Supplementary Information

Double thermoresponsive graft copolymers with different chain ends: feasible precursors for covalently crosslinked hydrogels

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1. Experimental set-up

An LED strip was stuck to the inner side of an aluminum cylinder with a diameter of about 16.5 cm (**Fig. S1**). The light intensity and wavelength were changed by a remote control. The light intensity was characterized by a S120UV photodiode sensor head from Thorlabs. The positions of the oil bath and the polymerization vial in the reactor were kept as constant as possible for every polymerization to ensure a satisfying reproducibility.
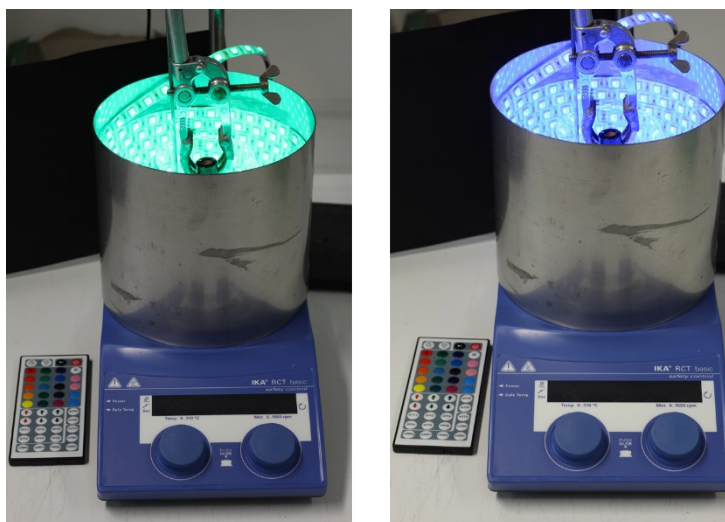

Fig. S1 Experimental set-up for photoiniferter RAFT polymerizations.

2. NMR analysis

2.1 Determination of the total conversion of OEGMA and BTPEMA

The total conversion (α) of OEGMA and BTPEMA was calculated through the decline of the proton signals from the monomers in the reaction mixture (**Fig. S2**):

$$\alpha = \left(1 - \frac{I_{O_1+B_1} + I_{O_1'+B_1'}}{I_{O_0+B_0} + I_{O_0'+B_0'}}\right) \times 100\% \tag{1}$$

$I_{O_0+B_0}$ and $I_{O_0'+B_0'}$ are the signal integrals at the beginning of the polymerization, while $I_{O_1+B_1}$ and $I_{O_1'+B_1'}$ are those in the end.
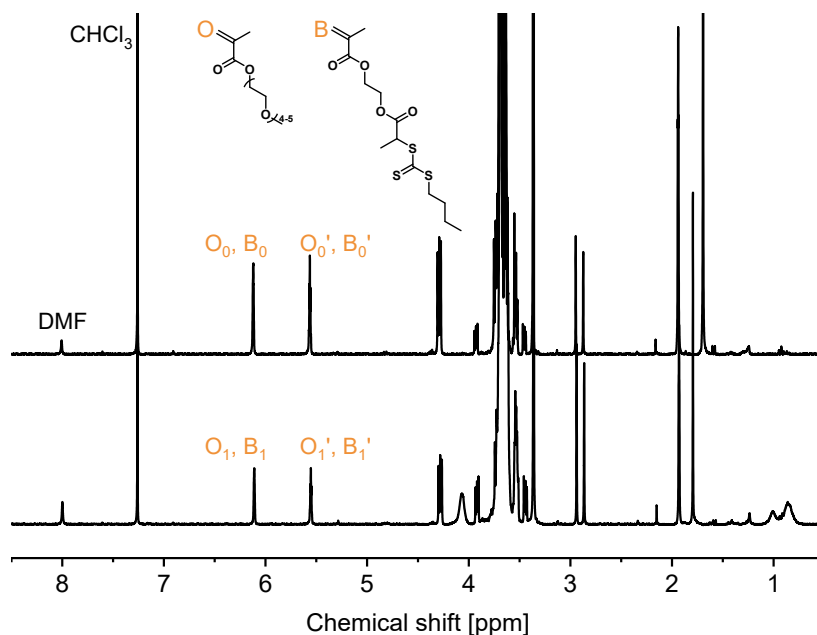

Fig. S2 Typical ^{1}H-NMR spectra of the reaction mixtures at the beginning of the polymerization (top) and at the end of the polymerization (bottom). The protons used for the conversion calculation are assigned to the signals.

