

Supporting Information

Synthesis of Water Soluble Polyrotaxanes by End-capping Polypseudorotaxanes of γ -CDs with PHEMA-PPO-PEO- PPO-PHEMA Using ATRP of MPC

Tao Kong, Jing Lin, Lin Ye, Ai-ying Zhang and Zeng-guo Feng*

School of Materials Science and Engineering, Beijing Institute of Technology

Beijing 100081, China.

E-mail: sainfeng@bit.edu.cn

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Materials

γ -CD (Wako, Japan), PPO-PEO-PPO comprising a central block of 90 PEO units and two flank blocks of 5 PO units having $M_n=4580$ (Zhejiang Huangma Chemical Industry Group Co., Ltd, China) and 2-Methacryloyloxyethyl phosphorylcholine (MPC) (Joy-nature Science and Technology Development institute of Nanjing, China) were used as received without further purification. 2-Hydroxyethyl methacrylate (HEMA) (TCI, Japan) was passed over a short basic alumina column to remove the inhibitor before polymerization. 2-Bromoisobutyryl bromide, 4-dimethylamino-pyridine (DMAP) and tris(2-(dimethylamino)ethyl)amine (Me_6TREN) were available from Alfa Aesar, USA. N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA) was purchased from Sigma, USA. Triethylamine (TEA) (VAS Chemical Reagents Company, China) was refluxed with *p*-toluenesulfonyl chloride and distilled under vacuum. Copper(I) chloride ($Cu(I)Cl$) was prepared from $CuCl_2$, purified by stirring in hydrochloric acid, washed with methanol and finally dried under vacuum prior to use, while Copper(I) bromide ($Cu(I)Br$) was treated with anhydrous acetic acid and refined in the same procedure. CH_2Cl_2 was stirred with CaH_2 and distilled under reduced pressure. DMF was supplied by Sinopharm Chemical Reagent Company, China and used without further purification. All other solvents and reagents were of analytical grade.

Measurements

1H NMR (400 MHz) and 2D-ROESY NMR spectra were recorded on a Bruker ARX-400 spectrometer at room temperature using $DMSO-d_6/D_2O$ (1:1, v/v) as solvent and tetramethylsilane (TMS) as internal standard. Gel permeation chromatographic (GPC) measurements were carried out at 30 °C on a HLC-8320GPC (TOSOH, Japan) instrument using DMF/H_2O (1:1, v/v) added 10 mmol/L LiBr as co-eluent at a flow rate of 0.3 mL/min. The transmittances of solutions of the resulting single-chain stranded γ -CD-based PRs were measured at 500 nm on a Hitachi U-2800 spectro-

photometer equipped with water circulated cell holder after thermostabilized for 10 minutes at each testing temperature point using a 1 cm quartz cell. The value for the cloud point of the mixing solution was defined as the temperature when the transmittance reaches the median in the range of phase transition. Fourier transform infrared spectroscopy (FTIR) spectra were measured using Shimadzu IRTracer-100 FTIR spectrometer at room temperature in the range between 4000 and 500 cm^{-1} , with a resolution of 2 cm^{-1} and 25 scans. Samples were prepared by mixed with dry KBr powder. TGA analyses were performed with a TA SDT 2960 instrument at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ purged with nitrogen, and the temperature was scanned from ambient temperature to 550 $^{\circ}\text{C}$. Wide-angle X-ray diffraction (WXR) measurements were carried out with powder samples using a Shimadzu XD-D1 X-ray diffractometer. The radiation source used was Ni-filtered, Cu $K\alpha$ radiation with a wavelength of 0.154 nm. The voltage was set to be 40 kV and the current 40 mA. Samples were placed on a sample holder and scanned from 4.5 to 60 $^{\circ}$ in 2θ at a speed of 5 $^{\circ} \text{min}^{-1}$. Transmission Electron Microscopy (TEM) image was acquired on a JEM-1200 (JEOL) electron microscope at 120 kV voltages, the sample was prepared by dropping a few microliters of the PR aqueous solution (0.3 %, w/w) onto the copper grid (300 mesh) and dried by slow evaporation for two days.

