Supporting Information

for

Bioinspired Dual Self-Folding of Single Polymer Chains via Reversible Hydrogen Bonding

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Materials

Styrene (St) (Sigma-Aldrich) and methyl methacrylate (MMA) (Sigma-Aldrich) were passed through a column of basic alumina (Acros) prior to use and subsequently stored at -19°C. 6-Bromohexanol (97%, ABCR GmbH and Co. KG), 11-bromoundecanol (97%, ABCR GmbH and Co. KG), ethylenediaminetetraacetic acid disodium salt (99%, Acros), 2,2-dimethoxypropane (99%, Acros), *p*-toluenesulfonic acid monohydrate (99%, Aldrich), 2,2-bis(hydroxymethyl)propionic acid (99%, Aldrich), cyanuric acid (CA) (99%, ABCR GmbH and Co. KG), 4-dimethylamino pyridine (DMAP) (99%, Acros), N,N-dicyclohexylcarbodiimide (DCC) (99%, Acros), N,N-dimethylformamide extra dry (DMF) (99.8%, Acros), tetrahydrofuran extra dry (THF) (99.8%, Acros), sodium azide (99.8%, Acros), α-bromo isobutyric acid (98%, Aldrich), 2-bromo-2-methylpropanoyl bromide (98%, Aldrich), 5-hydroxyisophthalic acid (97%, Aldrich), sulfuric acid (95%, Carl Roth GmbH and Co. KG), propargyl bromide, 80 wt.% solution in toluene (80%, Acros), 3,3-dimethylbutyryl chloride (99%, Aldrich), 2,6-diamino pyridine (98%, Aldrich), triethylamine (99.7%, ABCR GmbH and Co. KG), CuBr (99.9%, Acros) N,N,N',N'',N''-pentamethyldiethyltriamine (PMDETA) (99.9%, Merck), cupric sulfate pentahydrate (99.5%, Aldrich), (+)-sodium L-ascorbate (98%, Aldrich) were used as received. Methylene chloride (DCM) was distilled over phosphorus pentoxide and stored over molecular sieves. Toluene, diethyl ether, ethanol, methanol and chloroform were purchased as analytical grade (Aldrich) and used as received.

Characterization

Size Exclusion Chromatography (SEC)

SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 μm Mixed-C and one PLgel 3 μm Mixed-E columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using both linear poly(styrene) (PS) standards ranging from 160 to $6 \cdot 10^6$ g mol^{-1} and linear poly(methyl methacrylate) (PMMA) standards ranging from 700 to $6 \cdot 10^6$ g mol^{-1}. Calculation of the molecular weight proceeded via the Mark-Houwink parameters for these polymers, i.e. $K = 14.1 \cdot 10^{-5}$ dL·g^{-1}, $\alpha = 0.70$ (PS).[1]

Electrospray Ionization-Mass Spectrometry (ESI-MS)

Mass spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the m/z range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 3.5 kV and a dimensionless sheath gas of 8 and a sweep gas flow rate of 2 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature, were set to 60 V, 120 V and 275 °C, respectively.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The structures of the synthesized compounds were confirmed via ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker AM 400 MHz spectrometer for hydrogen nuclei and 100 MHz for carbon nuclei. Samples were dissolved in $CDCl_3$, DMSO-d_6 or CD_2Cl_2 (for the self-assembly study). The δ-scale was referenced with tetramethylsilane (δ = 0.00) as internal standard. Abbreviations used below in the description of the materials' syntheses include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

Static and Dynamic Light Scattering (SLS and DLS)

The solutions were prepared by dissolving the polymer in DCM at an appropriate concentration and then taking a part of this master solution to perform a serie of concentration by dilution. After waiting the equilibrium (around 4 hours) the solutions were filtered over 0,2μL filter and analysed by SLS and DLS.

SLS measurements were performed using a MALLS-detector (multi-angle laser light scattering detector) SLD 7000 from Polymer Standard Services (PSS), Mainz, Germany. Five concentrations of polymer from 1 to 10 $g \cdot L^{-1}$ to determine the weight-averaged molecular weight (M_w) and the second virial coefficient (A_2) were employed. The required d*n*/d*c* values where measured in the same solvent with a refractormeter Dn/Dc2010 also from PSS, Mainz, Germany. Typically, six concentrations of the polymer from 1 to 10 $g \cdot L^{-1}$ to determine d*n*/d*c*-values (d*n*/d*c* (PS standard in DCM) = 0.170 +/- $5 \cdot 10^{-4}$ $mL \cdot g^{-1}$ and d*n*/d*c* (**14** in DCM) = 0.166+/- $1 \cdot 10^{-3}$ $mL \cdot g^{-1}$) we used.

Hydrodynamic diameters where determined with dynamic light scattering (Nicomp 380 DLS spectrometer from Particle Sizing Systems, Santa Barabara, USA - laser diode: 90 mW, 658 nm). The measurements where performed in automatic mode and evaluated with a standard Gaussian and an advanced evaluation method, the latter using an inverse Laplace algorithmen to analyze for multimodal distributions. Numbers given in text are the volume weighted average values. All measurements were determined at 90° to the incident beam.

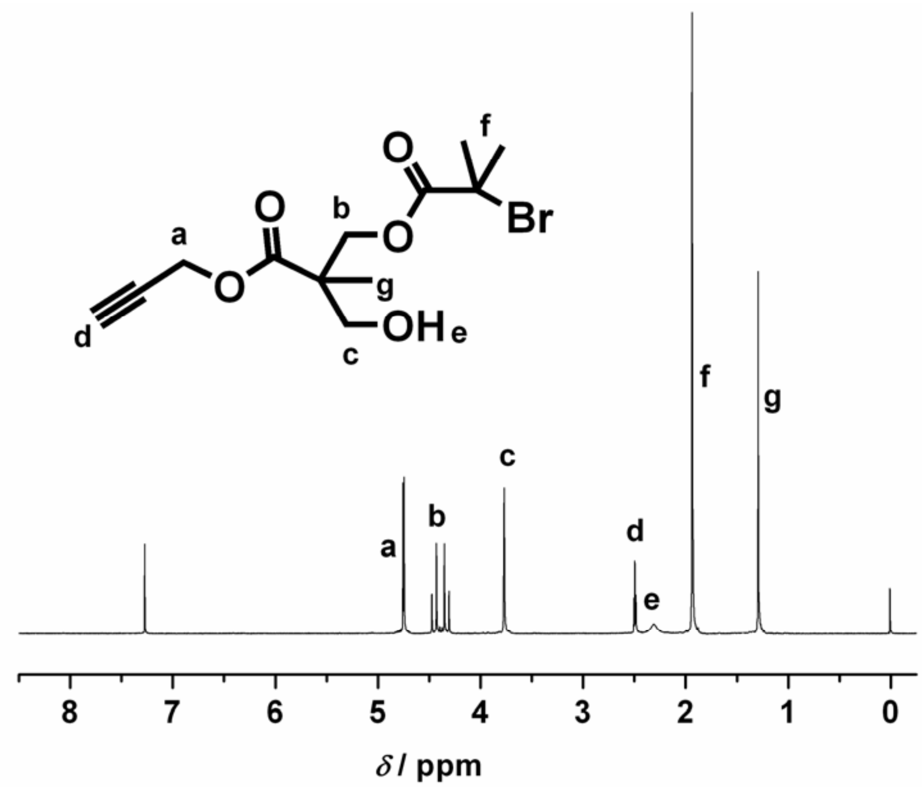


Figure S1. ^{1}H-NMR spectrum of 2-hydroxymethyl-2-(α-bromoisobutyloxymethyl)-propionate (**2**) in $CDCl_3$.

