$_2$**OH), 2.39 (s, 1H, CH_2O**H**), 1.90 (s, 3H, C**H$_3$**), 1.65 (m, 2H, (C=O)OCH_2C**H$_2$**), 1.54 (m, 2H, C**H$_2$**CH_2OH), 1.37 (m, 4H, CH_2C**H$_2$**C**H$_2$**CH_2); **ESI-MS**: *m\z* 209.2 $[M+Na]^+$.

6-(2-bromoacetoxy)hexyl methacrylate (8)

To a solution of **7** (0.8 g, 4.3 mmol) in dichloromethane, bromo acetyl bromide (1.354 g, 8.6 mmol) and triethylamine (1.2 mL, 8.6 mmol) were added. The reaction mixture was stirred for 2 h at room temperature and quenched adding 10% HCl solution. The organic phase was extracted twice with water and brine, dried with $MgSO_4$ and evaporated under *vacuo*. Purification by silica gel column chromatography (hexane:ethyl acetate 8:2) yielded the desired product **8** as colorless oil (0.86 g, 2.8 mmol, 66%).

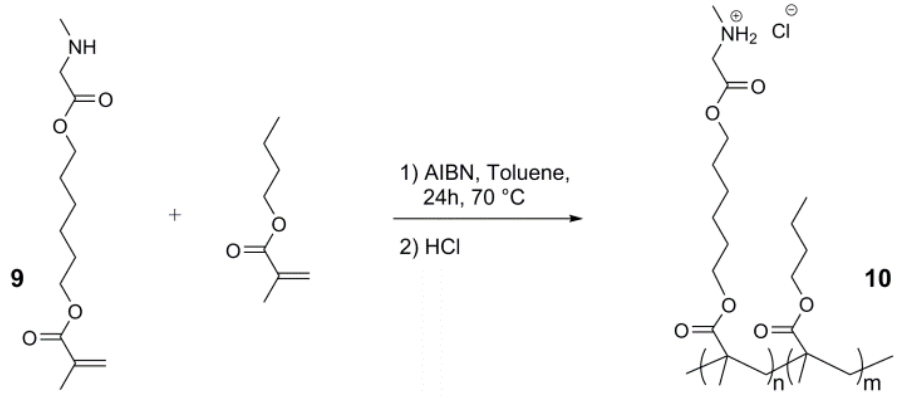
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 6.09 (s, 1H, **H$_{CIS}$**HC=C), 5.55 (s, 1H, **H$_{TRANS}$**HC=C), 4.19-4.13 (m, 4H, C**H$_2$**O), 3.83 (s, 2H, C**H$_2$**Br), 1.94 (s, 3H, C**H$_3$**), 1.69-1.67 (m, 4H, OCH_2C**H$_2$**), 1.45-1.42 (m, 4H, OCH_2CH_2C**H$_2$**); **ESI-MS**: *m/z* 308 $[M+H]^+$.

6-((methylglycyl)oxy)hexyl methacrylate (9)

8 (0.34 g, 1.12 mmol) was dissolved in acetonitrile and sodium iodide (0.25 g, 1.67 mmol) was added. After 5 minutes of stirring a solution of methylamine (0.6 mL, 22.4 mmol) in 3 mL of methanol was added. The solution was stirred at room temperature for 1 h. The reaction mixture was diluted with dichloromethane and the organic phase extracted twice with sat. aq. $NaHCO_3$ and water. The organic phase was dried with

anhydrous Na_2SO_4 and the solvent removed *in vacuo*. Purification by silica gel column chromatography (hexane:ethyl acetate 1:1) afforded the pure product **9** as colorless oil (0.25 g, 0.97 mmol, 87%).
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 6.11 (s, 1H, **H$_{CIS}$**HC=C), 5.57 (s, 1H, **H$_{TRANS}$**HC=C), 4.18-4.14 (m, 4H, C**H$_2$**O), 3.4 (s, 2H, NC**H$_2$**C(O)), 2.47 (s, 3H, NC**H$_3$**), 1.96 (s, 3H, C**H$_3$**), 1.73-1.66 (m, 4H, C**H$_2$**CH_2O), 1.44-1.40 (m, 4H, C**H$_2$**CH_2CH_2O); **ESI-MS**: *m/z* 258 $[M+H]^+$.