Preparation

Synthetic pathway of single-chain stranded PR-based multiblock copolymers is outlined in Scheme S1.

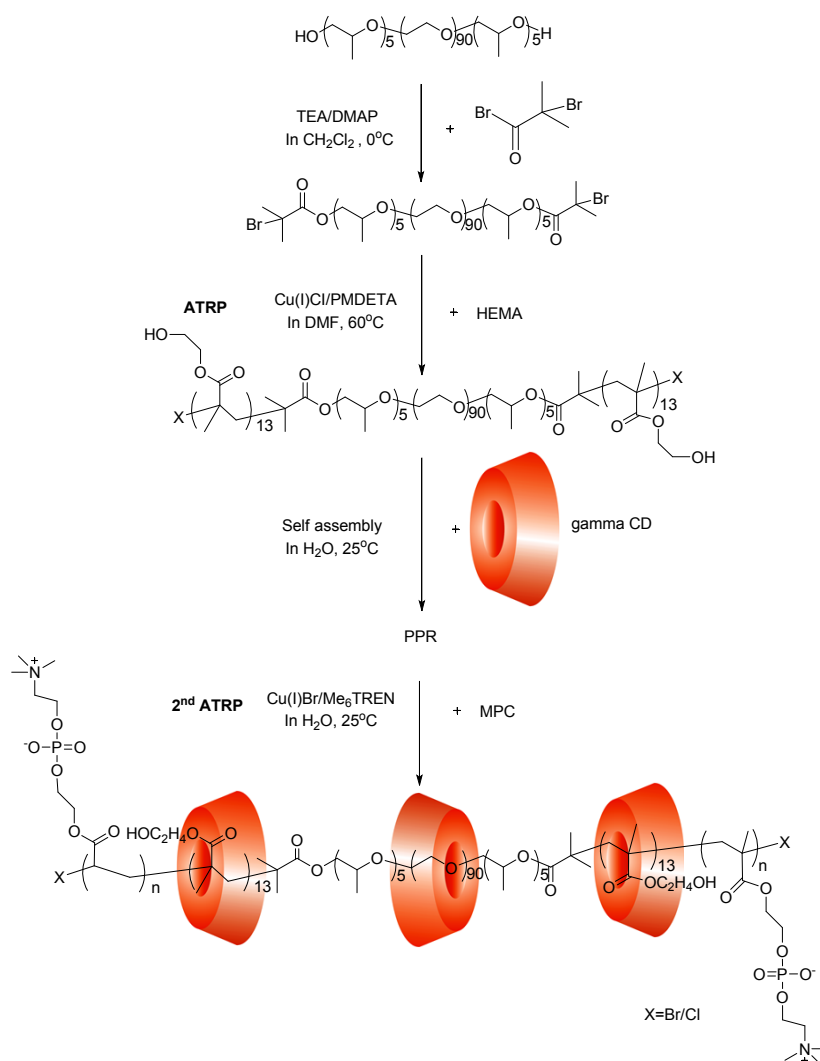
1. Synthesis of 2-bromoisobutyryl end-capped PPO-PEO-PPO (BrPEPBr)

As previously reported¹, PPO-PEO-PPO was converted to a corresponding ATRP macroinitiator through the end-capping reaction with 2-bromoisobutyryl bromide in CH_2Cl_2 in the presence of TEA and DMAP.

