Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Preparation of stereocomplex and pseudo-polyrotaxane with various cyclodextrins as wheel components using triblock copol-ymer of poly(ethylene glycol) and polylactide

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10. Analysis of SC samples

1. Materials and Instruments

1.1. Materials

Poly(ethylene glycol) (PEG), 3,5-dimethylbenzyl alcohol, chloroform and acetone were purchased from Wako Pure Chemical Industries. 3,5-dimethylphenyl isocyanate was purchased from Sigma-Aldrich Corp. (L,L)-lactide and (D,D)-lactide were purchased from Musashino Chemical Laboratory, Ltd and recrystallized in ethyl acetate: hexane (3:1, (v/v) and then dried in vacuo at 40 °C for overnight. Dibutyltin dilaurate (DBTDL), Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$), and □-cyclodextrin were purchased from Tokyo Chemical Industry Co. Ltd. *N*,*N*-dimethylformamide (DMF) and ethyl acetate were purchased from Nacalai Tesque Inc. Diethyl ether were purchased from AZBIO Corp., Japan. Anhydrous dichloromethane was purchased from Kanto Chemical Co. Inc. Deionized water (DIW) was made in our laboratory with a resistivity of 12 MΩ cm.

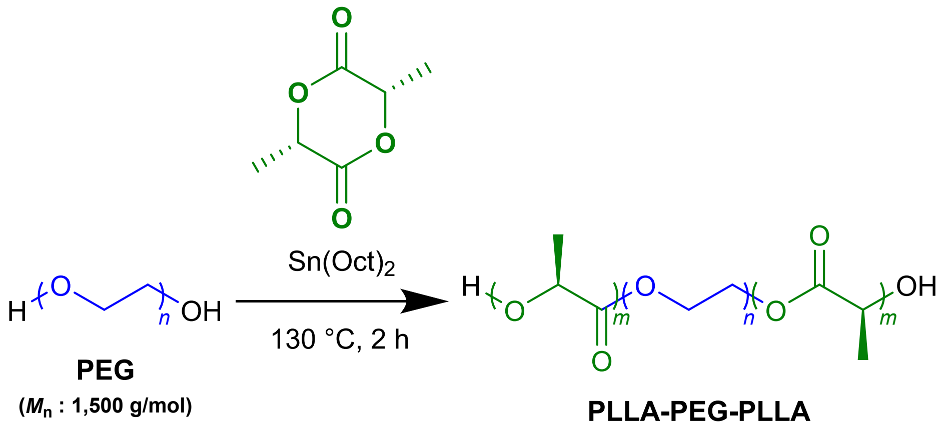
1.2. Instruments

Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured by a JEOL JNM-GSX400 system. Diffusion Ordered Spectroscopy (DOSY) spectra were measured by a JEOL JNM-ECA600 system. The number-average molecular weights (M_n) and polydispersity index (PDI) values were measured by size-exclusion chromatography (SEC). SPD-20A system (Shimadzu Corporation, Japan) using AS-2055 and RI-2031 was employed with polystyrene and polyethylene glycol standards at 40 °C. The column (TSKgel α-M) was used and DMF solution of polymer sample (1 mg/mL) was used as an eluent at 0.6 mL/min. FT-IR / ATR spectra were measured with a spectrum 100 FT-IR spectrometer (PerkinElmer) and IRAffinity-1S ATR Miracle A (Shimadzu). X-ray diffraction (XRD) was measured with Rigaku RINT-TTRIII/NM. Cu Kα (λ= 154 nm) was used as the X-ray source and operated at50 kV and 300 mA with a Ni filter at 2θ = 5° - 40° at scan speed of 0.5°/min. Thermogravimetric analysis (TGA) was performed by TGA-50 (Shimadzu Corporation, Japan) under a nitrogen atmosphere at the heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was measured by DSC-60 Plus and TAC/L systems heating and cooling rate of 5 °C/min. The DSC charts all samples showed 1st scan and obtained the melting point (T_m) of the samples. T_m and melting enthalpy (ΔH_m) were determined from each scan. The degree of crystallinity (X (%)) of all stereocomplex samples was obtained from the 1st heating scan using X (%) = $\Delta H_m / \Delta H^0_m \times 100$. ΔH^0_m was theoretical melting enthalpy of perfect stereocomplex crystal (142 J/g).

2. Syntheses of polymers, rotaxane and stereocomplex formation

2.1. Synthesis of axle components (ABA type BCPs)

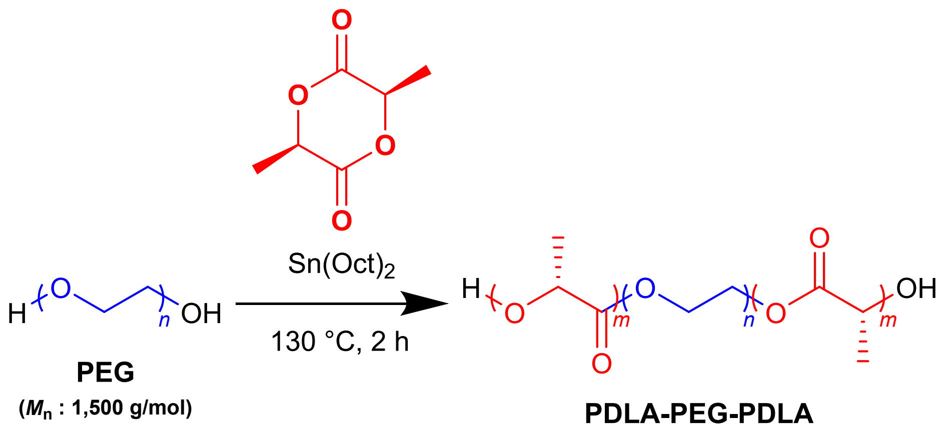
2.1.1. Synthesis of PLLA-PEG-PLLA (**1**)



(**1**)

PEG (7.72 g, 5 mmol (M_n : 1,540 g/mol)) was mixed with L,L-lactide (14.4 g, 100 mmol) and $Sn(Oct)_2$ (0.330 ml, 1 mmol), and the mixture was stirred for 2 h at 130 ºC. After the reaction, mixture was dissolved in chloroform (25 ml) and reprecipitated into diethyl ether (500 ml). The solution and precipitate was stand in refrigerator for overnight. The residue was collected using centrifugation (-10 ºC, 3500 rpm, 5 min) and dried at 60 ºC for overnight in vacuum and obtained PLLA-PEG-PLLA (**1**) (18.45 g, 81.8 %). M_n : 4,300 g/mol, M_w/M_n : 1.1, ^{1}H NMR (400 MHz, r.t., in DMSO-d_6) : δ 5.50 - 5.39 (m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 3.51 (s, PEG (4H)), 1.49 - 1.39 (m, PLA (3H)), 1.31 - 1.22 (m, terminal PLA (3H))

2.1.2. Synthesis of PDLA-PEG-PDLA (**2**)

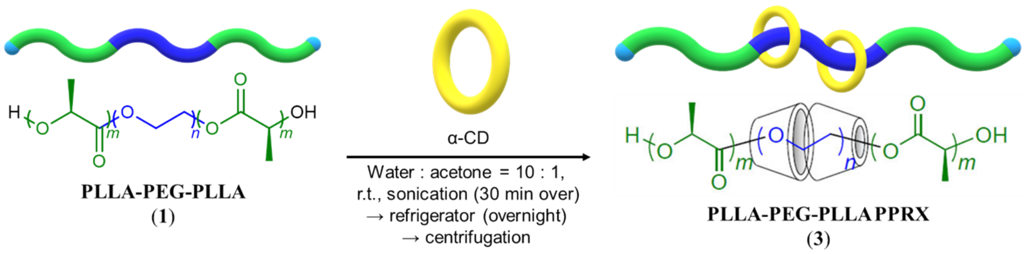


(**2**)

PEG (7.70 g, 5 mmol (M_n : 1,540 g/mol)) was mixed with D,D-lactide (14.4 g, 100 mmol) and $Sn(Oct)_2$ (0.330 ml, 1 mmol), and the mixture was stirred for 2 h at 130 ºC. After the reaction, mixture was dissolved chloroform (25 ml) and reprecipitated into diethyl ether (500 ml). The solution and precipitate was stand in refrigerator for overnight. The residue was collected using centrifugation (-10 ºC, 3500 rpm, 5 min) and dried at 60 ºC for overnight in vacuum and obtained PDLA-PEG-PDLA (**2**) (17.83 g, 79.2 %). M_n : 4,200 g/mol, M_w/M_n : 1.1, ^{1}H NMR (400 MHz, r.t., in DMSO-d_6) : δ 5.50 - 5.39 (m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 3.51 (s, PEG (4H)), 1.50 - 1.39 (m, PLA (3H)), 1.31 - 1.22 (m, terminal PLA (3H))

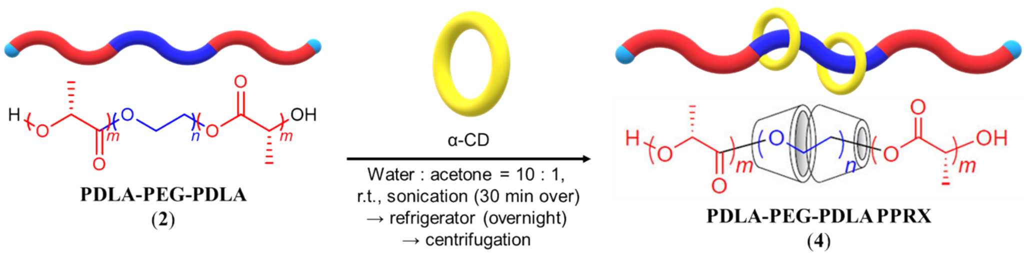
2.2. Formation of α-CD type PPRXs

2.2.1. Synthesis of PLLA-PEG-PLLA PPRX (**3**)



PLLA-PEG-PLLA (**1**) (0.51 g, 0.12 mmol (M_n : 4,300 g/mol)) was mixed with α-CD (3.01 g, 3.09 mmol) in water (100 ml) and acetone (10 ml). The solution was sonicated over 30 min at room temperature. After sonication, the solution was changed white colloid. The solution and residue was stand in refrigerator for overnight and the residue was collected using centrifugation (1 ºC, 3500 rpm, 5 min) and washed the new water : acetone = 10 : 1 solution using 40 ml on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained PLLA-PEG-PLLA PPRX (**3**) (0.78 g, 22.2 %). ^{1}H NMR (400 MHz, r.t., in DMSO-d_6) : δ 5.55 - 5.53 (d, J = 7.2 Hz, 6H), 5.50 - 5.40 (m, terminal PLA (1H)), 5.45 (d, J = 2.8 Hz, 6H), 5.23 - 5.10 (m, PLA (1H)), 4.80 - 4.79 (d, J = 3.2 Hz, 6H), 4.52 - 4.49 (t, J = 5.6 Hz, 6H), 3.80 - 3.75 (m, 6H), 3.70 - 3.57 (m, 18H), 3.51 (s, PEG (4H)), 3.41 - 3.36 (t, J = 9.2 Hz, 6H), 3.30 - 3.25 (m, 6H), 1.49 - 1.40 (m, PLA (3H)), 1.31 - 1.24 (m, terminal PLA (3H))

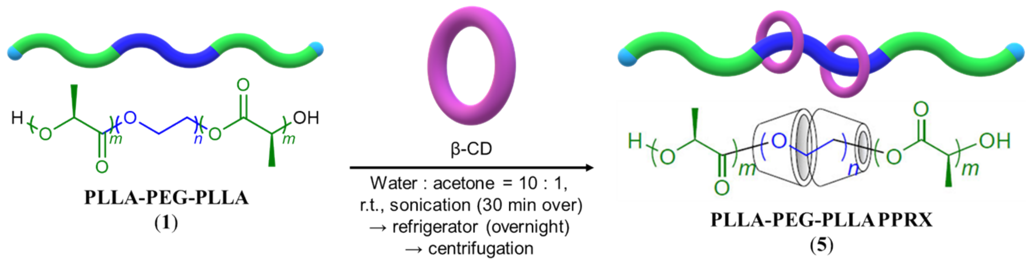
2.2.2. Synthesis of PDLA-PEG-PDLA PPRX (**4**)