Copolymerization between n-butyl methacrylate and 6-((methylglycyl)oxy)hexyl methacrylate (9) (PBMA-Sarc)
(10)



Scheme S2 Synthesis of PBMA-Sarc.

In a Schlenk with magnetic stirrer n-butyl methacrylate (3.9 mL, 24.84 mmol) and **9** (0.266 g, 1.03 mmol) were dissolved in toluene under nitrogen atmosphere. The solution was purged with nitrogen for 30 minutes and heated to 70 °C, then AIBN was added (85 mg) and the polymerization mixture kept for 24 h in these conditions. At the end of the reaction, the copolymer was purified by twice precipitation in 500 mL of cold methanol and after filtration, copolymer was dried *under vacuum* at room temperature (yield 70%). Subsequently the polymer was dissolved in toluene and under stirring gaseous HCl was bubbled through the solution. Gaseous HCl was produced by the addition of concentrated H_2SO_4 to dry NaCl. The polymer was precipitated twice from methanol.
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.96 (NC**H$_2$**C(O), C(O)OC**H$_2$**CH_2), 2.29 (NC**H$_3$**), 1.9-1.8 ([C**H$_2$**$C(CH_3)(C(O)OC_4H_9)]_n$), 1.63 ($C(O)OCH_2$C**H$_2$**), 1.43 (CH_2C**H$_2$**CH_3), 1.1-0.8 (CH_2CH_2C**H$_3$**, $[CH_2C($C**H$_3$**$)(C(O)OC_4H_9)]_n$); **IR** (solution casting on KBr plate): 3410 (ν_{N-H}), 2960 (asym ν_{C-H} CH_3), 2936 (asym ν_{C-H} CH_2), 2875 (sym ν_{C-H} CH_3), 1728 ($\nu_{C=O}$), 1466 (asym δ_{CH3}), 1385 (sym δ_{CH3}), 1268, 1242, 1177, 1154 (ν_{C-O-C}), 750 (ρ_{CH2}), 666 (Wagging N-H) cm^{-1}; **Elemental analysis**: theoretical C 66.41, H 9.81, N 0.38 %; found C 68.32, H 10.09, N 0.27 %; **GPC** ($CHCl_3$): $\overline{Mn}$: = 23200 Da, $\overline{Mw}$ = 36600 Da, PDI = 1.58.