2. Synthesis of PHEMA-PPO-PEO-PPO-PHEMA *via* first ATRP of HEMA

A typical procedure for the synthesis of PHEMA-PPO-PEO-PPO-PHEMA pentablock polymer *via* the ATRP of HEMA was as follows². In a sealable Pyrex reactor,

BrPEPBr (0.488 g, 0.1 mmol) was dissolved in 6 mL DMF to which HEMA (0.39 g, 3.0 mmol) and PMDETA (34.7 mg, 0.2 mmol) were added in sequence. The mixture was degassed by three freeze-pump-thaw cycles, then quenched in the liquid nitrogen to which Cu(I)Cl (19.8 mg, 0.2 mmol) was added. The reactants in the reactor were degassed three times by purging with nitrogen. The reactor was sealed under vacuum and the reaction started and maintained for 24 h at 60 °C under stirring. The reaction solution was diluted with 65 ml THF, then passed through basic alumina column to remove Cu complexes and concentrated to give PHEMA-PPO-PEO-PPO-PHEMA as macroinitiator for the second *in situ* ATRP which was precipitated in diethyl ethers followed by drying in yield of 61.6 %.



Scheme S1 Synthetic pathway of single-chain stranded PR-based multiblock copolymers.

3. Preparation of PR-based multiblock copolymers via second *in situ* ATRP of MPC

A protocol for the preparation of PR-based multiblock copolymer built from the self-assembly of PHEMA-PPO-PEO-PPO-PHEMA with γ -CDs was as follows. In a sealable Pyrex reactor, the pentablock polymer (0.10 g, 1.21×10^{-2} mmol) was added to an aqueous solution containing a predetermined amount of γ -CD and 2.5 g ultrapure H₂O, followed by vigorous stirring at 25 °C for 24 hours to produce white PPR slurry. A stoichiometric amount of MPC and 6.8 μ L Me₆TREN (2.5×10^{-2} mmol) were then added to the resulting suspension of PPR in sequence. The mixture was degassed by seven freeze-pump-thaw cycles, then quenched in the liquid nitrogen to which Cu(I)Br (3.6 mg, 2.5×10^{-2} mmol) was added. The reactants in the reactor were degassed three times by purging with nitrogen. The reactor was sealed under vacuum and the reaction started and maintained for 60 h at 25 °C under stirring. The polymerization stopped after breaking the Pyrex reactor, the product was dissolved in DMF/H₂O mixture and dialyzed using a cellulose membrane (molecular-weight cut-off (MWCO)=3500) to remove Cu complexes, residual free γ -CDs and MPC monomers before freeze-drying.