Once α after the polymerization is calculated, the theoretical molecular weight of the statistical copolymer can be calculated as follows:

$$\bar{M}_{n,th} = \alpha\left(\frac{[OEGMA]_0}{[RAFT]_0}M_{OEGMA} + \frac{[BTPEMA]_0}{[RAFT]_0}M_{BTPEMA}\right) + M_{RAFT} \tag{2}$$

$[OEGMA]_0$ and $[BTPEMA]_0$ are the initial concentrations of the monomers. $[RAFT]_0$ is the initial concentration of the RAFT agent. M_{OEGMA}, M_{BTPEMA}, and M_{RAFT} are the molecular weights of the monomers and RAFT agent, respectively.

2.2 Determination of the conversion of NIPAM

The conversion of NIPAM was also calculated through the decline of the proton signal from the monomer in the reaction mixture (**Fig. S3**):

2

$$\alpha = \left(1 - \frac{I_{N_1}}{I_{N_0}}\right) \times 100\% \tag{3}$$

I_{N_0} is the signal integral at the beginning of the polymerization, while I_{N_1} is that in the end.
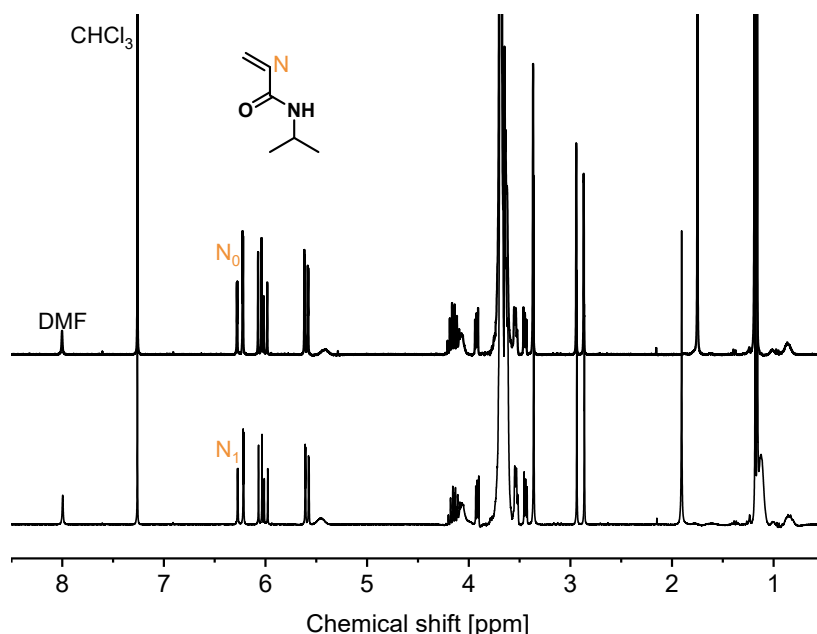

Fig. S3 Typical ^{1}H-NMR spectra of the reaction mixtures at the beginning of the polymerization (top) and at the end of the polymerization (bottom). The proton used for the conversion calculation is assigned to the signals.

Once α after the polymerization is calculated, the theoretical molecular weight of the graft copolymer can be calculated as follows:

$$\bar{M}_{n,th} = \alpha \frac{[NIPAM]_0}{[backbone]_0} M_{NIPAM} + \bar{M}_{n,th(backbone)} \tag{4}$$