PDLA-PEG-PDLA (**2**) (0.51 g, 0.12 mmol (M_n : 4,200 g/mol)) was mixed with α-CD (3.01 g, 3.09 mmol) in water (100 ml) and acetone (10 ml). The solution was sonicated over 30 min at room temperature. After sonication, the solution was changed white colloid. The solution and residue was stand in refrigerator for overnight and the residue was collected using centrifugation (1 ºC, 3500 rpm, 5 min) and washed the new water : acetone = 10 : 1 solution using 40 ml on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained PDLA-PEG-PDLA PPRX (**4**) (0.75 g, 21.1 %). ^{1}H NMR (400 MHz, r.t., in DMSO-d_6) : δ 5.49 (s, 12H of CD and m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 4.80 - 4.79 (d, J = 3.6 Hz, 6H), 4.50 (s, 6H of CD), 3.80 - 3.75 (m, 6H), 3.70 - 3.57 (m, 18H), 3.51 (s, PEG (4H)), 3.41 - 3.36 (t, J = 9.2 Hz, 6H), 3.30 - 3.25 (m, 6H), 1.49 - 1.40 (m, PLA (3H)), 1.31 - 1.24 (m, terminal PLA (3H))

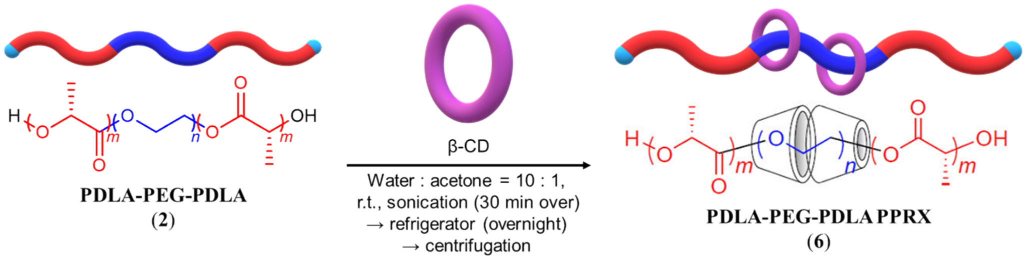
2.3. Formation of β-CD type PPRXs

2.3.1. Synthesis of PLLA-PEG-PLLA PPRX (**5**)



PLLA-PEG-PLLA (**1**) (0.50 g, 0.12 mmol (M_n : 4,300 g/mol)) was mixed with β-CD (3.00 g, 2.65 mmol) in water (100 ml) and acetone (10 ml). The solution was sonicated over 30 min at room temperature. After sonication, the solution was changed white colloid. The solution and residue was stand in refrigerator for overnight and the residue was collected using centrifugation (1 ºC, 3500 rpm, 5 min) and washed the new water : acetone = 10 : 1 solution using 40 ml on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained PLLA-PEG-PLLA PPRX (**5**) (0.51 g, 14.7 %). ^{1}H NMR (400 MHz, r.t., in DMSO-d_6) : δ 5.77 - 5.75 (d, J = 6.8 Hz, 7H), 5.70 (d, J = 2.0 Hz, 7H), 5.50 - 5.39 (m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 4.83 (d, J = 3.2 Hz, 7H), 4.49 - 4.46 (t, J = 5.2 Hz, 7H), 3.69 - 3.54 (m, 28H), 3.51 (s, PEG (4H)), 3.46 - 3.27 (m, 14H), 1.50 - 1.39 (m, PLA (3H)), 1.31 - 1.24 (m, terminal PLA (3H))

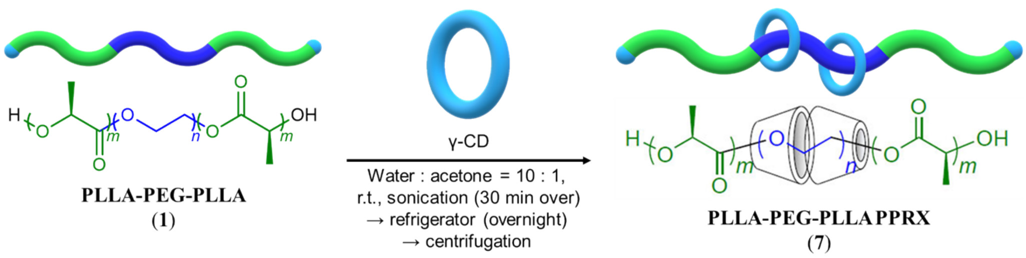
2.3.2. Synthesis of PDLA-PEG-PDLA PPRX (**6**)



PDLA-PEG-PDLA (**2**) (0.50 g, 0.12 mmol (M_n : 4,200 g/mol)) was mixed with β-CD (3.00 g, 2.65 mmol) in water (100 ml) and acetone (10 ml). The solution was sonicated over 30 min at room temperature. After sonication, the solution was changed white colloid. The solution and residue was stand in room temperature and the residue was collected using centrifugation (1 ºC, 3500 rpm, 5 min) and washed the new water : acetone = 10 : 1 solution using 40 ml on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained PDLA-PEG-PDLA PPRX (**6**) (0.51 g, 14.4 %). ^{1}H NMR (400 MHz, r.t., in DMSO-d_6): δ 5.76 - 5.75 (d, J = 7.2 Hz, 7H), 5.70 - 5.69 (d, J = 2.4 Hz, 7H), 5.50 - 5.39 (m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 4.83 - 4.82 (d, J = 3.6 Hz, 7H), 4.49 - 4.46 (t, J = 5.6 Hz, 7H), 3.69 - 3.54 (m, 28H), 3.51 (s, PEG (4H)), 3.46 - 3.27 (m, 14H), 1.49 - 1.39 (m, PLA (3H)), 1.31 - 1.24 (m, terminal PLA (3H))

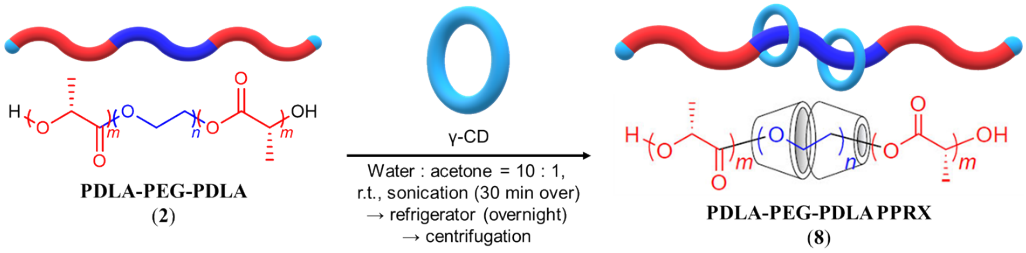
2.4. Formation of γ-CD type PPRXs

2.4.1. Synthesis of PLLA-PEG-PLLA PPRX (**7**)



PLLA-PEG-PLLA (**1**) (0.50 g, 0.12 mmol (M_n : 4,300 g/mol)) was mixed with γ-CD (3.00 g, 2.31 mmol) in water (100 ml) and acetone (10 ml). The solution was sonicated over 30 min at room temperature. After sonication, the solution was changed white colloid. The solution and residue was stand in room temperature and the residue was collected using centrifugation (1 ºC, 3500 rpm, 5 min) and washed the new water : acetone = 10 : 1 solution using 40 ml on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained PLLA-PEG-PLLA PPRX (**7**) (1.34 g, 38.2 %). ^{1}H NMR (400 MHz, r.t., in DMSO-d_6) : δ 5.79 (d, J = 2.4 Hz, 8H), 5.78 - 5.76 (d, J = 7.2 Hz, 8H), 5.50 - 5.40 (m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 4.89 (d, J = 3.6 Hz, 8H), 4.56 - 4.53 (t, J = 5.6 Hz, 8H), 3.62 - 3.52 (m, 32H), 3.51 (s, PEG (4H)), 3.43 - 3.29 (m, 16H), 1.50 - 1.41 (m, PLA (3H)), 1.31 - 1.24 (m, terminal PLA (3H))

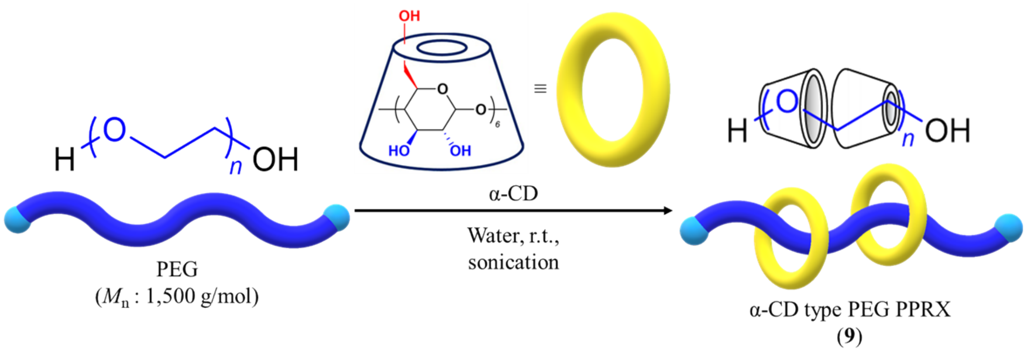
2.4.2. Synthesis of PDLA-PEG-PDLA PPRX (**8**)



PDLA-PEG-PDLA (**2**) (0.50 g, 0.12 mmol (M_n : 4,200 g/mol)) was mixed with γ-CD (3.00 g, 2.31 mmol) in water (100 ml) and acetone (10 ml). The solution was sonicated over 30 min at room temperature. After sonication, the solution was changed white colloid. The solution and residue was stand in room temperature and the residue was collected using centrifugation (1 ºC, 3500 rpm, 5 min) and washed the new water : acetone = 10 : 1 solution using 40 ml on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained PDLA-PEG-PDLA PPRX (**8**) (1.24 g, 35.4 %). ^{1}H NMR (400 MHz, r.t., in DMSO-d_6): δ 5.80 - 5.79 (d, J = 2.4 Hz, 8H), 5.79 - 5.77 (d, J = 7.2 Hz, 8H), 5.51 - 5.40 (m, terminal PLA (1H)), 5.23 - 5.10 (m, PLA (1H)), 4.89 - 4.88 (d, J = 3.6 Hz, 8H), 4.57 - 4.54 (t, J = 6.0 Hz, 8H), 3.62 - 3.52 (m, 32H), 3.51 (s, PEG (4H)), 3.41 - 3.29 (m, 16H), 1.50 - 1.41 (m, PLA (3H)), 1.31 - 1.23 (m, terminal PLA (3H))

2.5. Formation of PEG type PPRXs

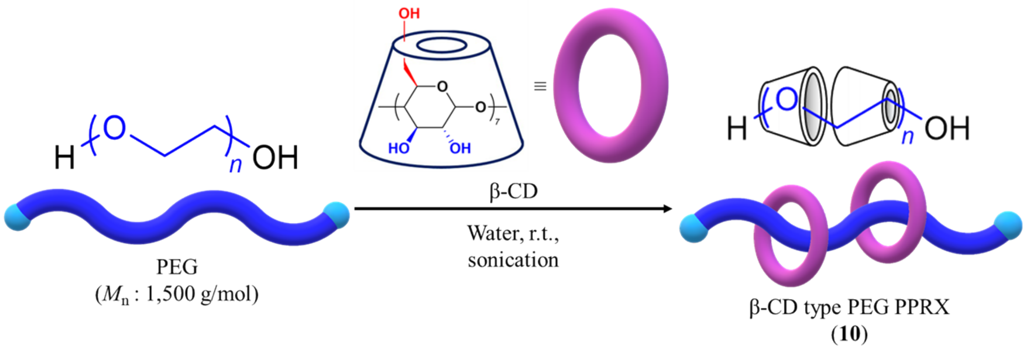
2.5.1. Synthesis of α-CD type PEG PPRX (**9**)



PEG (1.02 g, 0.662 mmol) was mixed with α-CD (3.00 g, 3.09 mmol) in 100 ml of water. The solution was sonicated over 1 hour at room temperature. After sonication, the solution was changed white colloid. The solution was stand at room temperature for one day. The solution and residue was stand in room temperature and the residue was collected using centrifugation (25 ºC, 3500 rpm, 5 min) and washed as the new water (40 ml) on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained the α-CD type PEG PPRX (**9**) (2.11 g, 52.5 %). ^{1}H NMR (600 MHz, 298 K, in