Supplementary Figures

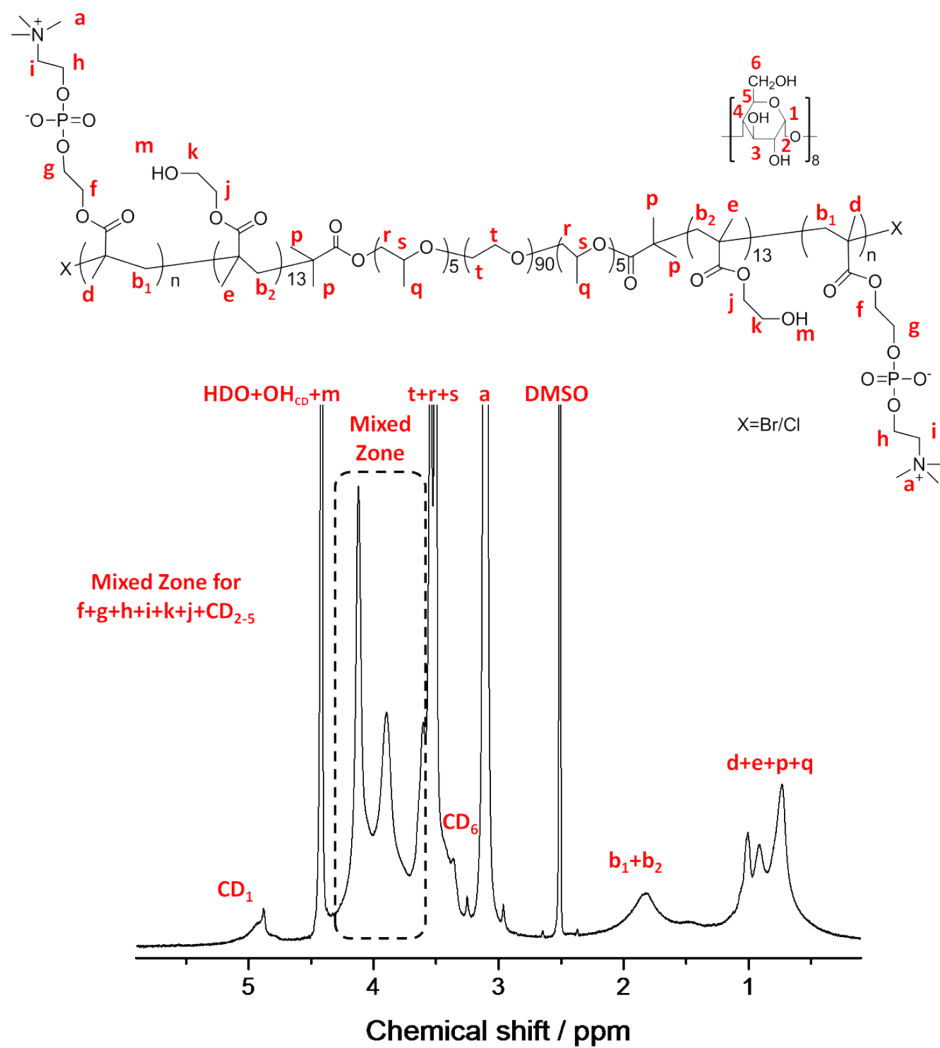


Figure S1 ¹H NMR spectrum of PEP26H29CD98M.