2.3 Determination of the molar ratio between OEGMA and BTPEMA

With the ^{1}H-NMR spectra of the statistical copolymers shown in **Fig. S4** and **Fig. S5**, the molar ratios (OEGMA/BTPEMA) in two backbones can be calculated by the signal integrals I_A and I_B:
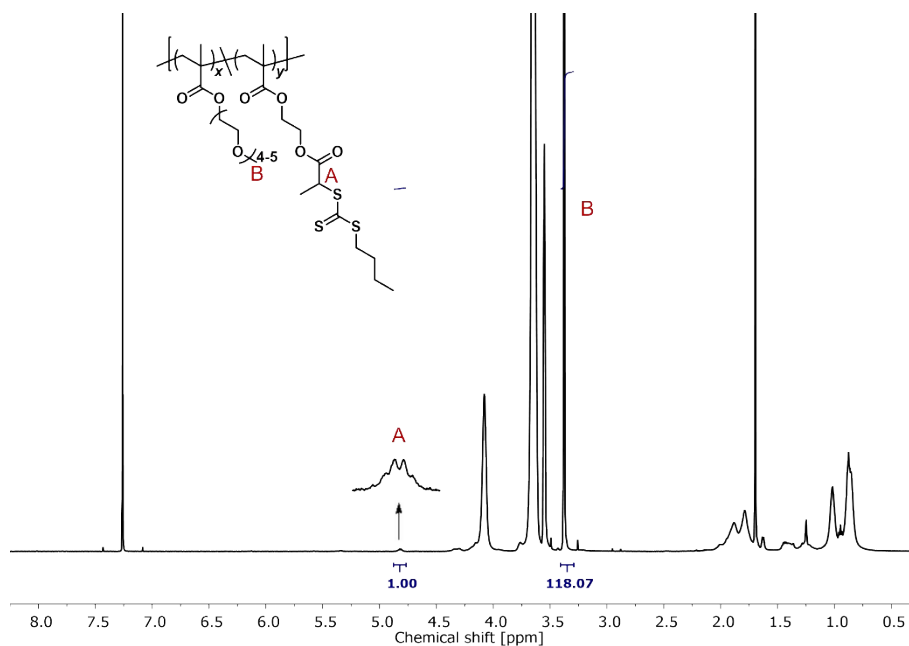
$$\frac{OEGMA}{BTPEMA} = \frac{I_B/3}{I_A} \tag{5}$$

3

Fig. S4 ^{1}H-NMR spectrum of P(O$_{245}$B$_6$) in CDCl$_3$ with the assignment of the proton signals (chain ends of the backbone are not shown here).
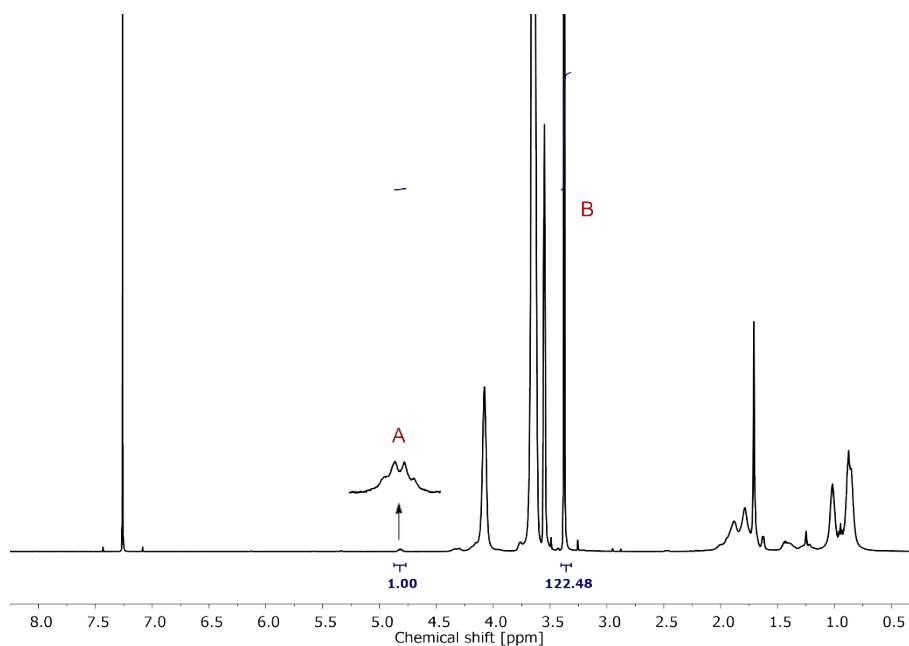

Fig. S5 ^{1}H-NMR spectrum of P(O$_{234}$B$_6$)-COOH in CDCl$_3$.

4

2.4 Determination of the molar ratio between OEGMA and NIPAM

With the ^{1}H-NMR spectra of the graft copolymers shown in **Fig. S6** and **Fig. S7**, the molar ratios (OEGMA/NIPAM) in two graft copolymers can be calculated by solving the following equations:

$$I_{A+C} = NIPAM + 2 \times OEGMA \tag{6}$$

$$I_B = 3 \times OEGMA \tag{7}$$

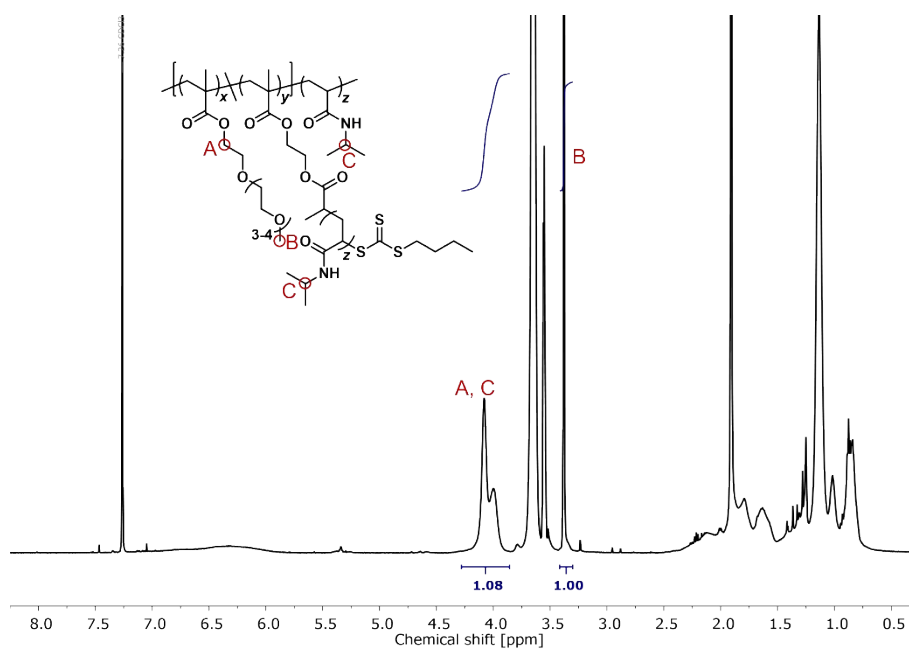**Fig. S6** ^{1}H-NMR spectrum of PO$_{245}$(PN$_{40}$)$_7$ in CDCl$_3$ with the assignment of the proton signals (chain ends of the backbone are not shown here).
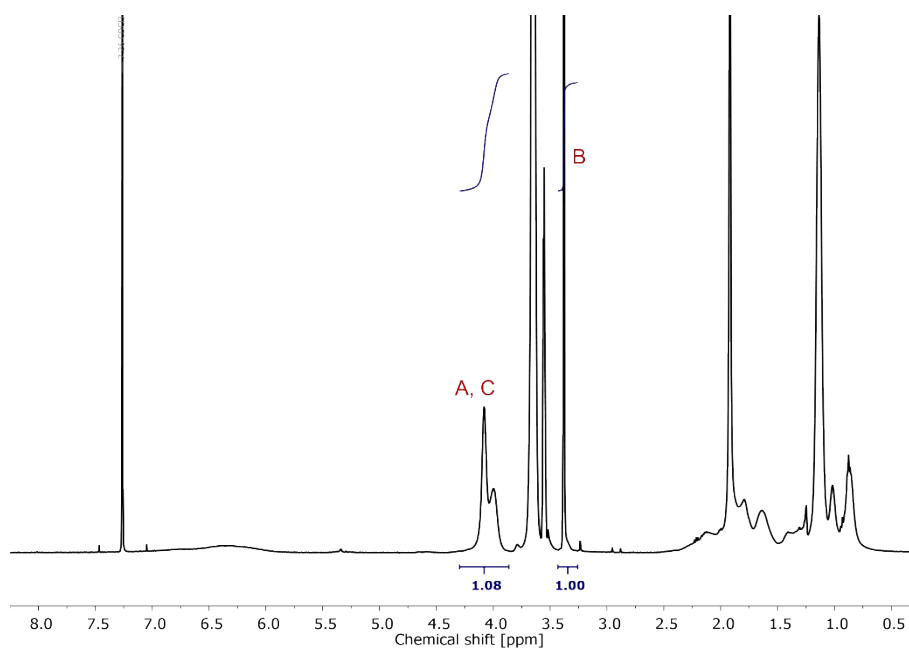
Fig. S7 ^{1}H-NMR spectrum of PO$_{234}$(PN$_{43}$)$_7$-COOH in CDCl$_3$.

