

Supporting Information

**A new story of cyclodextrin as a bulky pendent
group causing uncommon behaviour to
random copolymers in solution**

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Characterization The Zimm plots and $^1\text{H-NMR}$ spectrums for the characterization of PNiCD copolymers and PNIPAM for control are shown in Figure S1 and Figure S2, respectively. The concentrations of the series of solution for Zimm plot were 0.4, 0.6, 0.8 mg/mL for PNiCDs and 0.2, 0.4, 0.8 mg/mL for PNIPAM. The samples for ^1H NMR spectrum were measured in deuterium oxide solution, and the monomer ratio was calculated from the integrated area ratio between the peak for the proton on the first carbon of the glucose unit of the cyclodextrin (4.9 ppm) and the methyl proton of the NIPAM monomer (0.95 ppm).

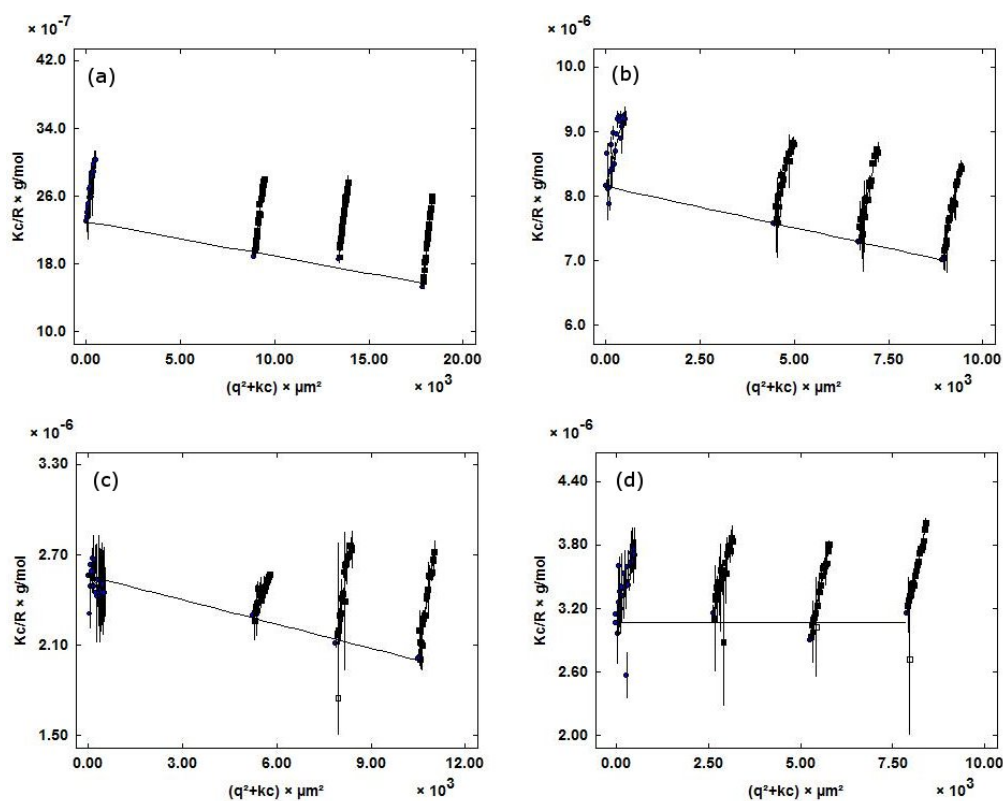


Fig. S1: The Zimm plots of the (a)PNiCD1-1, (b)PNiCD1-2, (c)PNiCD0.5, and (d)PNIPAM.

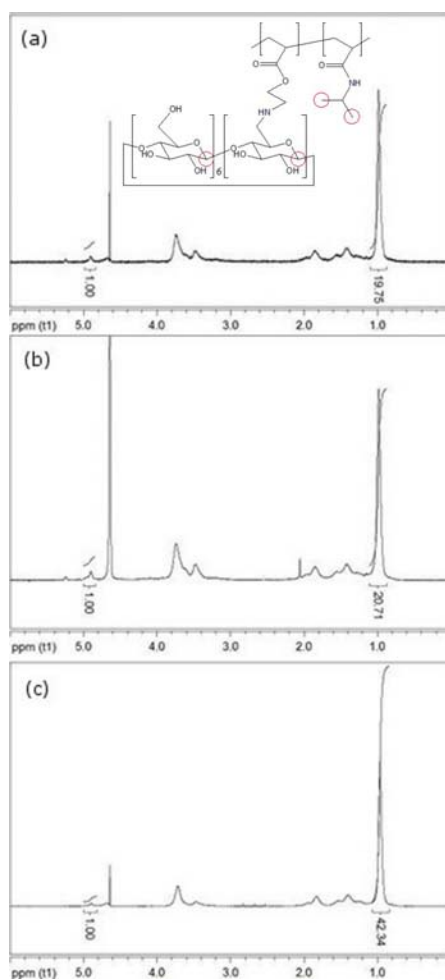


Fig. S2 : The ^1H NMR spectrum for (a)PNiCD1-1, (b)PNiCD1-2, and (c)PNiCD0.5 in deuterium oxide solution.