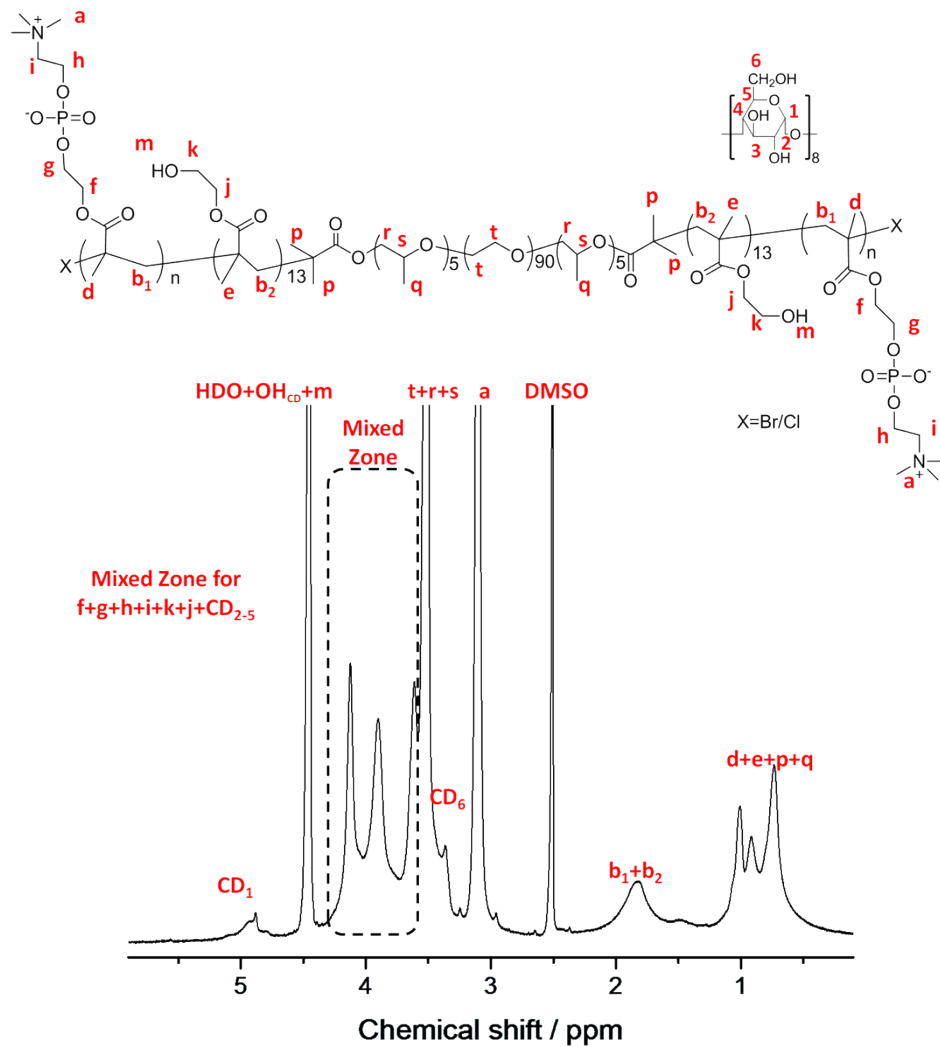


Figure S2 ¹H NMR spectrum of PEP26H29CD70M.

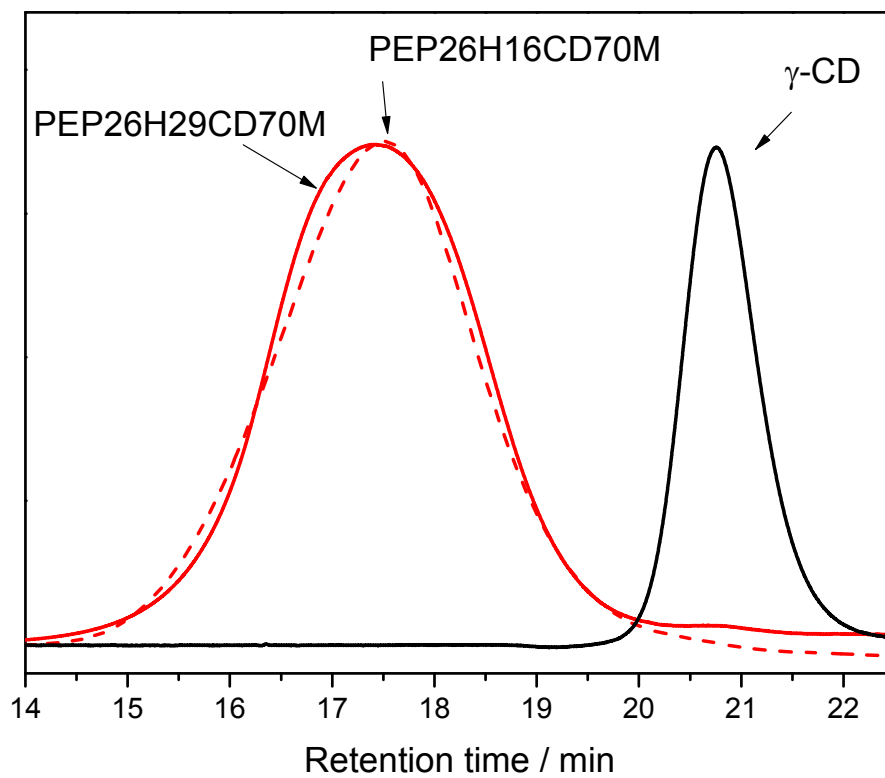


Figure S3 GPC traces of γ -CD, PEP26H16CD70M and PEP26H29CD70M.