3. Kinetic study of chain extension
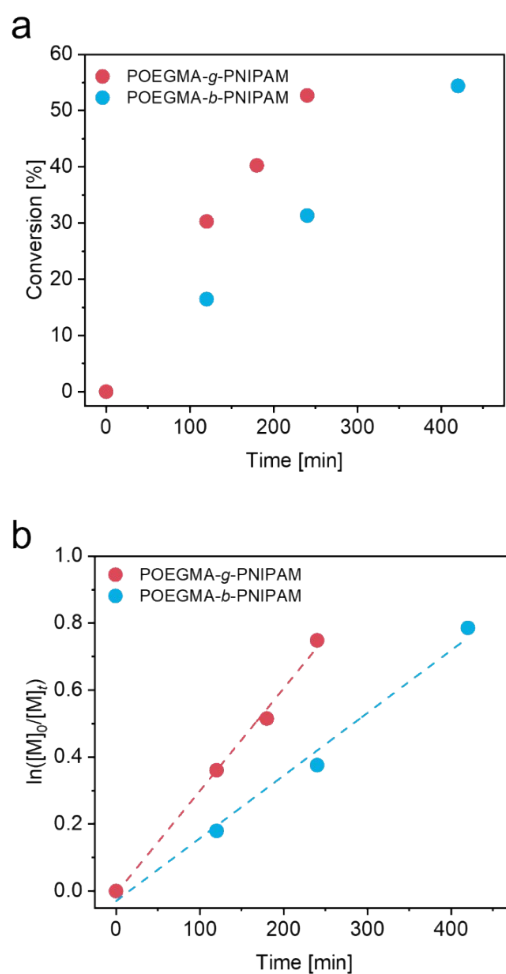
Fig. S8 (a): Monomer conversions of chain extensions from PO$_{234}$-COOH and P(O$_{234}$B$_6$)-COOH. A block copolymer and a graft copolymer were supposed to be obtained, respectively; (b): pseudo first-order kinetics plots of both chain extensions.

4. Static light scattering (SLS) measurements

The aqueous solution of $PO_{234}(PN_{43})_7$-COOH with a fixed concentration ($c = 0.1\%$ [w/w]) was measured at 25 °C and 40 °C by SLS. The range of the scattering angles of the measurements was from 30° to 150° with a step of 10°. The results are shown in **Fig. S9**.
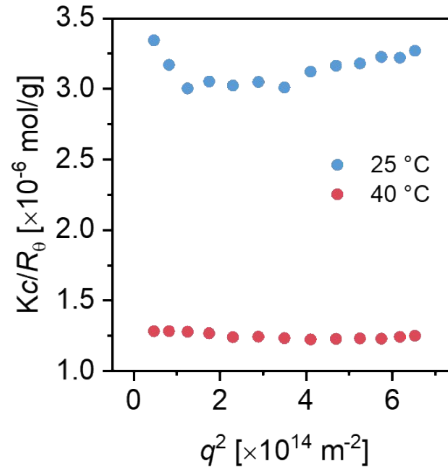

Fig. S9 SLS data of the aqueous solution of $PO_{234}(PN_{43})_7$-COOH ($c = 0.1\%$ [w/w]) at two different temperatures.

The weight average molecular weights ($\bar{M}_w$) at both temperatures were estimated by the partial Zimm approach:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w}\left(1 + \frac{R_g^2 q^2}{3}\right) \tag{8}$$

where K, c, R_θ, R_g, and q are the optical constant, concentration, difference in the Rayleigh ratio between the polymer solution and the solvent, radius of gyration, and scattering vector, respectively.

According to the SLS results, the absolute $\bar{M}_w$ of the formed micelles ($\bar{M}_{w,agg}$) at 40 °C was about 784 kDa. The absolute $\bar{M}_w$ of the unimers ($\bar{M}_{w,uni}$) dissolved at 25 °C was about 324 kDa. The deviation from the theoretical value could be attributed to the inaccurate concentration, but it has no influence on the estimation of the aggregation number ($N_{agg} = \bar{M}_{w,agg}/\bar{M}_{w,uni}$).

5. Cumulant approach for evaluation of dynamic light scattering (DLS) data

In the DLS measurements, the obtained intensity correlation function ($g_2(\tau)$) for one size distribution was fitted with the following standard function:

$$g_2(\tau) = B + \beta exp\left(-2\bar{\Gamma}\tau\right)\left(1 + \frac{\mu_2}{2!}\tau^2 - \frac{\mu_3}{3!}\tau^3 + ...\right)^2 \tag{9}$$

where B represents the baseline, β denotes the stretching factor (contrast), $\bar{\Gamma}$ is the mean decay rate, μ_2, and μ_3 are the cumulants. The hydrodynamic radius R_H is calculated through the Stokes-Einstein equation:

$$R_H = \frac{k_B T q^2}{6\pi\eta\bar{\Gamma}} \tag{10}$$

where k_B is the Boltzmann constant, T is the temperature, q is the scattering vector and η is the viscosity.