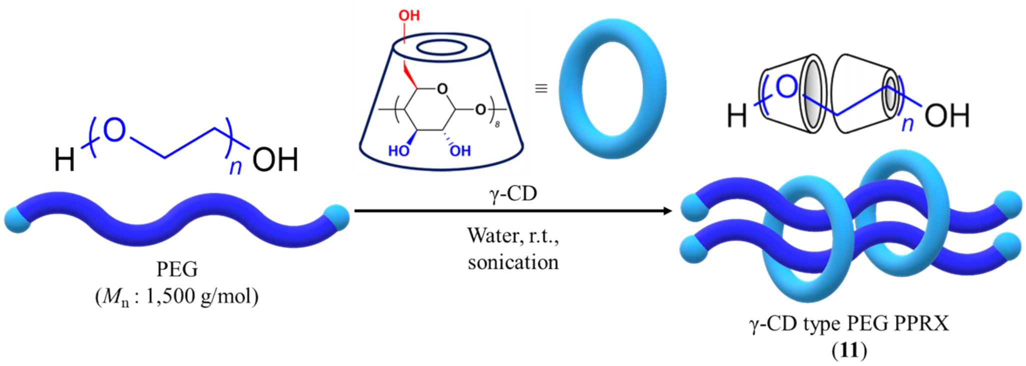
DMSO-d_6): δ 5.53 - 5.51 (d, J = 7.2 Hz, 6H)), 5.44 (d, J = 2.4 Hz, 6H), 4.80 - 4.79 (d, J = 3.6 Hz, 6H), 4.50 - 4.48 (t, J = 6.0 Hz, 6H), 3.80 - 3.75 (m, 6H), 3.69 - 3.57 (m, 18H), 3.51 (s, PEG), 3.41 - 3.36 (t, J = 6.0 Hz, 6H), 3.29 - 3.26 (m, 6H)

2.5.2. Synthesis of β-CD type PEG PPRX (**10**)



PEG (1.00 g, 0.650 mmol) was mixed with β-CD (3.01 g, 2.65 mmol) in 100 ml of water. The solution was sonicated over 1 hour at room temperature. After sonication, the solution was changed white colloid. The solution was stand at room temperature for one day. The solution and residue was stand in room temperature and the residue was collected using centrifugation (25 ºC, 3500 rpm, 5 min) and washed as the new water (40 ml) on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained the β-CD type PEG PPRX (**10**) (1.72 g, 51.2 %). ^{1}H NMR (600 MHz, 298 K, in DMSO-d_6): δ 5.75 - 5.74 (d, J = 4.8 Hz, 7H)), 5.69 (s, 7H), 4.83 (d, J = 3.0 Hz, 7H), 4.48 - 4.46 (t, J = 5.4 Hz, 7H), 3.65 - 3.53 (m, 28H), 3.51 (s, PEG), 3.45 - 3.30 (m, 14H)

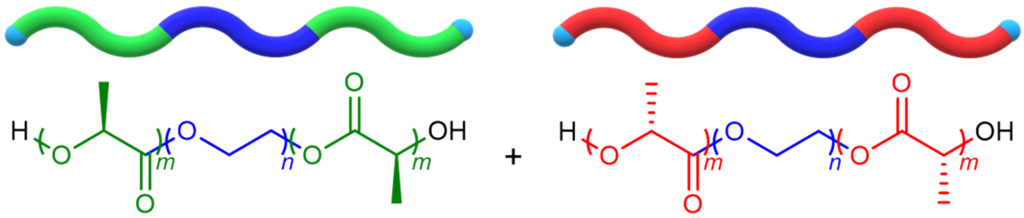
2.5.3. Synthesis of γ-CD type PEG PPRX (**11**)



PEG (1.01 g, 0.653 mmol) was mixed with γ-CD (3.01 g, 2.32 mmol) in 100 ml of water. The solution was sonicated over 1 hour at room temperature. After sonication, the solution was changed white colloid. The solution was stand at room temperature for one day. The solution and residue was stand in room temperature and the residue was collected using centrifugation (25 ºC, 3500 rpm, 5 min) and washed as the new water (40 ml) on 3 times. The residue was dried at 60 ºC for overnight in vacuum and obtained the γ-CD type PEG PPRX (**11**) (2.06 g, 51.2 %). ^{1}H NMR (600 MHz, 298 K, in DMSO-d_6): δ 5.77 (d, J = 1.8 Hz, 8H)), 5.76 - 5.75 (d, J = 6.6 Hz, 8H), 4.89 - 4.88 (d, J = 3.0 Hz, 8H), 4.54 - 4.52 (t, J = 5.4 Hz, 8H), 3.63 - 3.49 (m, 32H), 3.51 (s, PEG), 3.42 - 3.25 (m, 16H)

2.6. Formation of stereocomplex using ABA type BCPs

2.6.1. Synthesis of ABA type BCP SC (**12**)

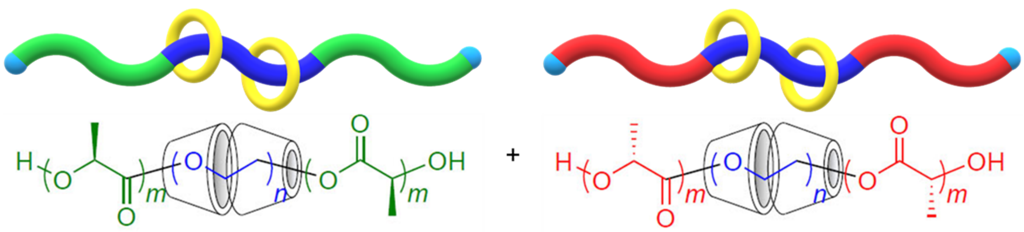


PLLA-PEG-PLLA (1) + **PDLA-PEG-PDLA (2)**

PLLA-PEG-PLLA (**1**) (1.5 g, 0.349 mmol (M_n : 4,300 g/mol)) and PDLA-PEG-PDLA (**2**) (1.5 g, 0.358 mmol (M_n : 4,200 g/mol)) was mixed in chloroform (20 ml). The solution was stand in 60 ºC for overnight and collected by drying the chloroform. The residue was obtained white solid (PLA-PEG-PLA BCP SC (**12**)).

2.7. Formation of stereocomplex using α-CD type PPRXs

2.7.1. Synthesis of α-CD type PPRX SC (**13**)

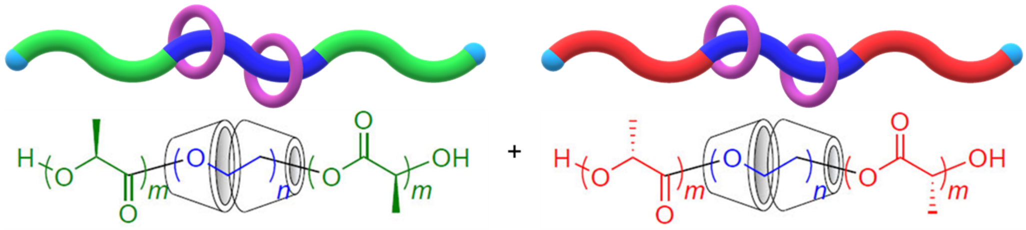


PLLA-PEG-PLLA PPRX (3) + **PDLA-PEG-PDLA PPRX (4)**

PLLA-PEG-PLLA PPRX (**3**) (0.1 g) and PDLA-PEG-PDLA PPRX (**4**) (0.1 g) was mixed in chloroform (10 ml). The solution was stand in 60 ºC for overnight and collected by drying the chloroform. The residue was obtained white solid (α-CD type PPRX SC (**13**)).

2.8. Formation of stereocomplex using β-CD type PPRXs

2.8.1. Synthesis of β-CD type PPRX SC (**14**)

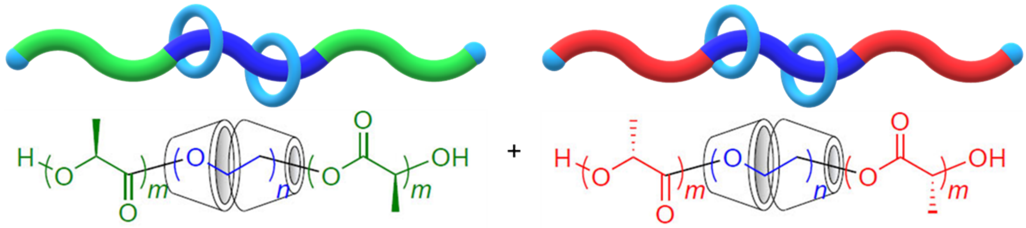


PLLA-PEG-PLLA PPRX (5) + **PDLA-PEG-PDLA PPRX (6)**

PLLA-PEG-PLLA PPRX (**5**) (0.1 g) and PDLA-PEG-PDLA PPRX (**6**) (0.1 g) was mixed in chloroform (10 ml). The solution was stand in 60 ºC for overnight and collected by drying the chloroform. The residue was obtained white solid (β-CD type PPRX SC (**14**)).

2.9. Formation of stereocomplex using γ-CD type PPRXs

2.9.1. Synthesis of γ-CD type PPRX SC (**15**)



PLLA-PEG-PLLA PPRX (7) + **PDLA-PEG-PDLA PPRX (8)**

PLLA-PEG-PLLA PPRX (**7**) (0.1 g) and PDLA-PEG-PDLA PPRX (**8**) (0.1 g) was mixed in chloroform (10 ml). The solution was stand in 60 ºC for overnight and collected by drying the chloroform. The residue was obtained white solid (γ-CD type PPRX SC (**15**)).

Table S1. Solubility test of BCP, PPRX, and CD. [a]

Entry	Sample name	Type of Structure	Water	Acetone	$CHCl_3$	DMF	DMSO
1	PLLA-PEG-PLLA (**1**)	BCP	×	○	○	○	○
2	PDLA-PEG-PDLA (**2**)	BCP	×	○	○	○	○
3	PLLA-PEG-PLLA PPRX (**3**)	PPRX	×	×	×	○	○
4	PDLA-PEG-PDLA PPRX (**4**)	PPRX	×	×	×	○	○
5	PLLA-PEG-PLLA PPRX (**5**)	PPRX	×	×	×	○	○
6	PDLA-PEG-PDLA PPRX (**6**)	PPRX	×	×	×	○	○
7	PLLA-PEG-PLLA PPRX (**7**)	PPRX	×	×	×	○	○
8	PDLA-PEG-PDLA PPRX (**8**)	PPRX	×	×	×	○	○
9	α-CD type PEG PPRX (**9**)	PPRX	×	×	×	○	○
10	β-CD type PEG PPRX (**10**)	PPRX	×	×	×	○	○
11	γ-CD type PEG PPRX (**11**)	PPRX	×	×	×	○	○
12	α-CD	CD	○	×	×	○	○
13	β-CD	CD	○	×	×	○	○
14	γ-CD	CD	○	×	×	○	○

[a] 10 mg/mL at room temperature.

Table S2. Characterization of BCPs in this chapter.

Entry	Sample name	Yield (%) [a]	M_n (kDa) [b]	PDI (M_w/M_n) [b]
1	PLLA-PEG-PLLA (**1**)	81.8	4.3	1.1
2	PDLA-PEG-PDLA (**2**)	79.2	4.2	1.1

[a] Diethyl ether insoluble part. [b] Determined by GPC with DMF as an eluent using polystyrene standards.

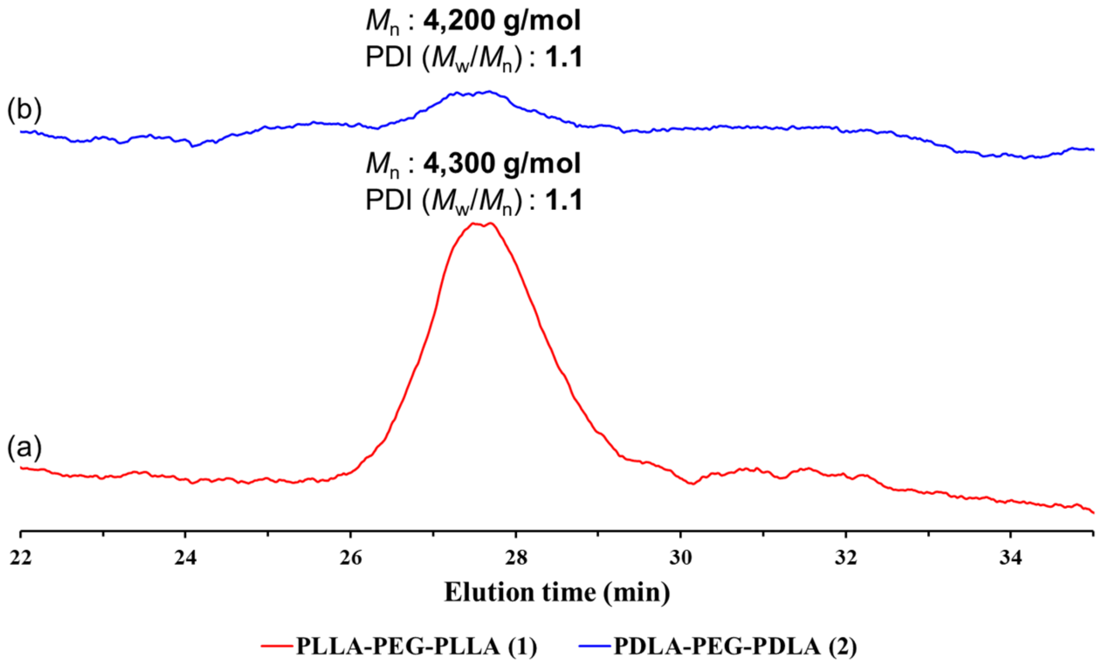


Figure S1. GPC curves of ABA-type BCPs: PLLA-PEG-PLLA (**1**) (a) and PDLA-PEG-PDLA (**2**) (b).