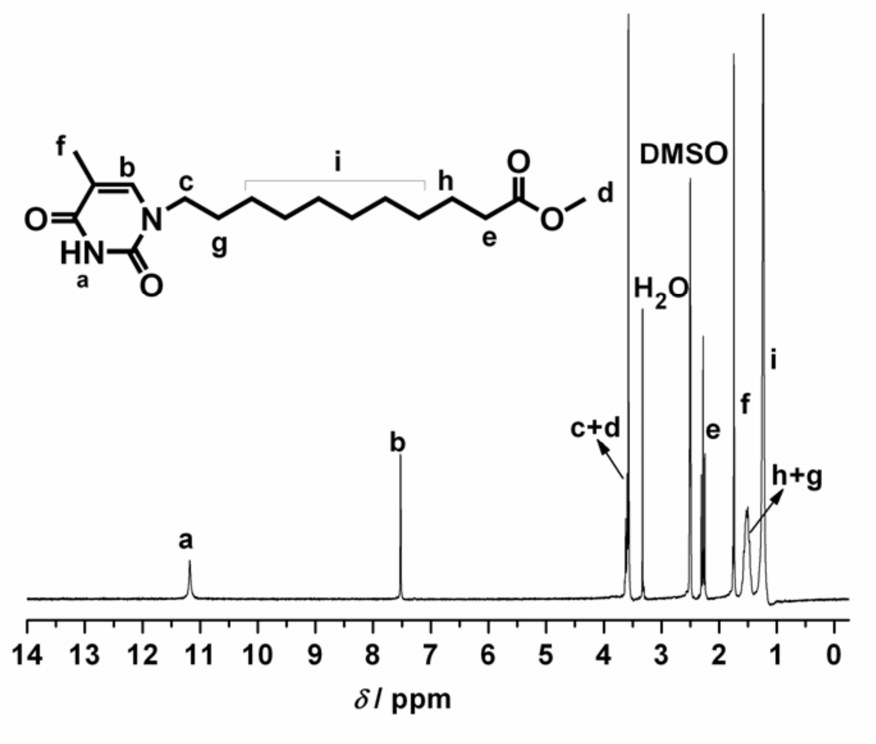


Figure S2. ^{1}H-NMR spectrum of methyl 11-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)undecanoate (**4**) in DMSO-d_6.

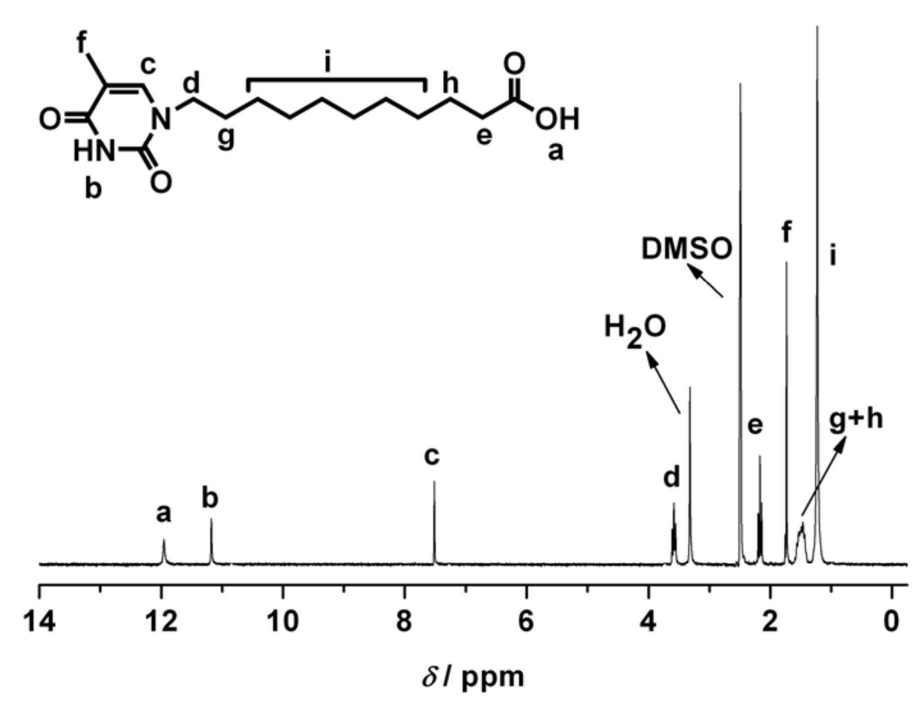


Figure S3. ^{1}H-NMR spectrum of 11-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)undecanoic acid (**5**) in DMSO-d_6.