The Maldi TOF MS spectra of MPEG2k, MPEG-ADA, and MPEG-Azo are shown in Figure S3. The peaks were shifted to high M_w and the displacement of peaks between MPEG2k and MPEG-ADA, MPEG-Azo is $(30+44\times n)$ and $(16+44\times n)$, respectively, which are both consistent with the mass increment by the modification of end function group. 2,5-dihydroxybenzoic acid was used as matrix. ^1H

NMR (CDCl_3) of MPEG-ADA: $\delta = 4.22-4.20$ (d, 2H, COOCH), 3.65-3.55(d, $4\text{H} \times n$, CH_2O in PEG unit), 3.26-3.24 (s, 3H, CH_3), 2.1-1.7 (m, 15H, ADA H). ^1H NMR (CDCl_3) of MPEG-Azo: $\delta = 7.95-7.89$ (m, 4H, Azo H), 7.54-7.44 (m, 3H, in Azo H), 7.27-7.25 (d, 2H, Azo H), 4.29-4.27 (d, 2H, COOCH), 3.65-3.55(d, $4\text{H} \times n$, CH_2O in PEG unit), 3.26-3.24 (s, 3H, CH_3), 2.92-2.90 (d, 2H, CHCOO), 2.81-2.79 (d, 2H, CHCOO).

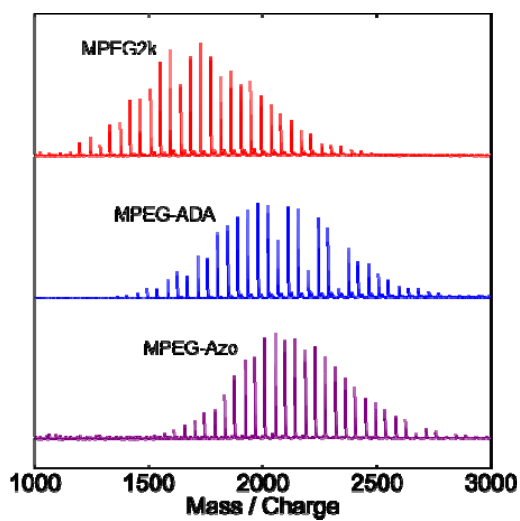


Fig. S3: The Maldi TOF MS spectrum of the MPEG2k, MPEG-ADA, MPEG-Azo.

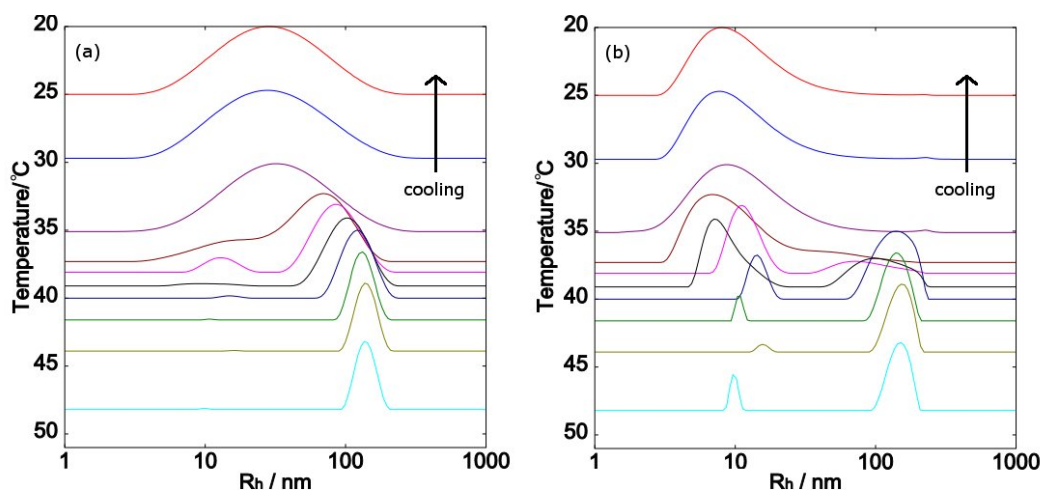


Fig. S4 (a) Unweighted and (b) mass-weighted size distribution plots during stepwise cooling process of PNiCD1-1 after the stepwise heating process.

DLS measurement The dissociation process of the PNiCD1-1 aggregation prepared in stepwise heating is observed by the DLS measurements, and the unweighted and mass-weighted size distribution is plotted in **Fig. S4**. The cooling procedure is composed in stepwise by 1°C for every 30 min (0.033°C/min).