3. [1]H NMR

3.1. [1]H NMR spectra of ABA type BCPs (1 and 2)

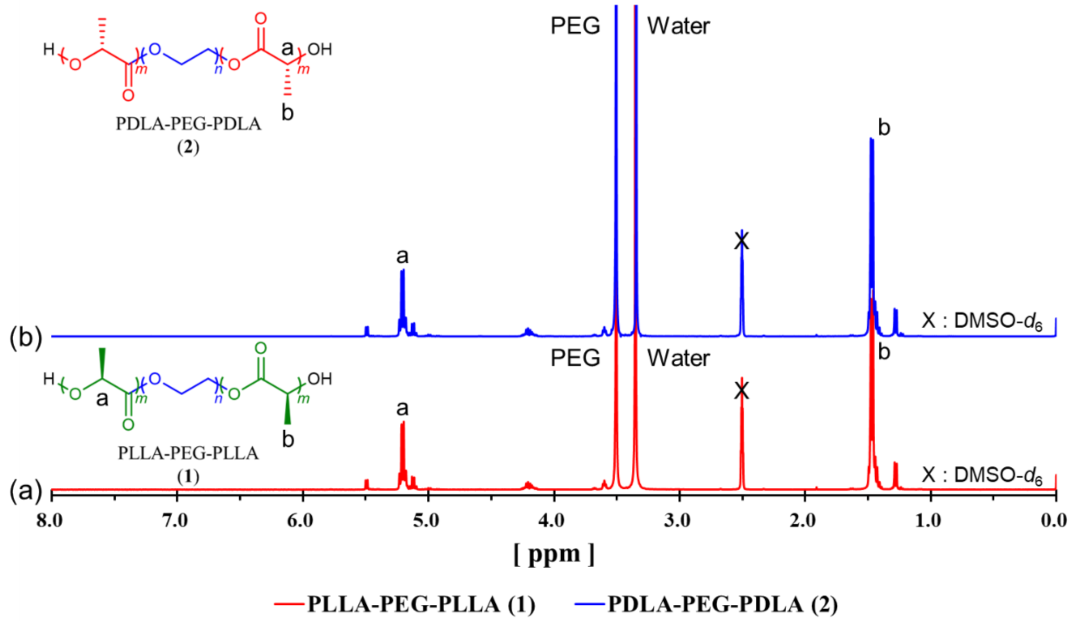


Figure S2. [1]H NMR of ABA type BCPs: PLLA-PEG-PLLA (**1**) (a) and PDLA-PEG-PDLA (**2**) (b). (400 MHz, r.t., DMSO-d_6)

3.2. ^{1}H NMR spectra of α-CD type PPRXs (3 and 4)

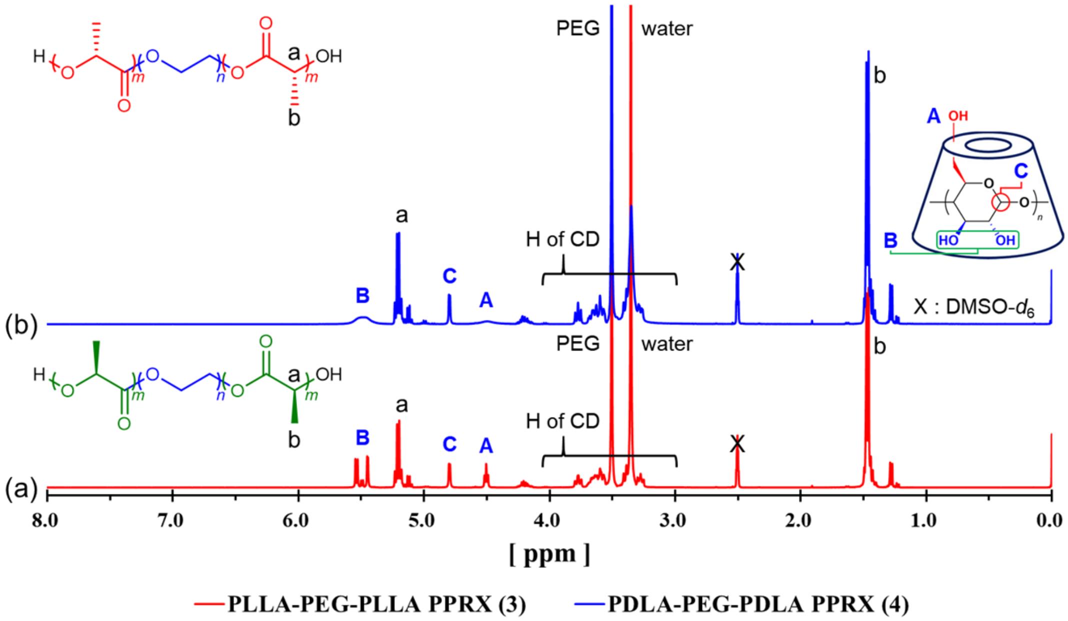


Figure S3. ^{1}H NMR of α-CD type PPRXs: PLLA-PEG-PLLA PPRX (**3**) (a) and PDLA-PEG-PDLA PPRX (**4**) (b). (400 MHz, r.t., DMSO-d_6)

3.3. ^{1}H NMR spectra of β-CD type PPRXs (5 and 6)

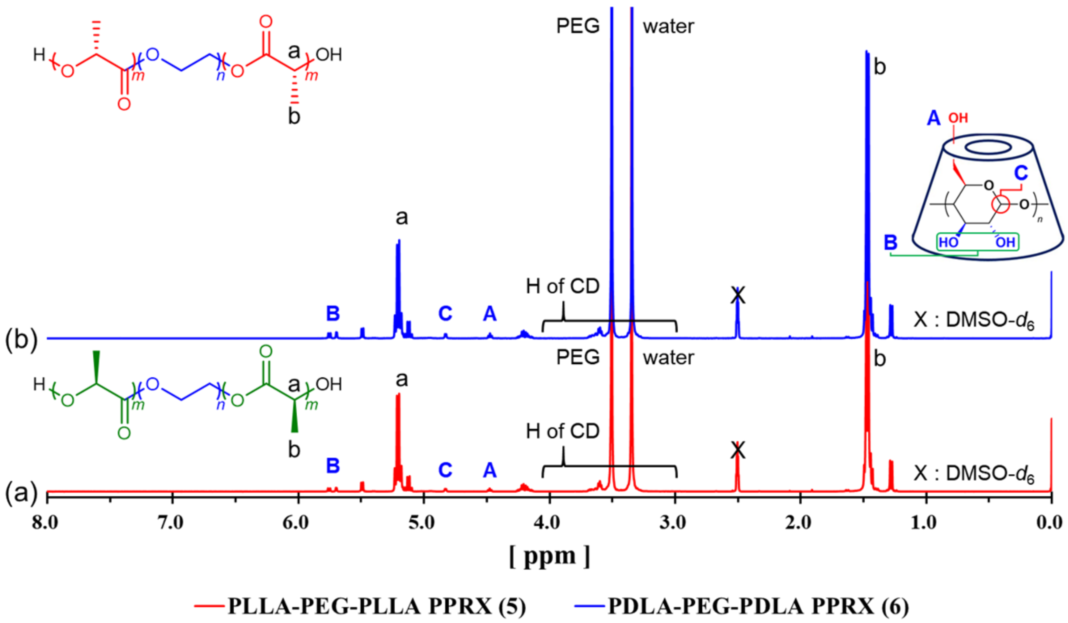


Figure S4. ^{1}H NMR of β-CD type PPRXs: PLLA-PEG-PLLA PPRX (**5**) (a) and PDLA-PEG-PDLA PPRX (**6**) (b). (400 MHz, r.t., DMSO-d_6)

3.4. ^{1}H NMR spectra of γ-CD type PPRXs (**7** and **8**)

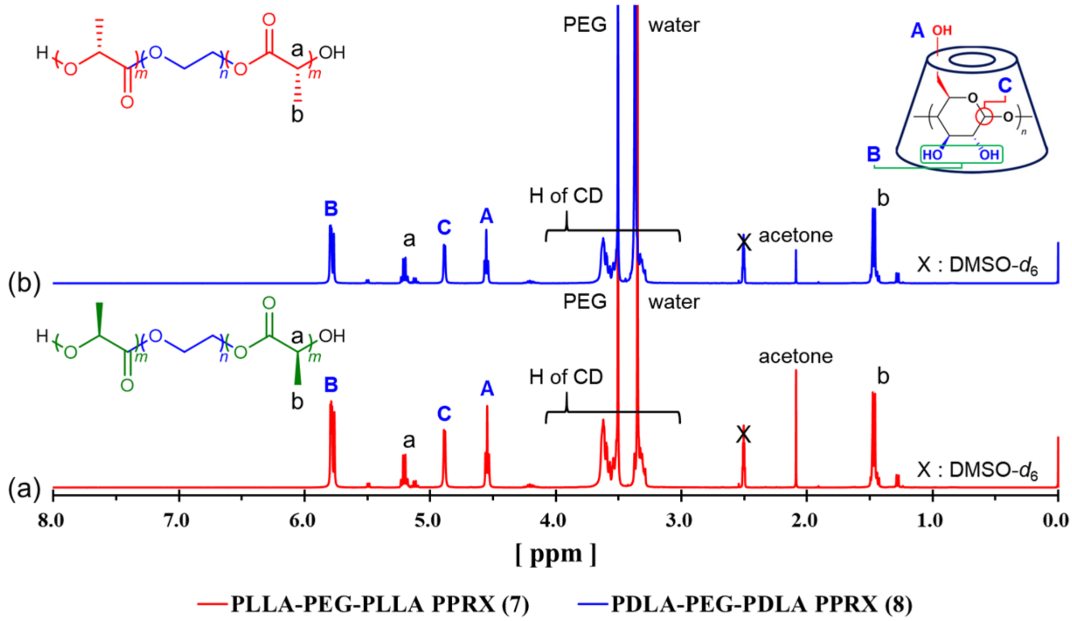


Figure S5. ^{1}H NMR of γ-CD type PPRXs: PLLA-PEG-PLLA PPRX (**7**) (a) and PDLA-PEG-PDLA PPRX (**8**) (b). (400 MHz, r.t., DMSO-d_6)

3.5. ^{1}H NMR spectra of PEG PPRXs (**9**, **10** and **11**)

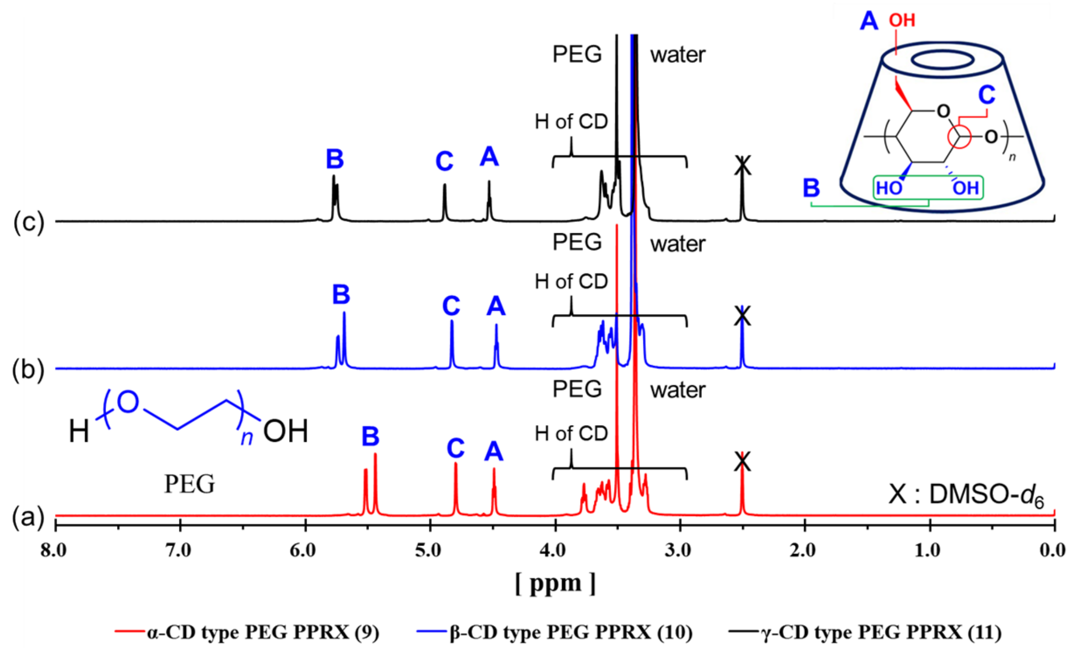


Figure S6. ^{1}H NMR of α-CD type PEG PPRX (**9**) (a), β-CD type PEG PPRX (**10**) (b) and γ-CD type PEG PPRX (**11**) (600 MHz, 298 K, DMSO-d_6)

Table S3. Preparation and analysis of PPRXs.