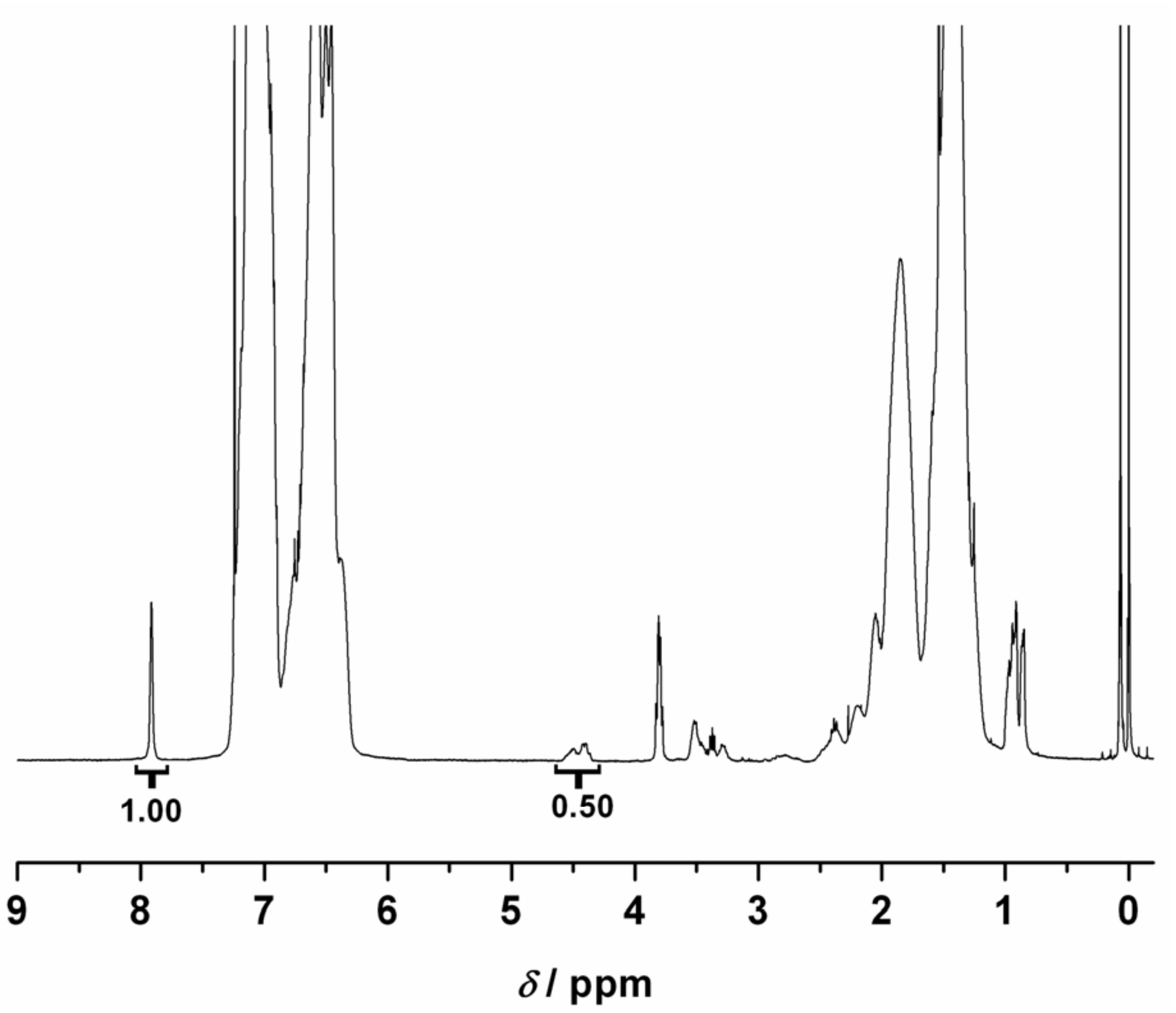


Figure S4. ^{1}H NMR spectrum of **8** in $CDCl_3$ at ambient temperature. From the ratio of the peak areas **N*H₂*** of CA to **C*H*Br** (integral values shown), the end group functionalization can be deduced as being close to ~100 %.

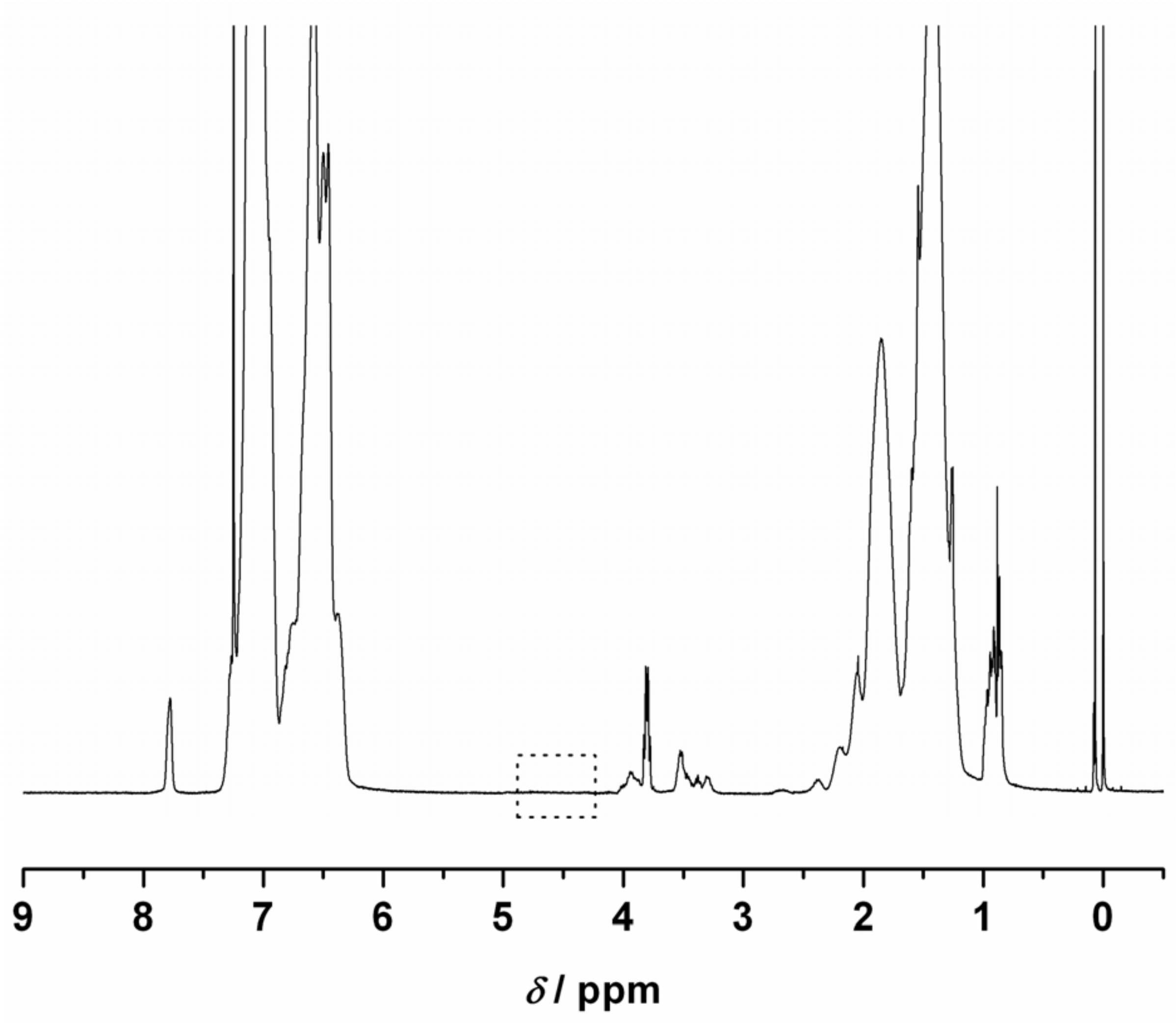


Figure S5. ^{1}H NMR spectrum of **8** with azide functionality in $CDCl_3$ at ambient temperature. The dashed box within the figure shows that **C*H*-Br** of polymer **8** was quantitively converted to its azide functionality.