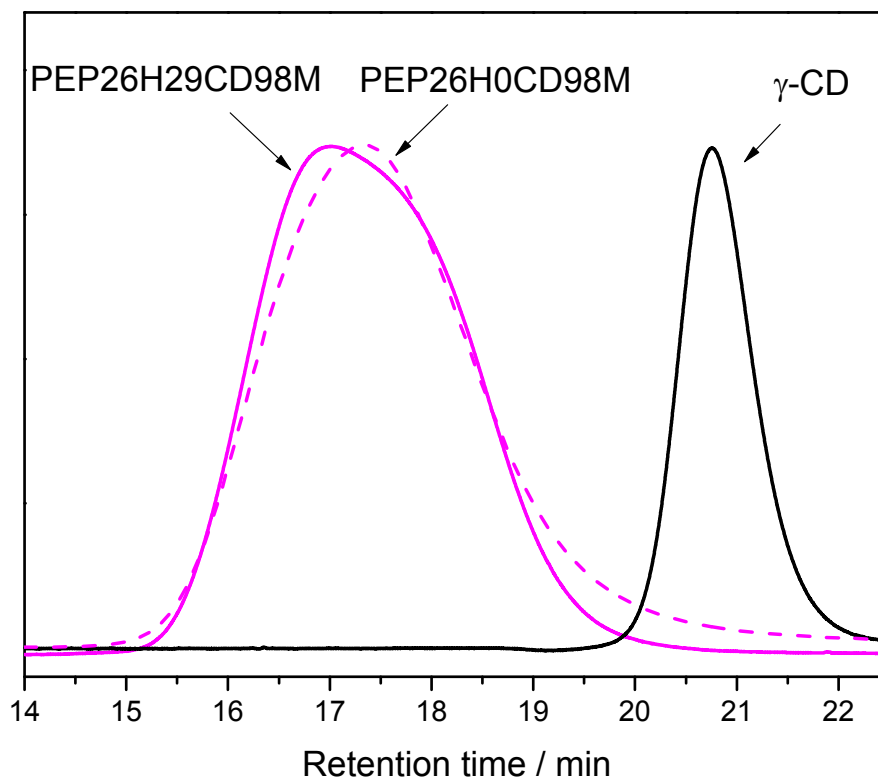


Figure S4 GPC traces of γ -CD, PEP26H0CD98M and PEP26H29CD98M.