Entry	Sample name	Yield (%)	Number of CD
1	α-CD type PEG PPRX (**9**)	52.5 [a]	10 (10.16) [b]
2	β-CD type PEG PPRX (**10**)	43.0 [a]	21 (20.80) [b]
3	γ-CD type PEG PPRX (**11**)	51.2 [a]	12 (11.85) [b, c]

[a] Water insoluble part. [b] Calculated the assuming 35-repeated unit of ethylene part (140 H) of PEG 1,500 by ^{1}H NMR spectra in DMSO-d_6 by 600 MHz NMR. [c] Calculated the number of γ-CD, it could form the PPRX structure with two PEG chains, so, the number of γ-CD × 2.

3.6. ^{1}H NMR spectra of α-, β- and γ-CD

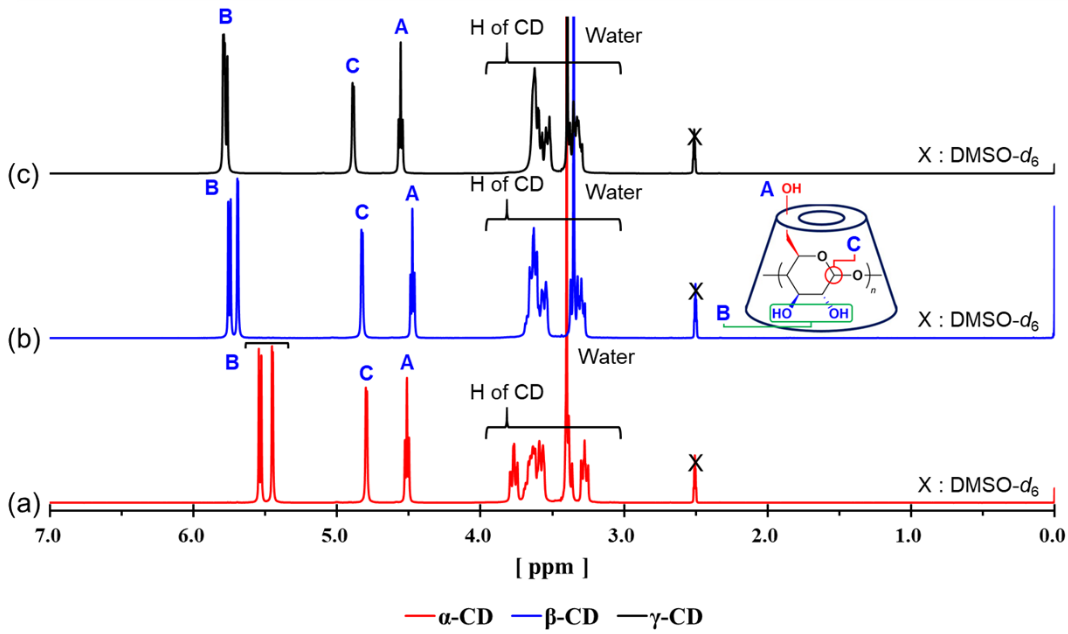


Figure S7. ^{1}H NMR spectra of α-CD (a), β-CD (b), and γ-CD (c). (400 MHz, r.t., DMSO-d_6)

4. DOSY

4.1. DOSY NMR spectrum of α-CD type PPRX (PLLA-PEG-PLLA PPRX (3))

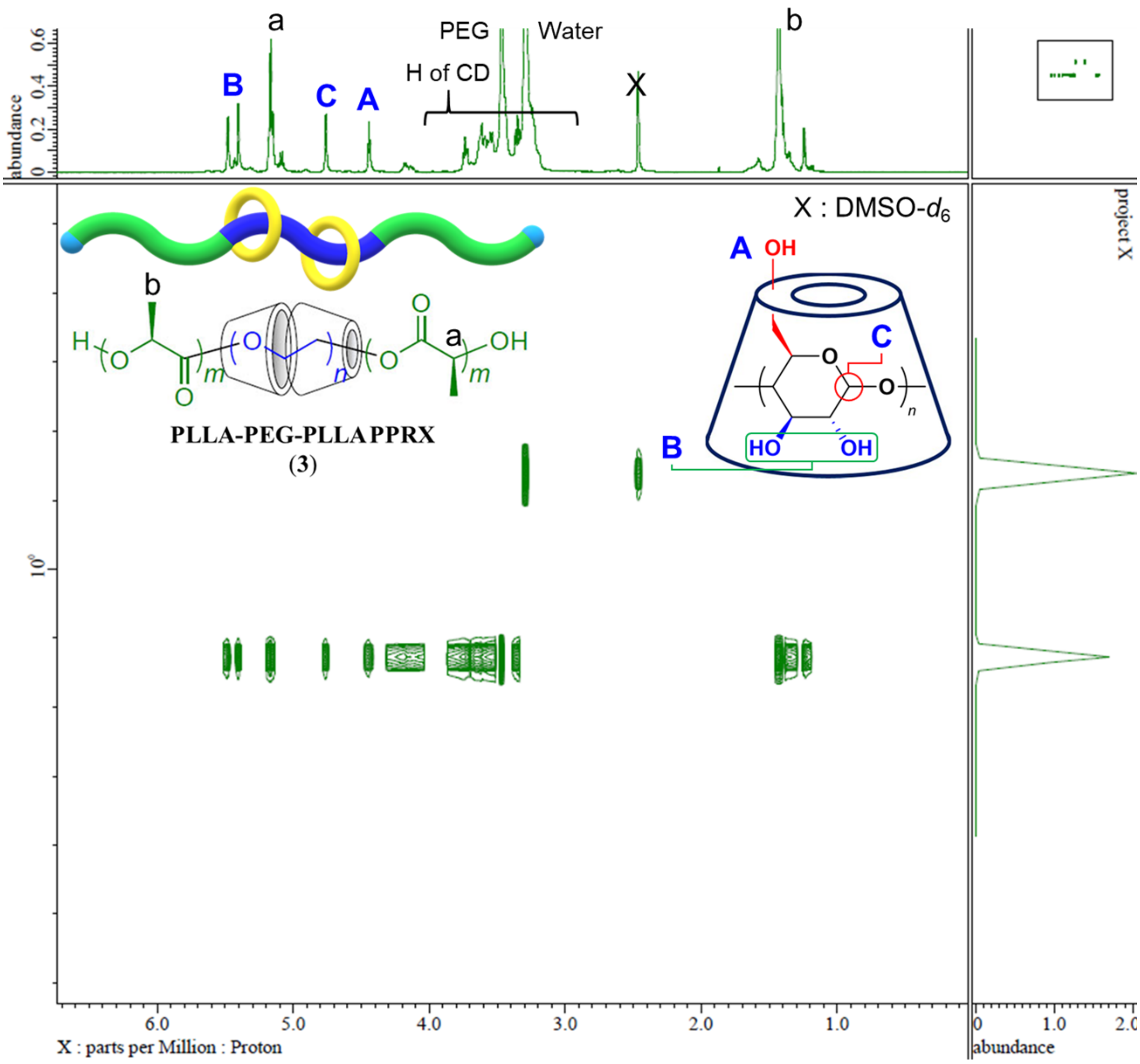


Figure S8. DOSY NMR spectrum of α-CD type PPRX (PLLA-PEG-PLLA PPRX (**3**)) (600 MHz, DMSO-d_6, 298 K).

In Figure S8, the DOSY analysis of α-CD L-type PPRX (**3**) resulted in the same values of diffusion coefficient around 10^0 μm^{2}ms^{-1} at 3.5 ppm as the PEG moiety, around 5.3 and 1.5 ppm of the PLLA moiety, and as around 5.5, 4.8, 4.5 and broad region from 4.0 to 3.0 ppm of outside protons of α-CD moieties. This can be assigned to formation of unique structure by same diffusion coefficient with PLLA-PEG-PLLA (**1**) as the axle components and α-CD as the wheel components.

4.2. DOSY NMR spectrum of α-CD type PPRX (PDLA-PEG-PDLA PPRX (4))

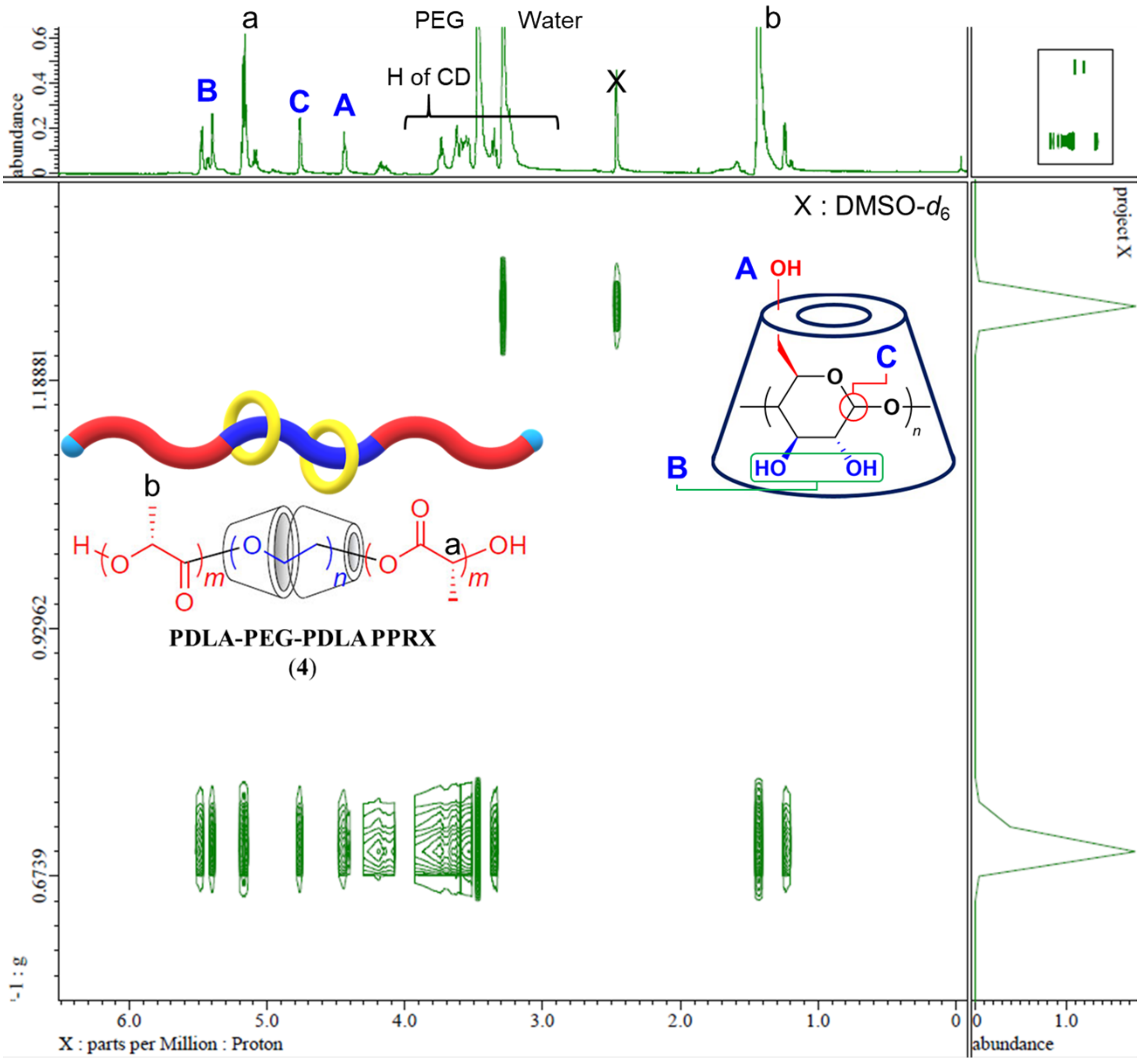


Figure S9. DOSY NMR spectrum of α-CD type PPRX (PDLA-PEG-PDLA PPRX (**4**)) (600 MHz, DMSO-d_6, 298 K).