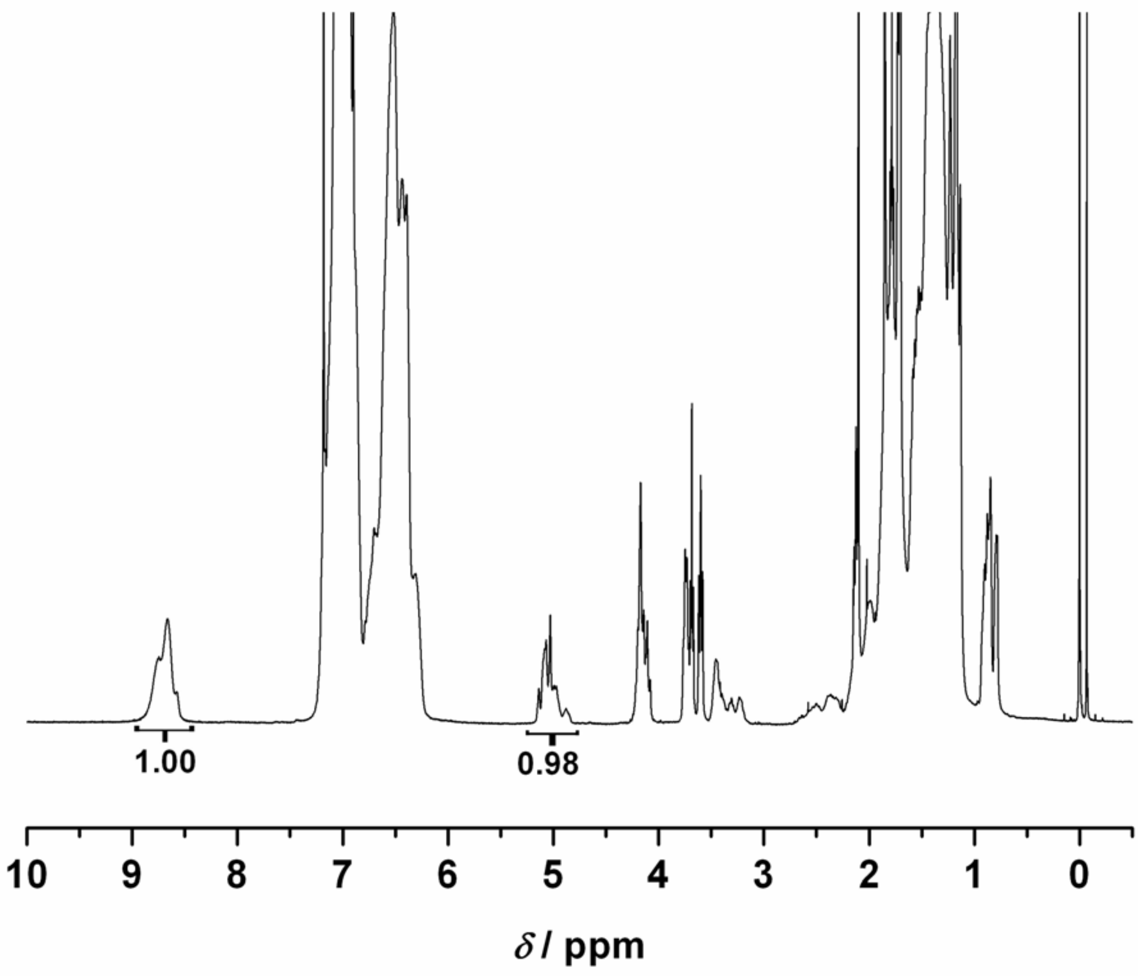


Figure S6. ^{1}H NMR spectrum of **9** in $CDCl_3$ at ambient temperature. . From the ratio of the peak areas $\mathbf{N}\boldsymbol{H_2}$ of CA to $\mathbf{C}\boldsymbol{H_2}$ and $\mathbf{C}\boldsymbol{H}$ (next to triazole ring) (integral values shown), the end group functionalization can be deduced as being close to ~98 %.

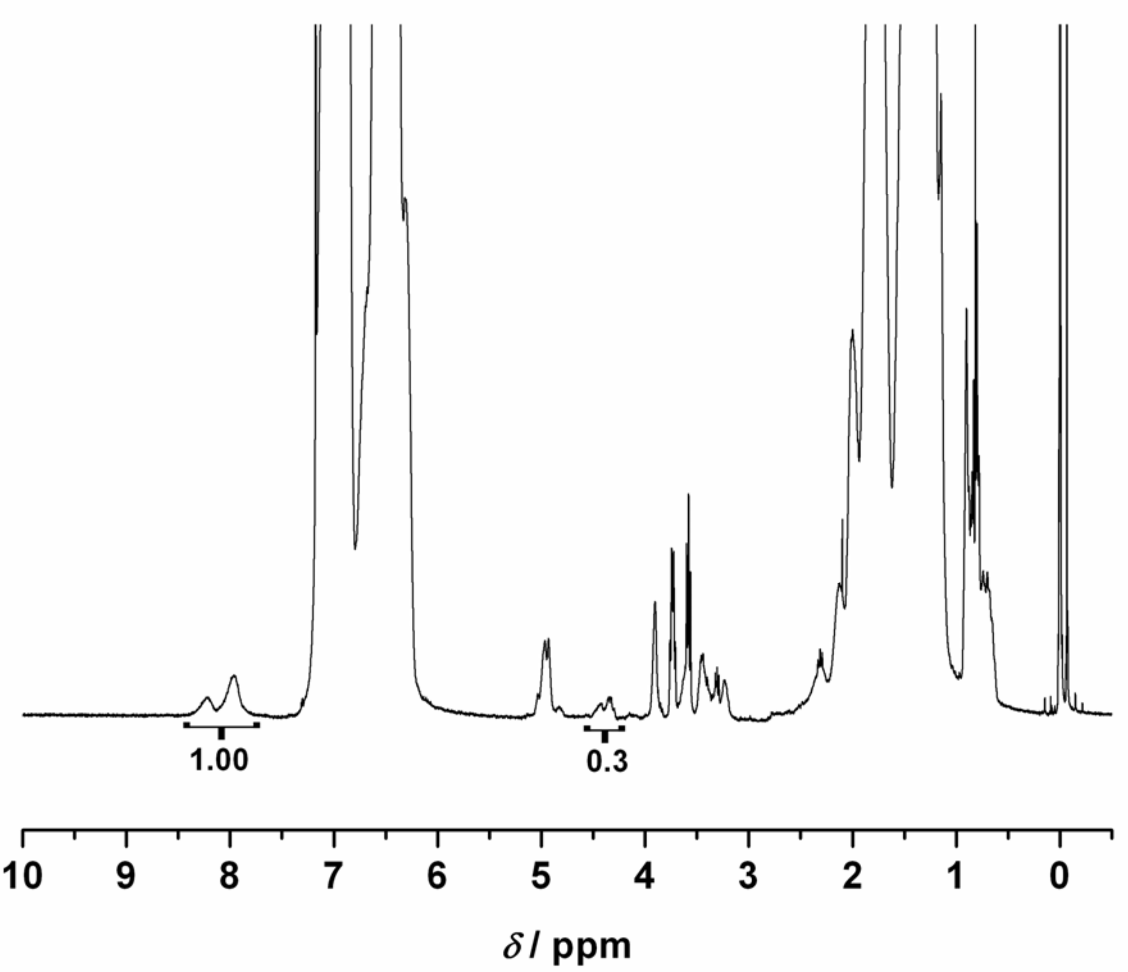


Figure S7. ^{1}H NMR spectrum of **10** in $CDCl_3$ at ambient temperature. From the ratio of the peak areas **N*H*** (three protons) of CA and Thy to **C*H*Br** (one proton) (integral values shown), the end group functionalization can be deduced as being close to ~87 %.