PBMA-Sarc Characterization

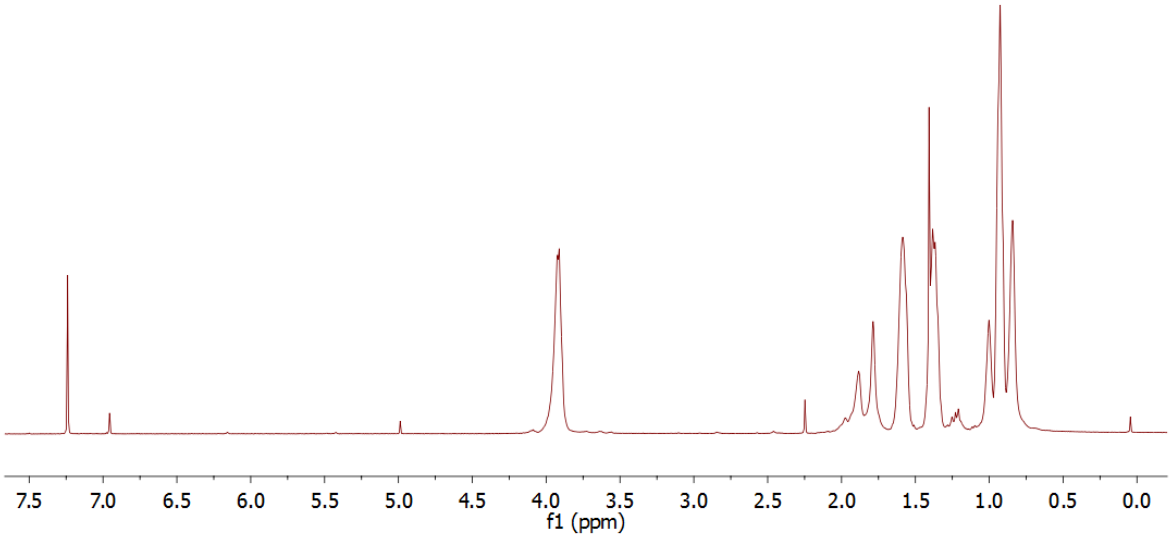


Figure S10 ^{1}H NMR ($CDCl_3$, 400 MHz) of PBMA-Sarc.

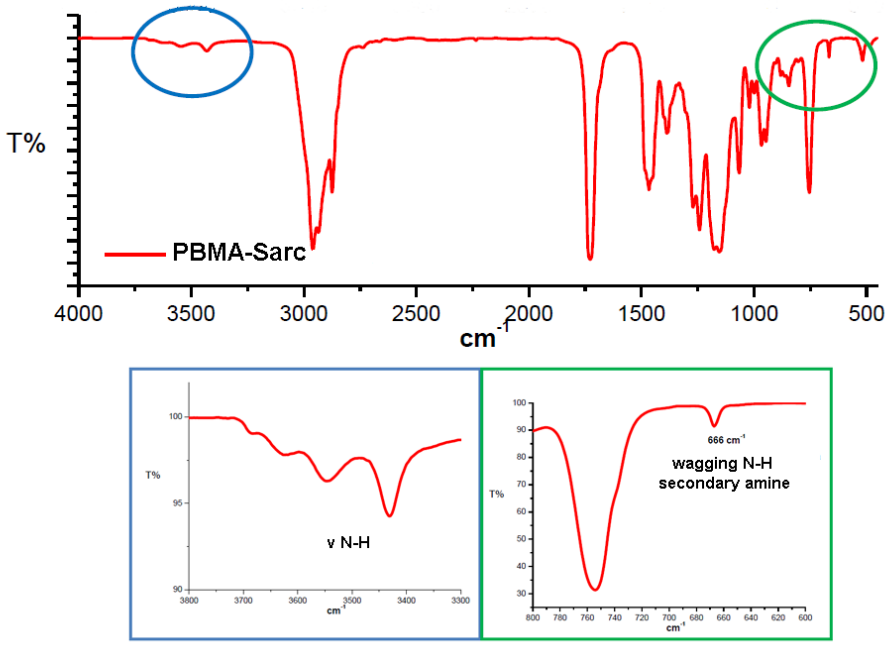


Figure S11 FT-IR of PBMA-Sarc.

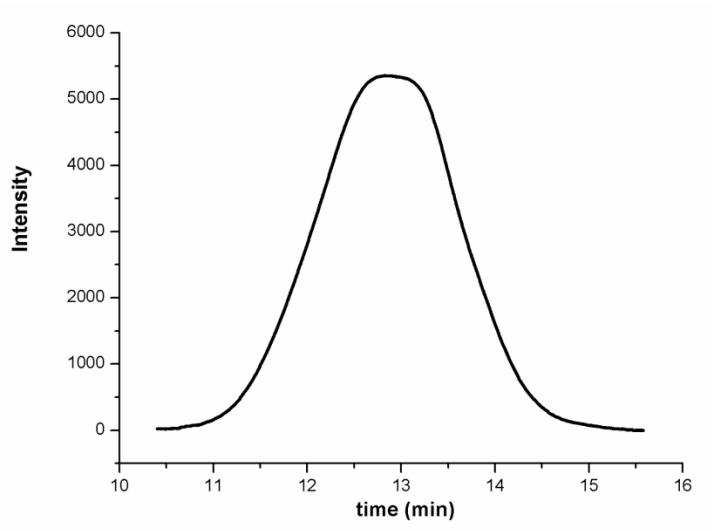


Figure S12 RI chromatographic trace of PBMA-Sarc.