In Figure S9, the DOSY spectra of α-CD D-type PPRX (**4**) is analyzed. Based on the X-axis, it can see the α-CD, PLA, PEG components, and the peak of the solvent. It has also the same values of diffusion coefficient around 10^0 $\mu m^2 ms^{-1}$ at 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PDLA moiety, and around 5.5, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of α-CD moieties. As with PLLA-PEG-PLLA PPLX (**1**), this shows the formation of single structure by same diffusion coefficient with PDLA-PEG-PDLA (**2**) as the axle components and α-CD as the wheel components. As a result, α-CD type PPRXs are able to confirm that both L and D types had successful PPRX structures.

4.3. DOSY NMR spectrum of β-CD type PPRX (PLLA-PEG-PLLA PPRX (5))

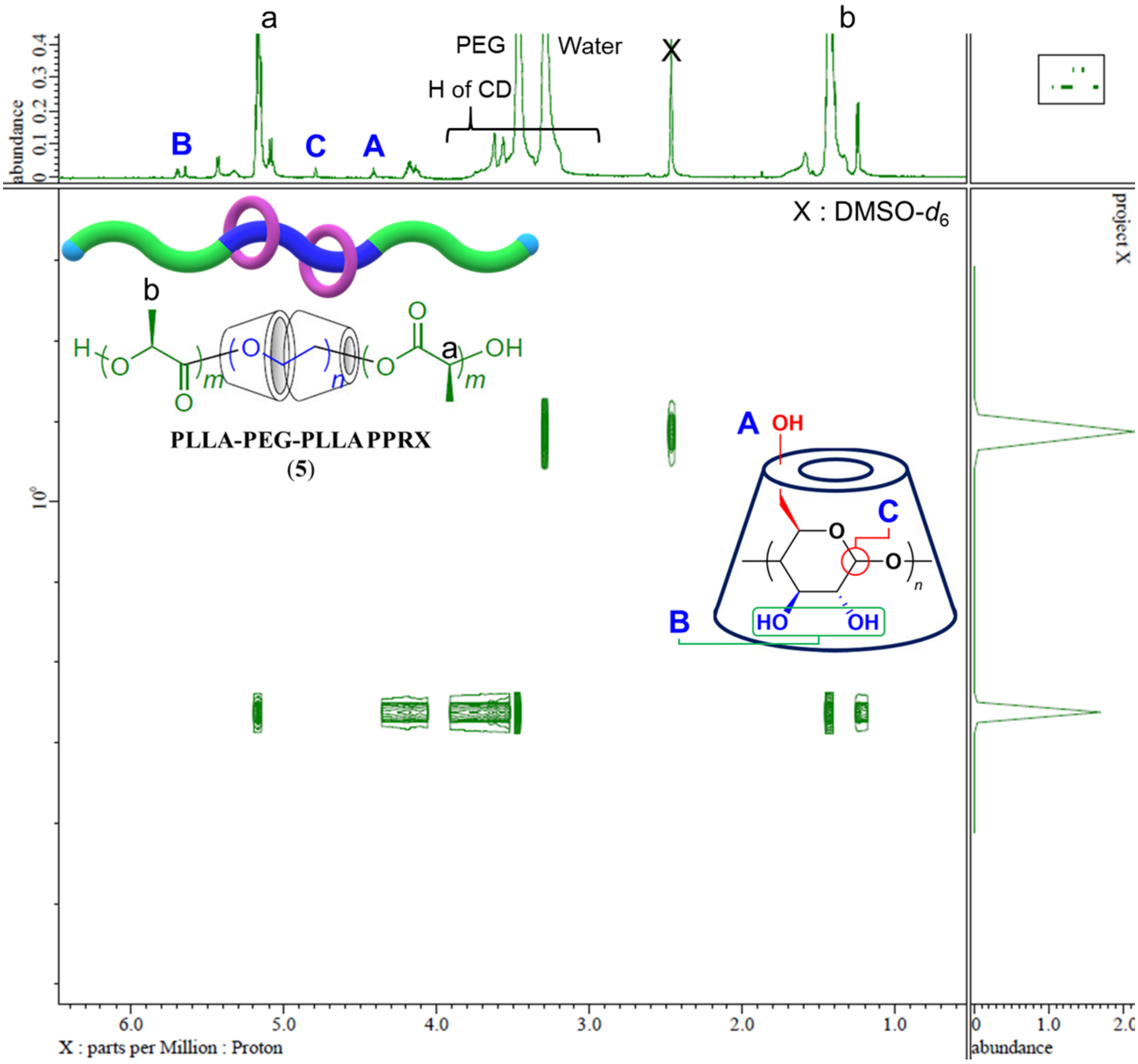


Figure S10. DOSY NMR spectrum of β-CD type PPRX (PLLA-PEG-PLLA PPRX (**5**)) (600 MHz, DMSO-d_6, 298 K).

In Figure S10, the DOSY spectra of β-CD L-type PPRX (**5**) is analyzed. The same values of diffusion coefficient between 10^0 μm^{2}ms^{-1} and 10^{-1} μm^{2}ms^{-1} at 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PLLA moiety, around 5.8, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of β-CD moieties. This can be attributed to formation of single structure of PLLA-PEG-PLLA (**1**) with the axle components and β-CD as the wheel components. As a result, L type PPRX with β-CD is able to confirm the PPRX structures.

4.4. DOSY NMR spectrum of β-CD type PPRX (PDLA-PEG-PDLA PPRX (6))

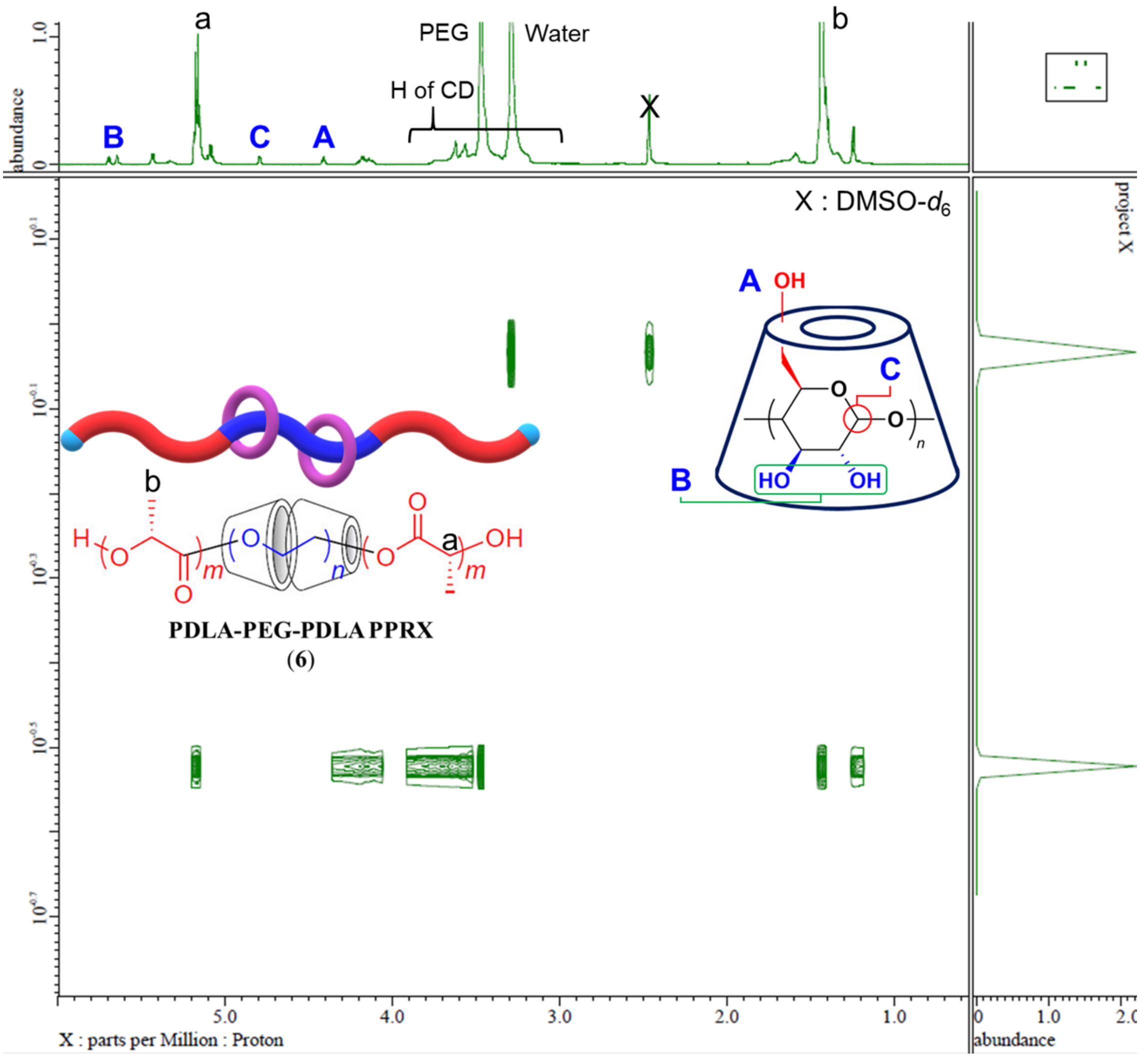


Figure S11. DOSY NMR spectrum of β-CD type PPRX (PDLA-PEG-PDLA PPRX (**6**)) (600 MHz, DMSO-d_6, 298 K).

In Figure S11, the DOSY spectra of β-CD L-type PPRX (**6**) is analyzed. Based on the X-axis, it can see the β-CD, PLA, PEG components, and the peak of the solvent. It has also the same values of diffusion coefficient around $10^{-0.5}$ $\mu m^2 ms^{-1}$ at 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PDLA moiety, and around 5.8, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of β-CD moieties. This shows single structure with PDLA-PEG-PDLA (**2**) as the axle components and β-CD as the wheel components. As a result, β-CD type PPRXs are able to confirm that both L and D types had successful PPRX structures.

4.5. DOSY NMR spectrum of γ-CD type PPRX (PLLA-PEG-PLLA PPRX (7))

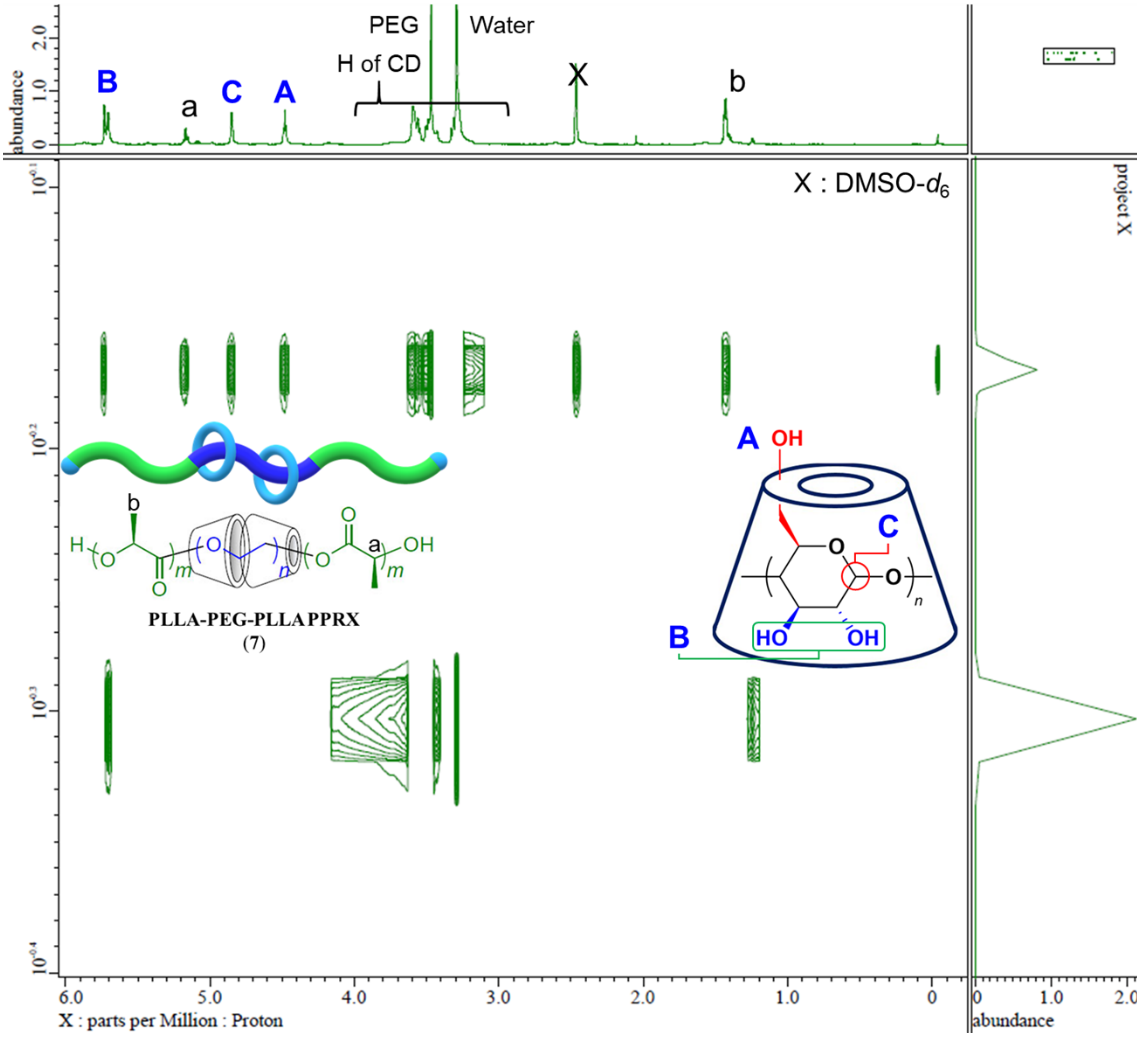


Figure S12. DOSY NMR spectrum of γ-CD type PPRX (PLLA-PEG-PLLA PPRX (**7**)) (600 MHz, DMSO-d_6, 298 K).