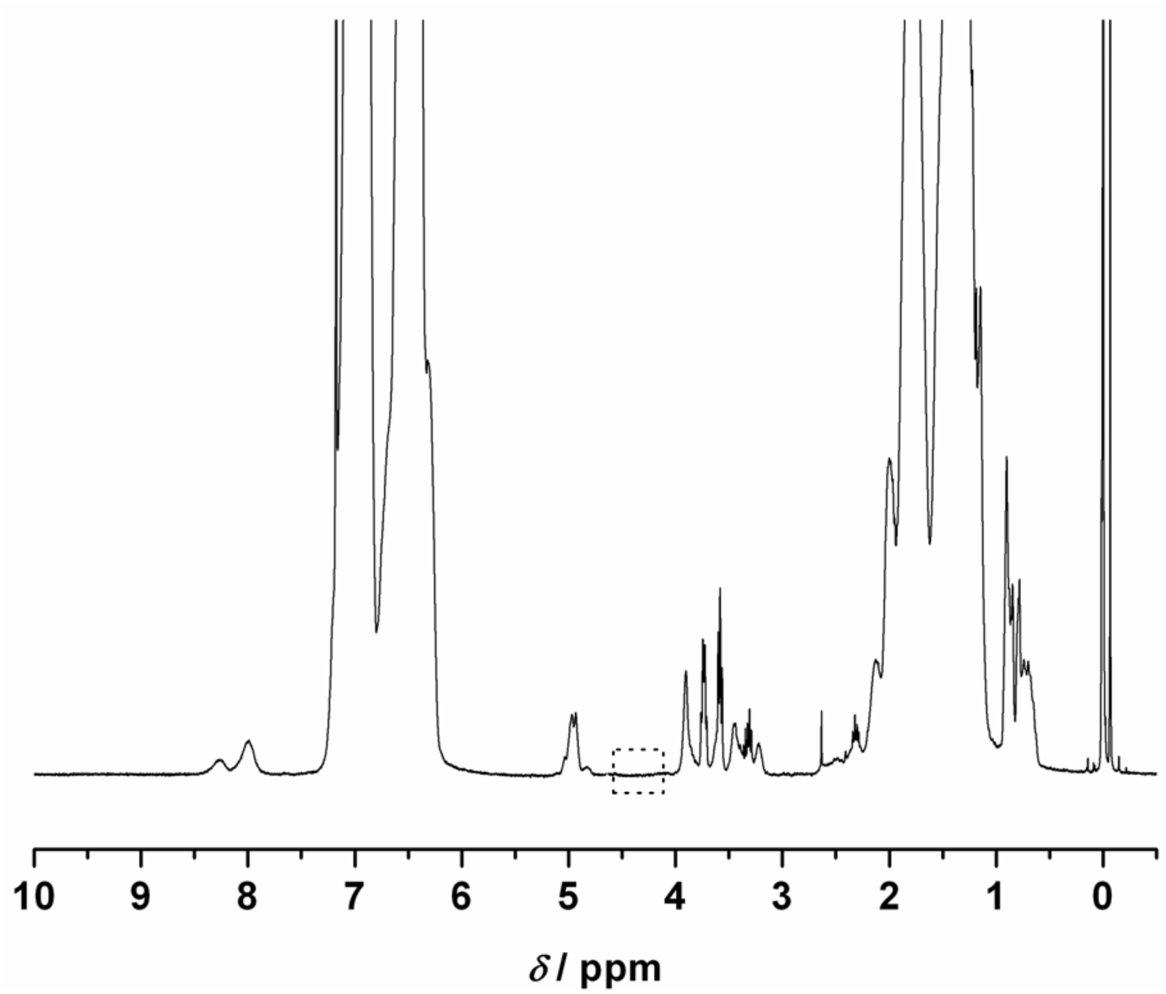


Figure S8. ^{1}H NMR spectrum of **10** with azide functionality in $CDCl_3$ at ambient temperature. The dashed box within the figure shows that **C*H*-Br** of polymer **10** was quantitively converted to its azide functionality

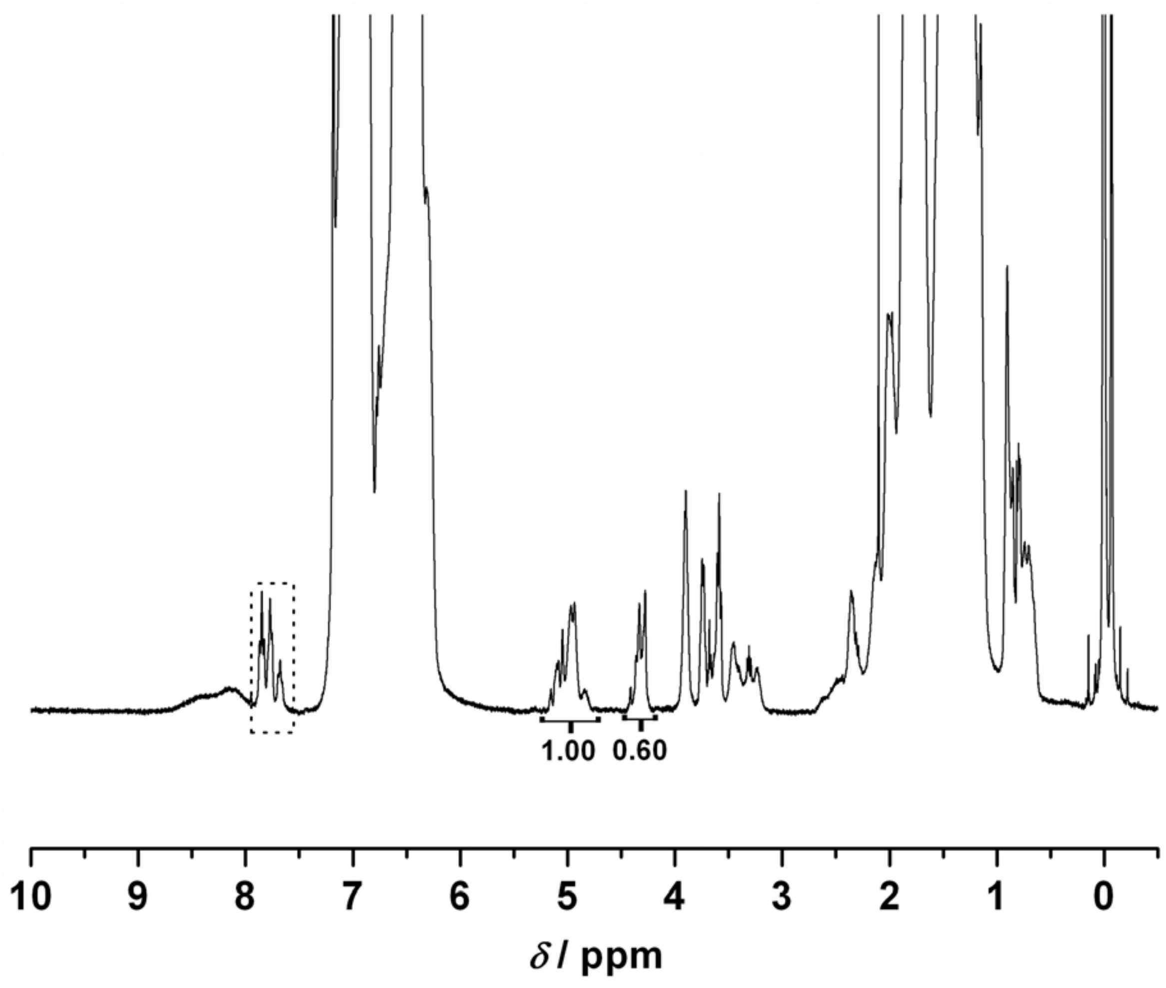


Figure S9. ^{1}H NMR spectrum of **11** in $CDCl_3$ at ambient temperature. From the ratio of the peak areas (**C***H_2*)$_2$ and (**C***H*)$_2$ (next to triazole ring) and C(**OC***H_2*)$_2$ (integral values shown), the end group fidelity can be deduced as being close to ~91 %. The dashed box within the figure shows that the aromatic protons of the compound **3**.