For two size distributions, the data were fitted with the sum of two exponential decay functions:

$$g_2(\tau) = B + \beta\left(\sum_{i=1}^{2} f_i \exp\left(-\bar{\Gamma}_i\tau\right)\left(1 + \frac{\mu_{2,i}}{2!}\tau^2 - \frac{\mu_{3,i}}{3!}\tau^3 + ...\right)\right)^2 \tag{11}$$

where f_i represents the fraction of different particle species. The hydrodynamic radius $R_{H,i}$ of each specie is calculated through the Stokes-Einstein equation:

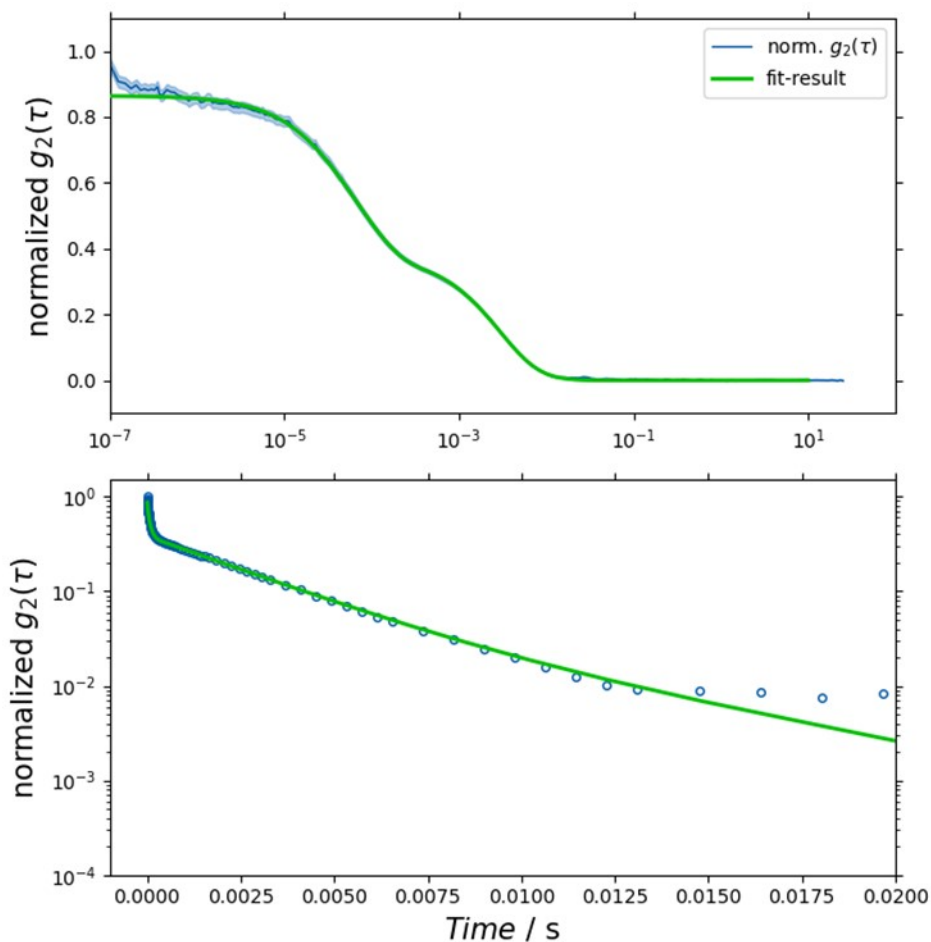$$R_{H,i} = \frac{k_B T q^2}{6\pi\eta\bar{\Gamma}_i} \tag{12}$$

Fig. S10 DLS data of $PO_{245}(PN_{40})_7$ at 40 °C (blue curve) and fit result by using Equation 11 (green curve).
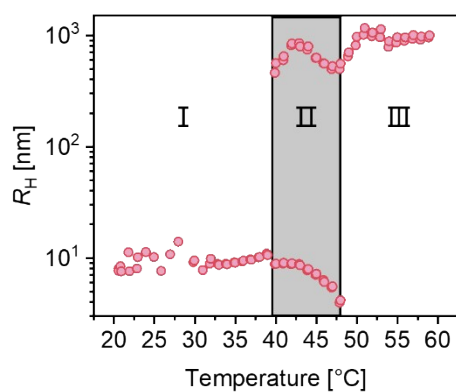

Fig. S11 Evolution of R_H of $PO_{218}(PN_{32})_7$ in a dilute aqueous solution ($c = 0.05\%$ [w/w]) during heating followed by DLS.