In Figure S12, the DOSY spectra of γ-CD L-type PPRX (**7**) is analyzed. The parts of the γ-CD, PLA, PEG, and the peaks of the solvent are shown. As with L type PPRX, each components has the same values of diffusion coefficient between $10^{-0.2}$ $\mu m^2 ms^{-1}$ and $10^{-0.1}$ $\mu m^2 ms^{-1}$ at 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PLLA moiety, around 5.8, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of γ-CD moieties. In this PPRX, the top part (between $10^{-0.2}$ $\mu m^2 ms^{-1}$ and $10^{-0.1}$ $\mu m^2 ms^{-1}$) is PPRX, with both axle and wheel components, and the bottom part (around $10^{-0.3}$ $\mu m^2 ms^{-1}$) is the part where water and the inside of the CD are in interaction. This result suggests the relationship between the stereospecific properties of the hydroxyl group inside the γ-CD and methyl group of PLA.

4.6. DOSY NMR spectrum of γ-CD type PPRX (PDLA-PEG-PDLA PPRX (8))

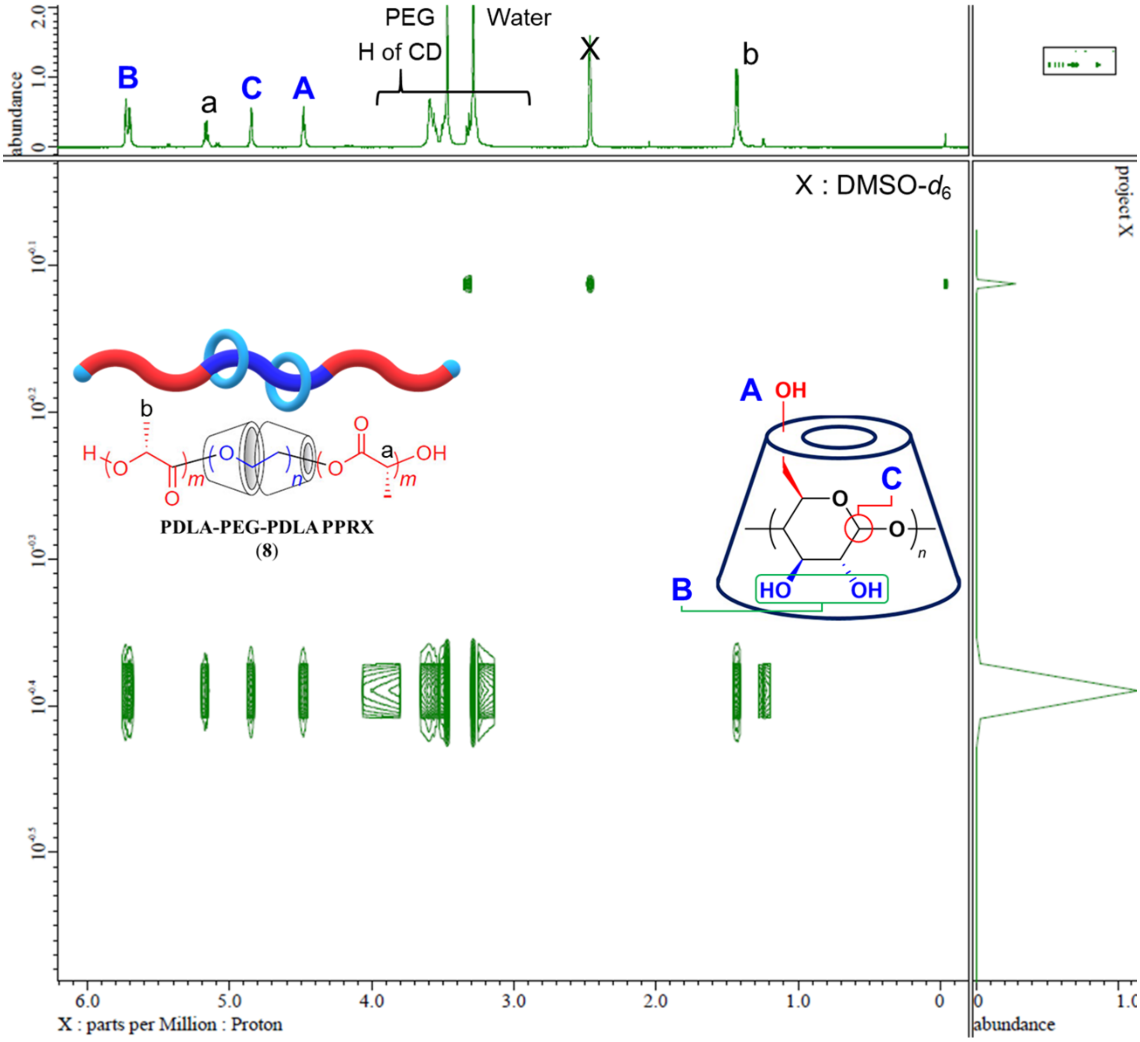


Figure S13. DOSY NMR spectrum of γ-CD type PPRX (PDLA-PEG-PDLA PPRX (**8**)) (600 MHz, DMSO-d_6, 298 K).

In Figure S13, the DOSY spectra of γ-CD D-type PPRX (**8**) is analyzed. Based on the X-axis, it can see the γ-CD, PLA, PEG components, and the peak of the solvent. It is also the same values of diffusion coefficient around $10^{-0.4}$ $\mu m^2 ms^{-1}$ at 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PDLA moiety, and as those at around 5.8, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of γ-CD moieties.

4.7. DOSY NMR spectrum of α-CD type PEG PPRX (α-CD type PEG PPRX (9))

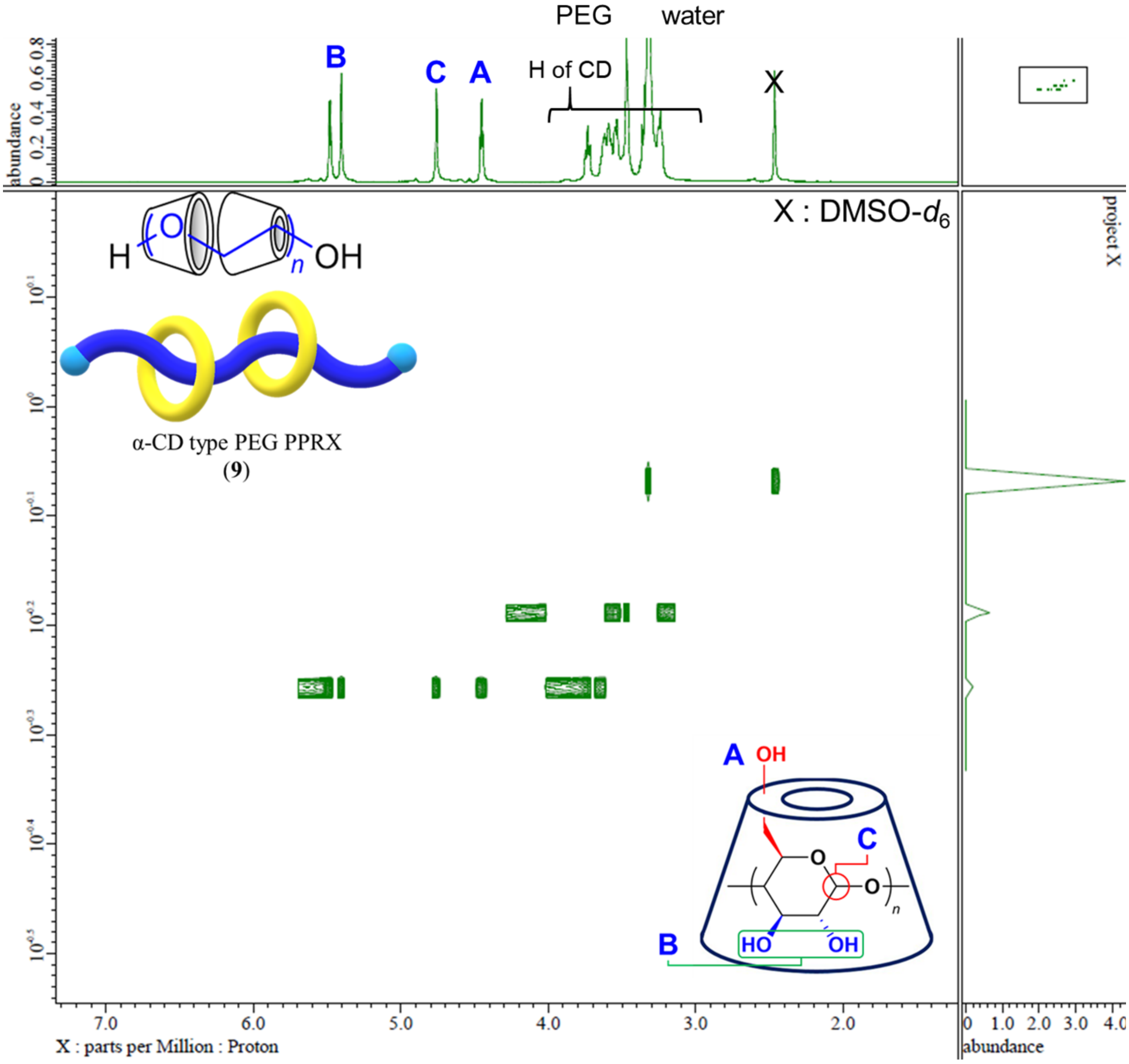


Figure S14. DOSY NMR spectrum of α-CD type PEG PPRX (**9**) (600 MHz, DMSO-d_6, 298 K).

In Figure S14, the DOSY spectra of α-CD type PEG PPRX (**9**) is analyzed. The α-CD, PEG, and the peaks of the solvent. The same values of diffusion coefficient between $10^{-0.3}$ μm^{2}ms^{-1} and $10^{-0.2}$ μm^{2}ms^{-1} at 3.5 ppm of the PEG moiety, and around 5.5, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of α-CD moieties. In this PPRX, three parts are divided but only one part exists the PPRX structure between $10^{-0.3}$ μm^{2}ms^{-1} and $10^{-0.2}$ μm^{2}ms^{-1}.