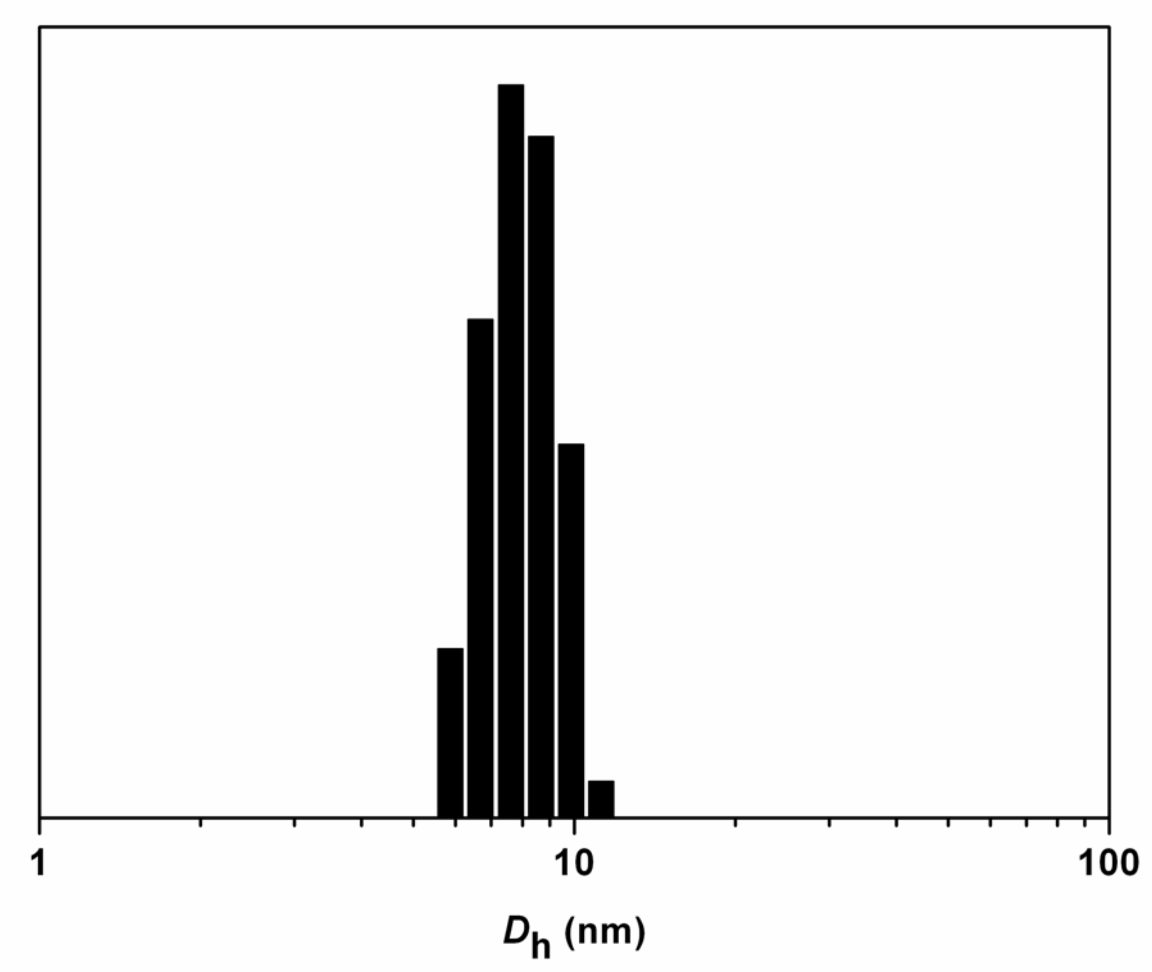


Figure S10. The mean diameter of self-folded single polymer chain **14** in 2 mM concentration in dichloromethane at ambient temperature.

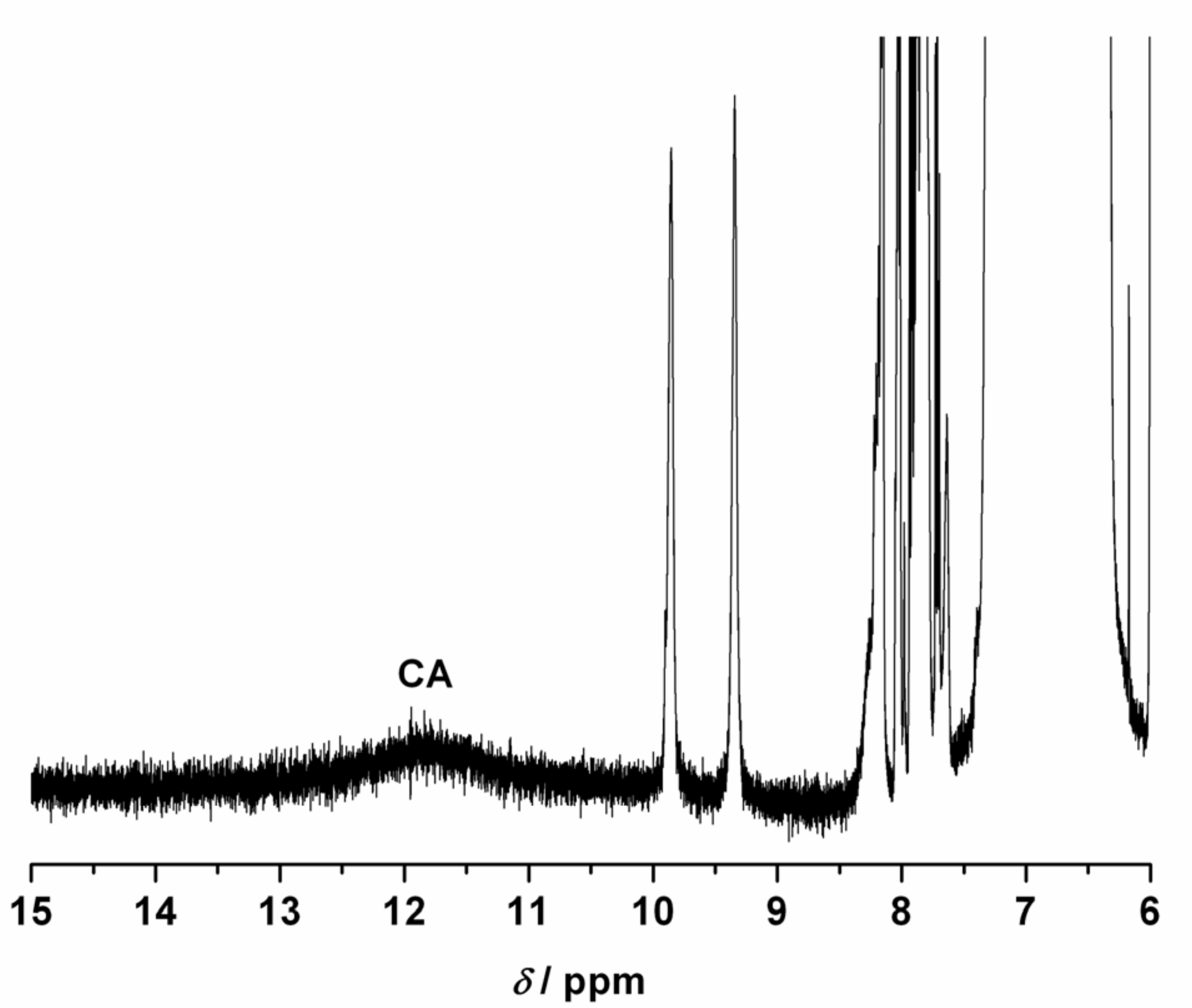


Figure S11. Magnified ^{1}H NMR of single chain self-folded of the polymer **14** in [D_2] tetrachloroethane at +40 °C showing bound imide protons of cyanuric acid (CA).