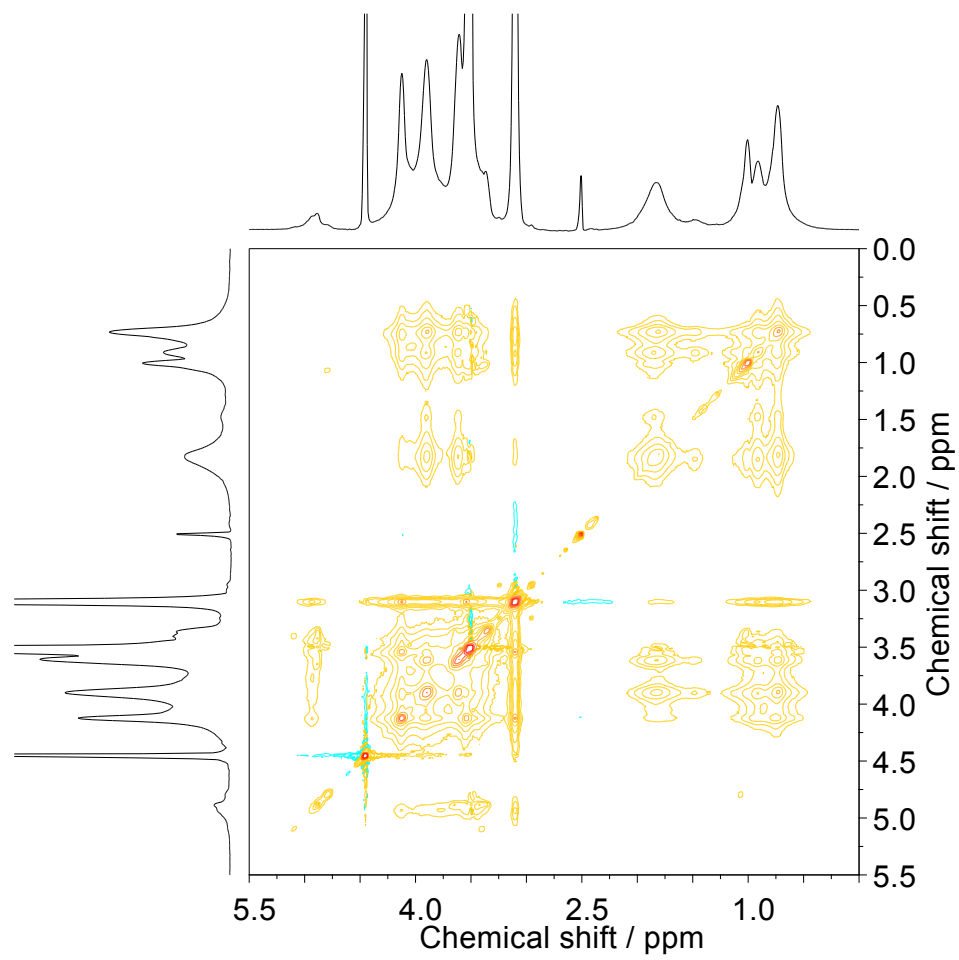


Figure S5 2D-NOESY NMR spectrum of PEP26H29CD42M in DMSO- d_6 /D $_2$ O (1:1, v/v) at 25 °C.

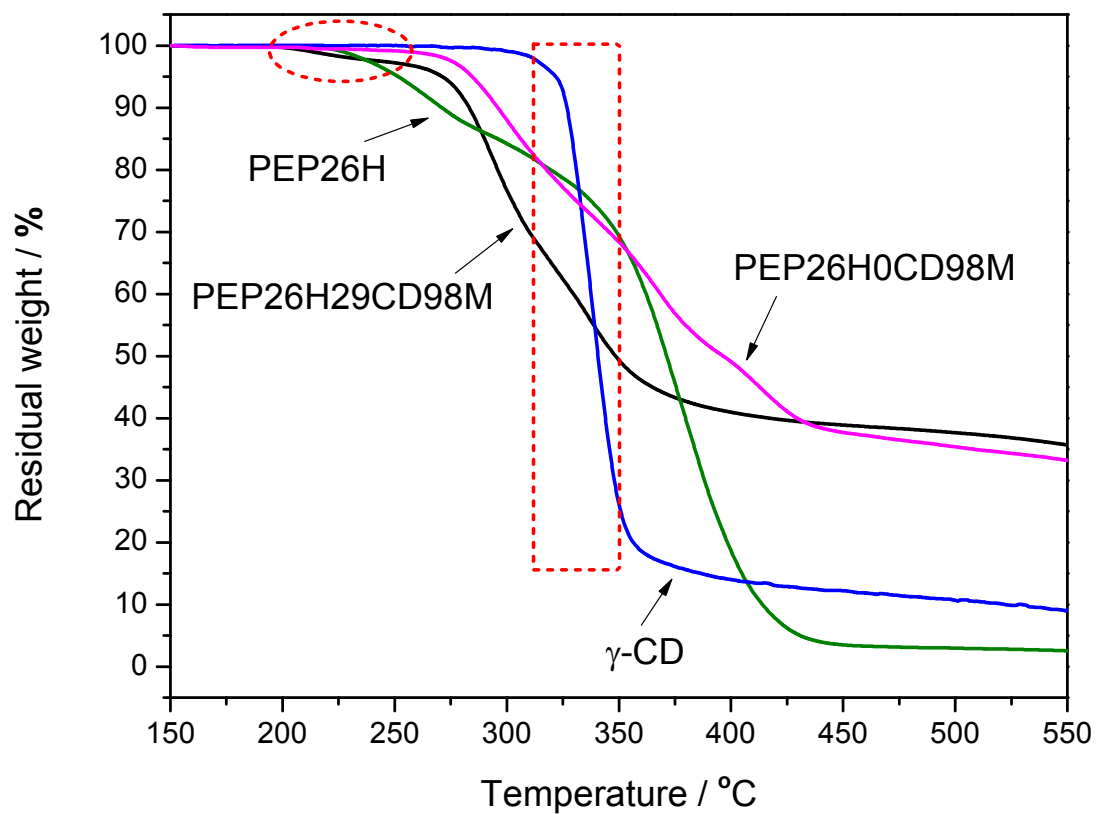


Figure S6 TGA curves of γ -CD, PEP26H, PEP26H0CD98M and PEP26H29CD98M.