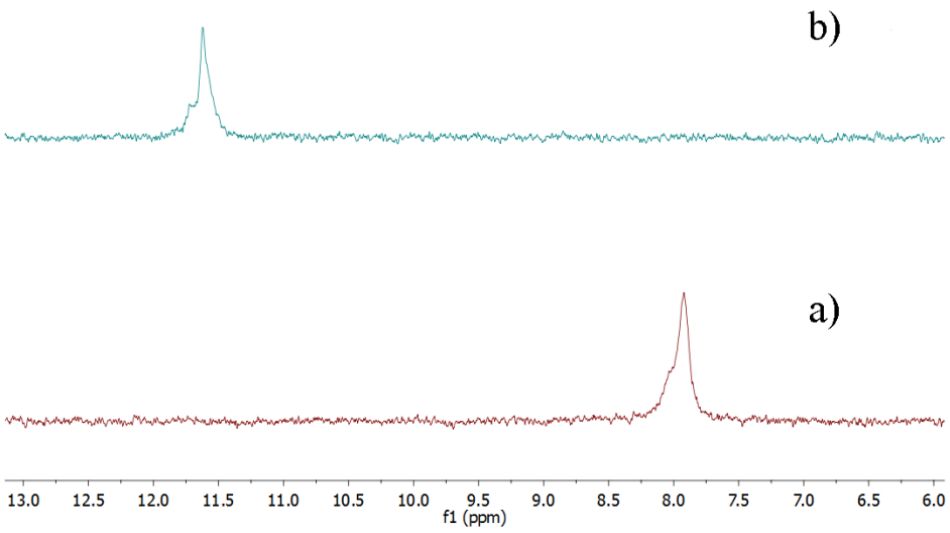


Figure S13 ^{31}P NMR spectra in $CDCl_3$ a) PS-Host (0.5 mM), b) PS-Host:PBMA-Sarc 1:1 (0.5 mM).

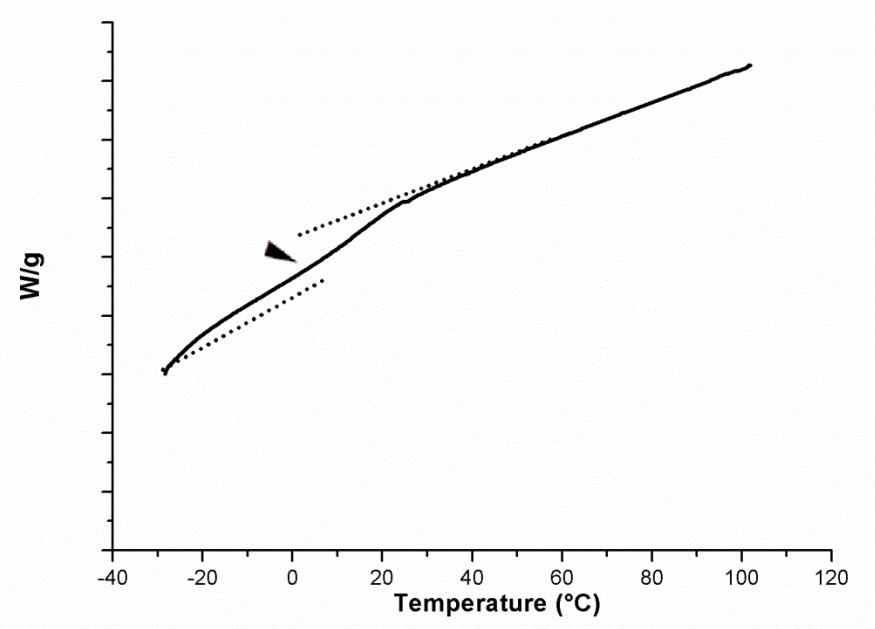


Figure S14 DSC thermogram of PBMA-Sarc