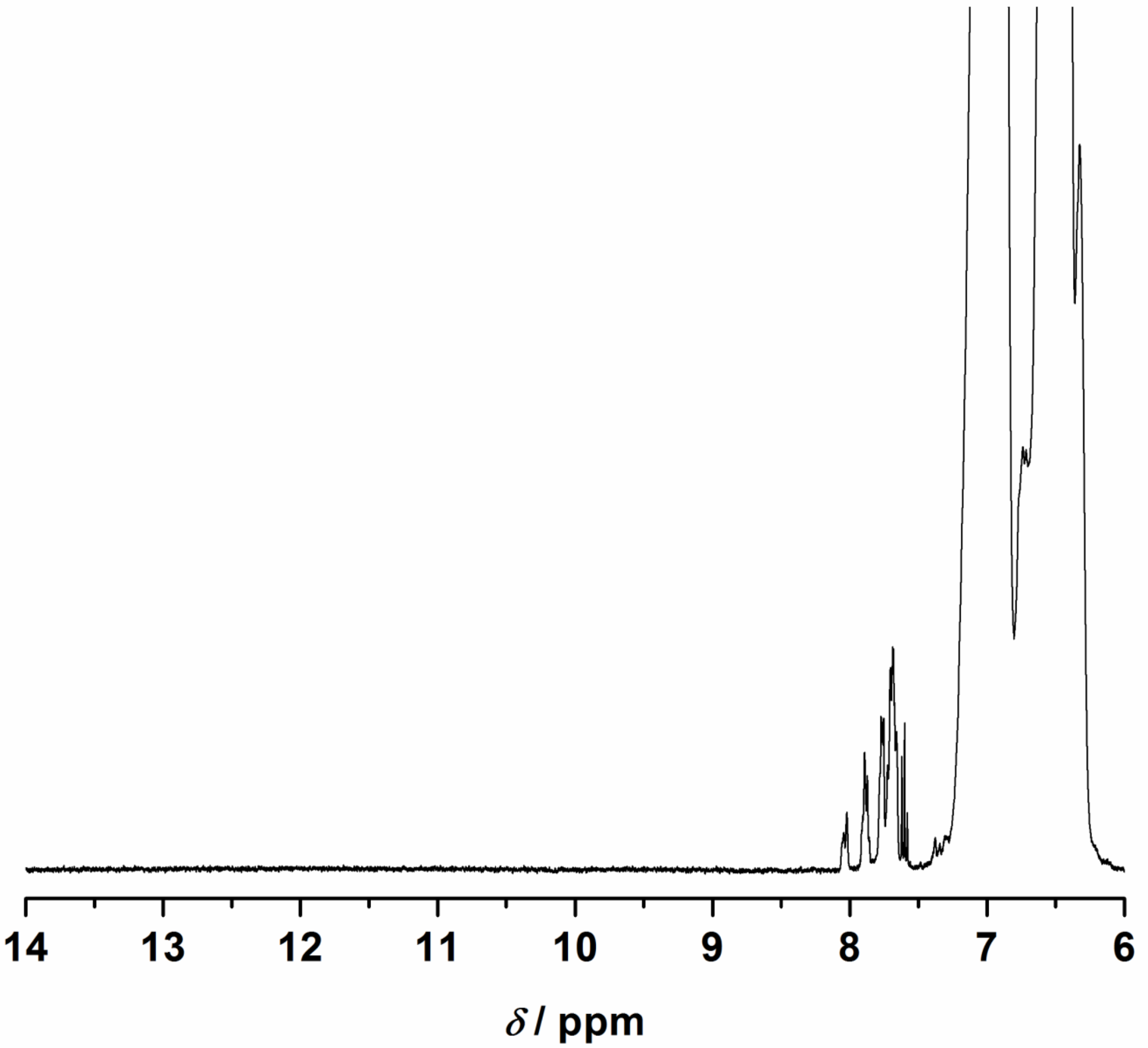


Figure S12. Magnified ^{1}H NMR of polymer **14** in CD_2Cl_2 and CD_3OD ($c_{\text{d-methanol}}$ = 0.17 mol·L^{-1}) in 2 mM concentration at the ambient temperature.

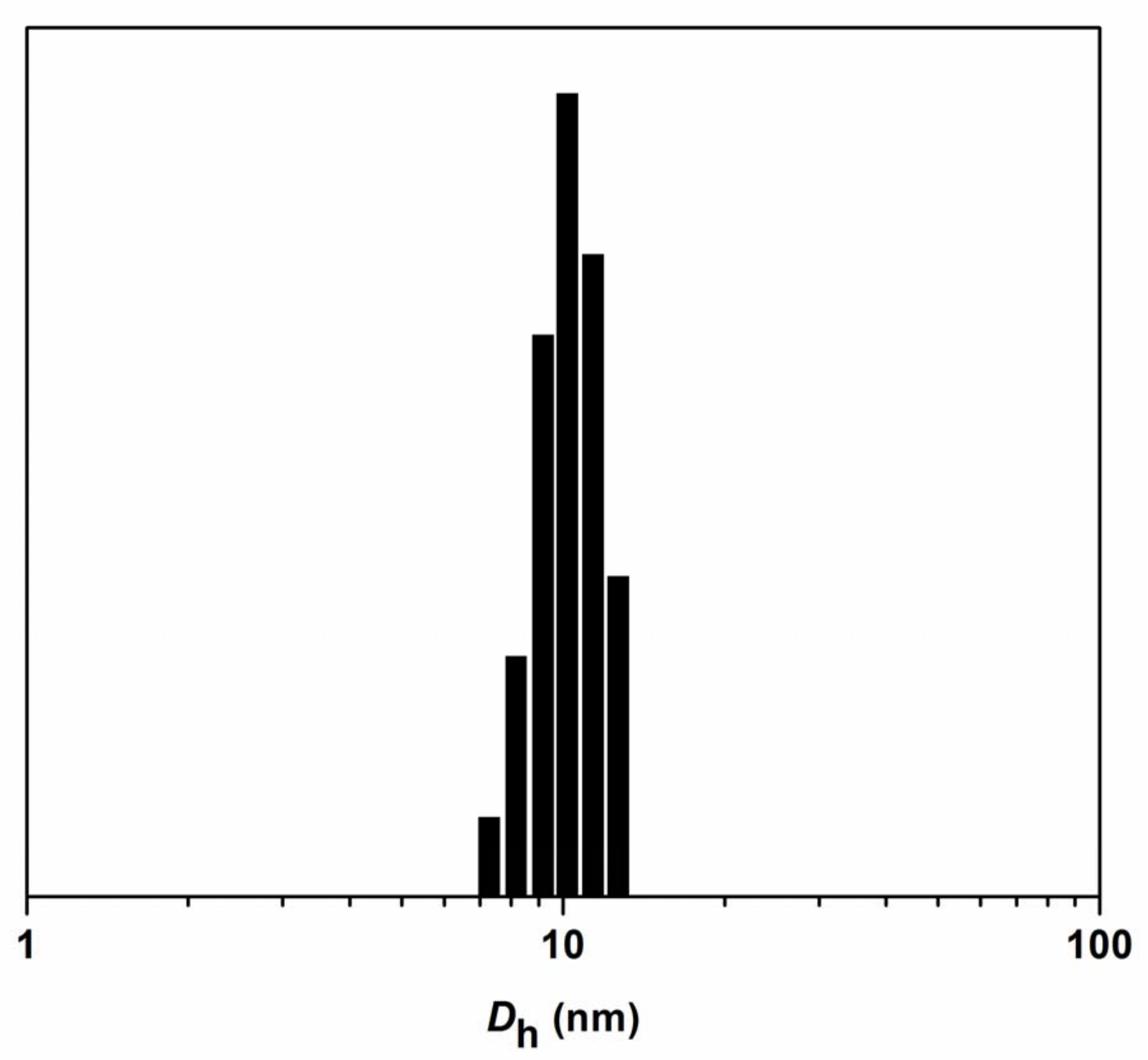


Figure S13. The mean diameter of the single polymer chain **14** determined at 90°,in 2 mM concentration in dichloromethane and methanol (c_{methanol} = 0.17 mol·L^{-1}) at ambient temperature.