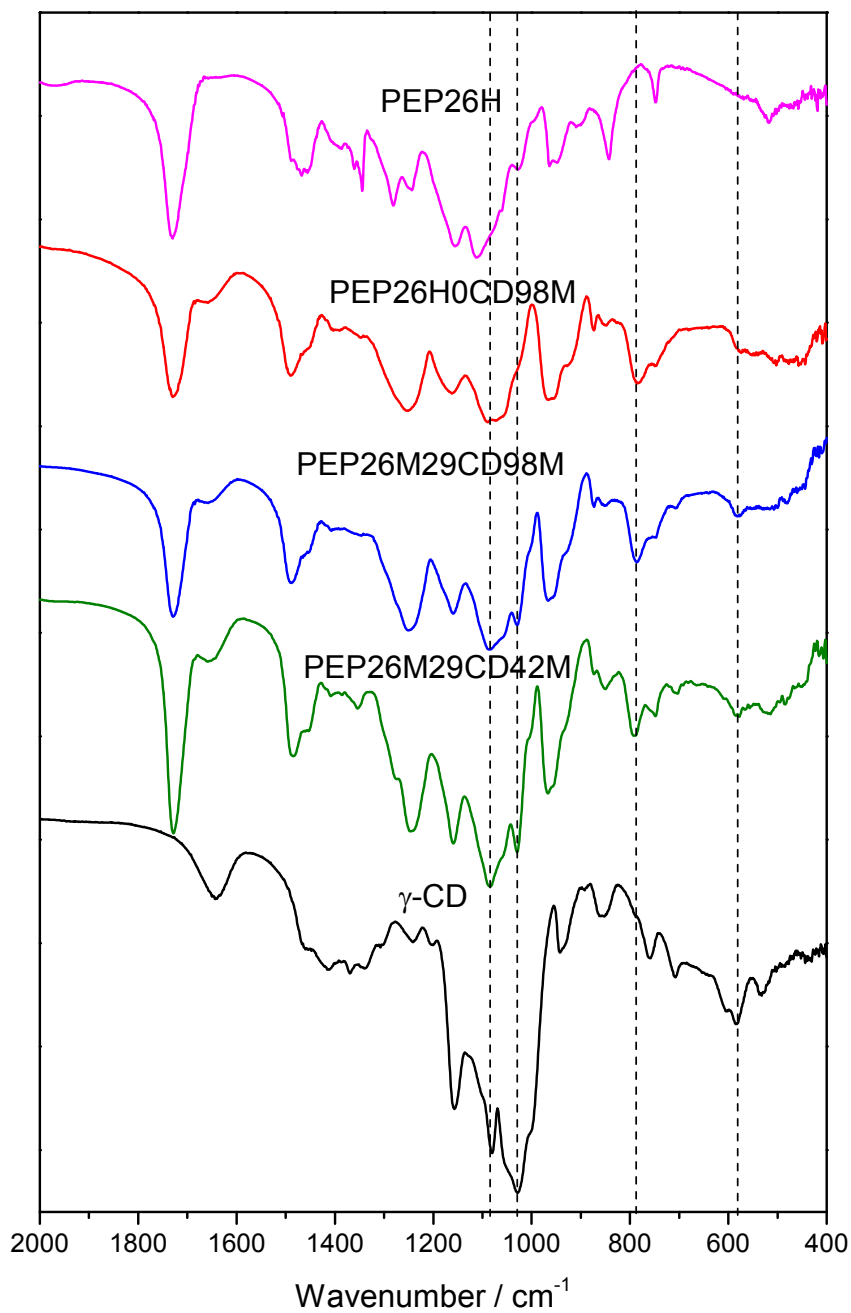


Figure S7 FTIR spectra of γ -CD, PEP26H, PEP26H0CD98M, PEP26H29CD98M and PEP26H29CD42M.

References

1. T. Kong, L. Ye, A. Y. Zhang and Z. G. Feng, *Beilstein journal of organic chemistry*, 2014, **10**, 2461-2469.
2. S. B. Lee, A. J. Russell and K. Matyjaszewski, *Biomacromolecules*, 2003, **4**, 1386-1393.