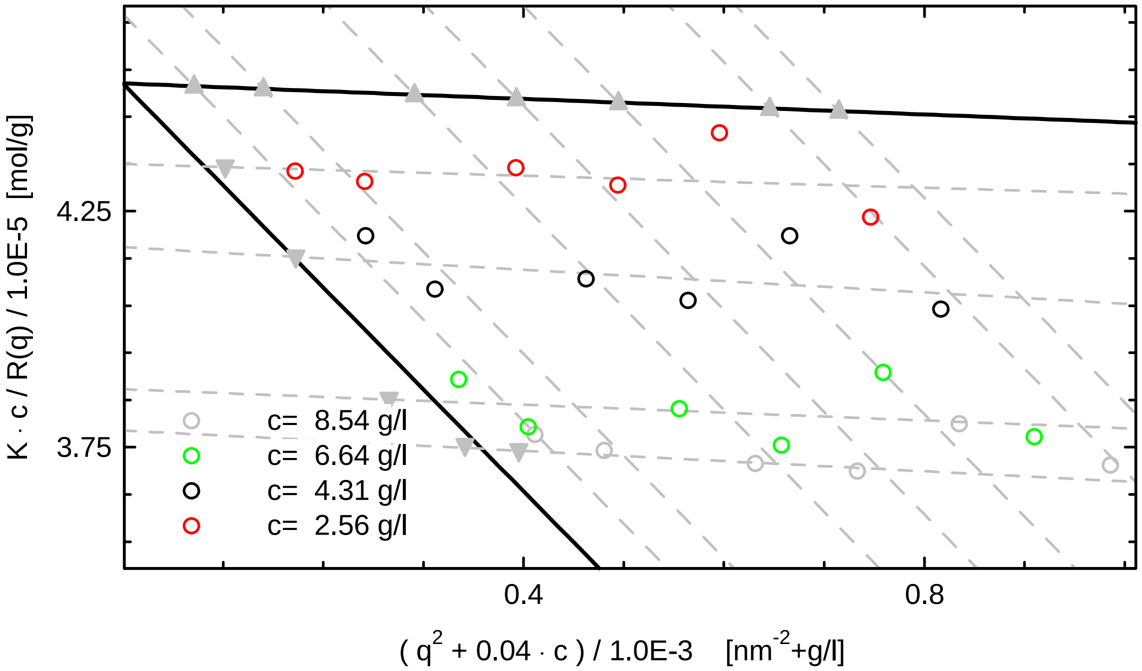


Figure S14. Zimm-plot obtained by SLS measurement for polymer **14** dissolved in dichloromethane.

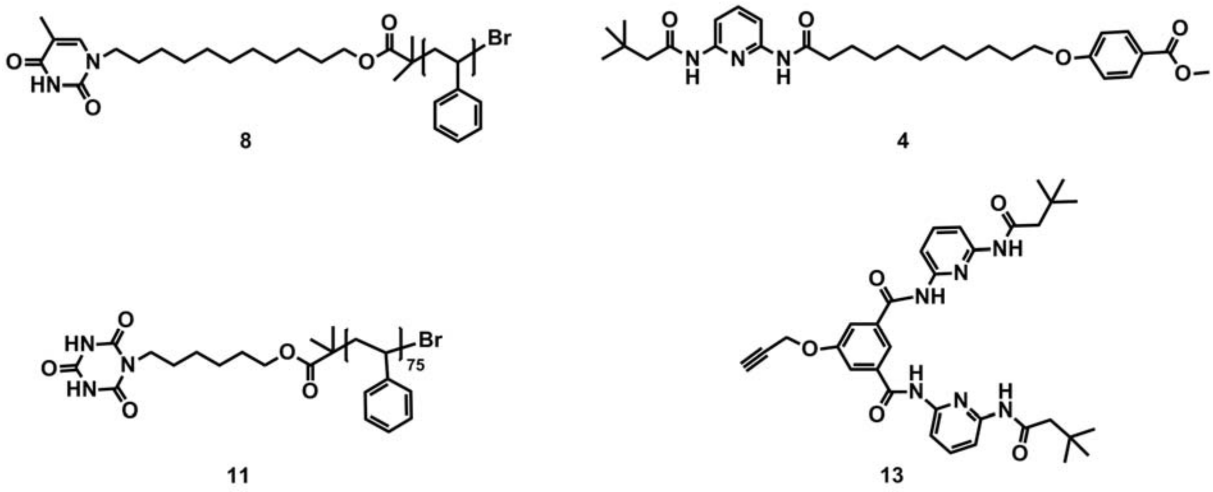
Mathematical model chosen to determine K_{ass}: The data were fitted to the following equation to provide K_{ass}:

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{H}} + \frac{(\delta_{\mathrm{HG}}-\delta_{\mathrm{H}})\{\left([\mathrm{H_t}]+[\mathrm{G_t}]+\frac{1}{\mathrm{K_a}}\right)-(\left([\mathrm{H_t}]+[\mathrm{G_t}]+\frac{1}{\mathrm{K_a}}\right)^2-4[\mathrm{H_t}][\mathrm{G_t}])^{1/2}\}}{2[\mathrm{H_t}]} \qquad \text{(eq. 1S)}$$

where the experimentally determined parameters are as follows: $[\mathrm{G_t}]$ and $[\mathrm{H_t}]$, the total guest and host concentrations, respectively, δ_{obs} the observed shift, and δ_{H}, the shift of the host in the absence of guest and δ_{HG} the shift in the fully associated system. K_{a} is obtained by implicitly solving the above equation via a fitting exercise to match the resulting δ_{obs} with its experimentally found value.

Table S1. Chemical shifts and concentrations of the recognition units, which are used in the mathematical model above. The values provided in the table are taken from our previous study where the small molecule association between Thy (polymer terminus) **8** and DAP (small molecule) **4** as well as CA (polymer terminus) **11** and HW (small molecule) **13** (see Scheme S1 below) was followed by ^{1}H-NMR in a concentration dependent series going to full association (to obtain δ_{HG}), whose values are listed in the below table.[2]

Recognition Units	Concentrations	δ_{obs} / ppm	δ_{H} / ppm[2]	δ_{HG} / ppm[2]
Thymine	1×10^{-3} mol L^{-1}	9.10	7.87	11.83
Cyanuric acid	1×10^{-3} mol L^{-1}	13.39	7.98	13.50



Scheme S1. Structures of the association units employed in ref. 2

References and Notes

1 C. Strazielle, H. O. Benoit, O. Vogl, O. *Eur. Polym. J.*, 1978, **14**, 331-334.

2 O. Altintas, T. Rudolph, C. Barner-Kowollik, *J. Polym. Sci. Part A: Polym. Chem.* 2011, **49**, 2566-2576.