4.8. DOSY NMR spectrum of β-CD type PEG PPRX (β-CD type PEG PPRX (10))

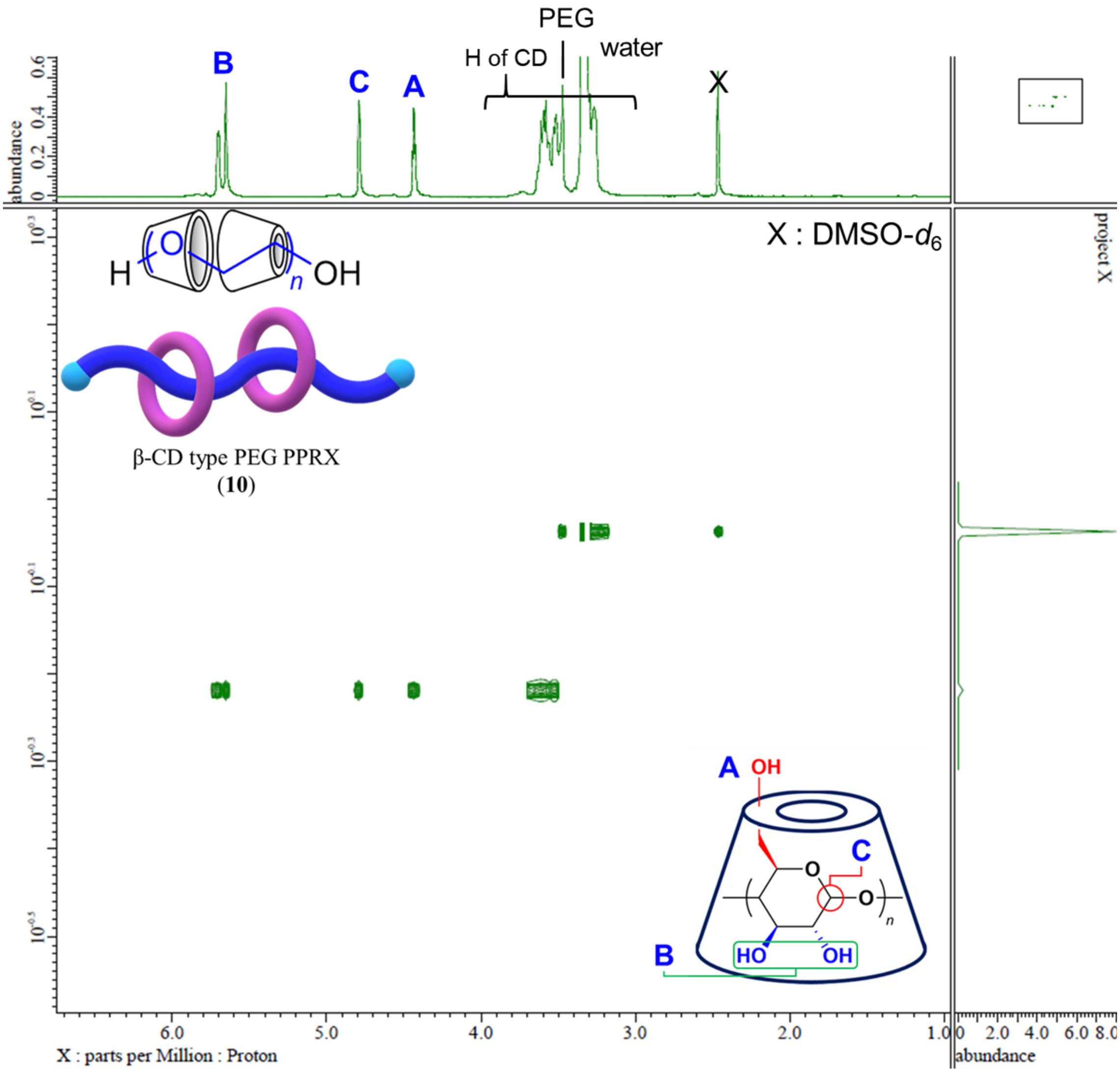


Figure S15. DOSY NMR spectrum of β-CD type PEG PPRX (**10**) (600 MHz, DMSO-d_6, 298 K).

In Figure S15, the DOSY spectra of the β-CD type PEG PPRX (**10**) is analyzed. The β-CD, PEG, and the peaks of the solvent. It can be confirmed that each components has the same values of diffusion coefficient between $10^{-0.3}$ $\mu m^2 ms^{-1}$ and $10^{-0.1}$ $\mu m^2 ms^{-1}$ at 3.5 ppm of the PEG moiety, and around 5.8, 4.8, 4.5, and broad peak from 4.0 to 3.0 ppm of outside protons of β-CD moieties.

4.9. DOSY NMR spectrum of γ-CD type PEG PPRX (γ-CD type PEG PPRX (11))

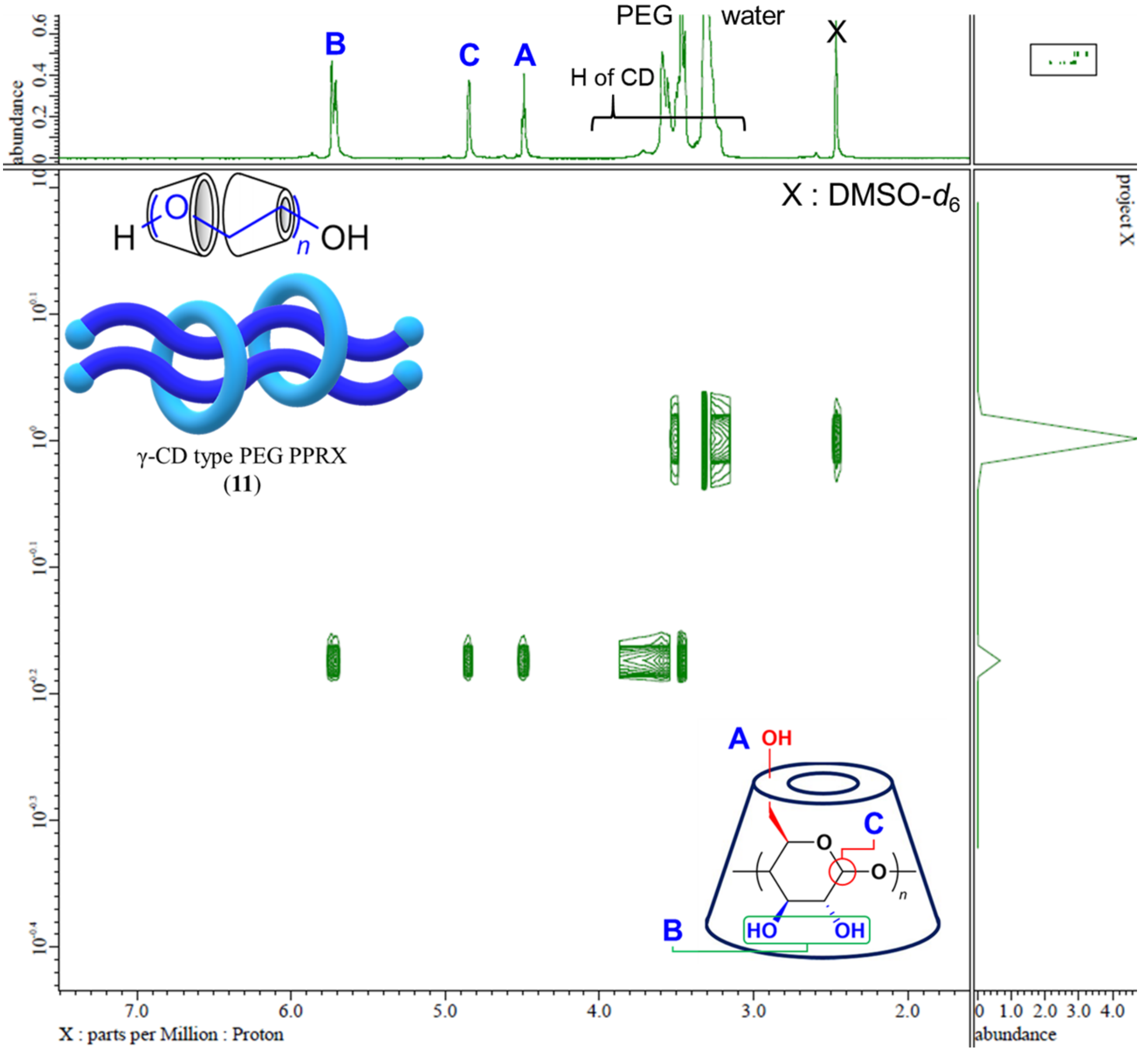


Figure S16. DOSY NMR spectrum of γ-CD type PEG PPRX (**11**) (600 MHz, DMSO-d_6, 298 K).

In Figure S16, the DOSY spectra of the γ-CD type PEG PPRX (**11**) is analyzed. The γ-CD, PEG, and the peaks of the solvent. It can be confirmed that each components has the same values of diffusion coefficient between $10^{-0.2}$ $\mu m^2 ms^{-1}$ and $10^{-0.1}$ $\mu m^2 ms^{-1}$ at 3.5 ppm of the PEG moiety, and around 5.8, 4.8, 4.5, and the broad peak from 4.0 to 3.0 ppm of outside protons of γ-CD moieties. Meanwhile, the γ-CD can form the PPRX structure with two PEG chains, so the structure may be composed of two polymer chains.

5. NOESY

5.1. NOESY NMR spectrum of α-CD type PPRX (PLLA-PEG-PLLA PPRX (3))

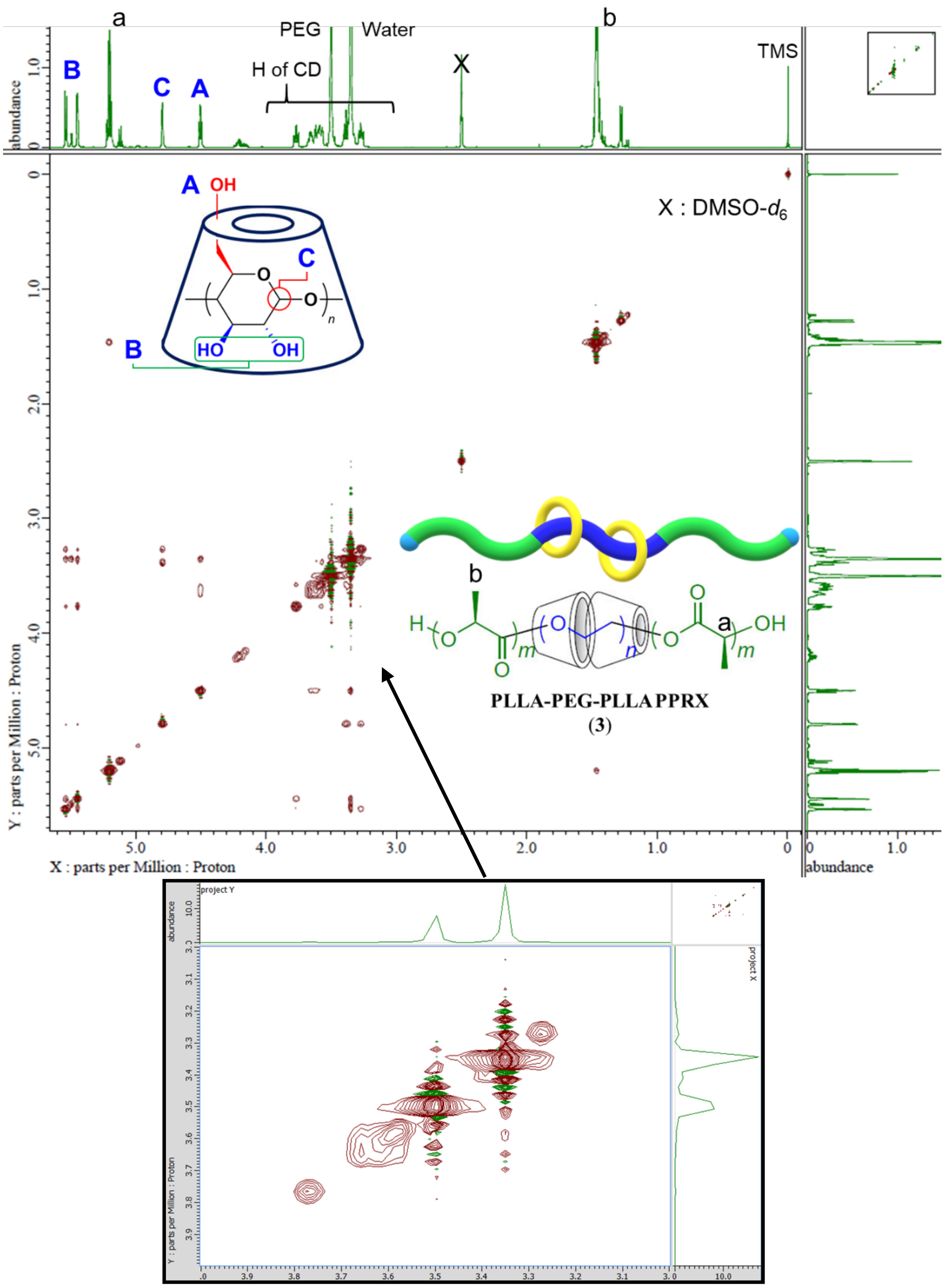


Figure S17. NOESY NMR spectrum of α-CD type PPRX (PLLA-PEG-PLLA PPRX (**3**)) (600 MHz, DMSO-d_6, 298 K).

5.2. NOESY NMR spectrum of α-CD type PPRX (PDLA-PEG-PDLA PPRX (4))

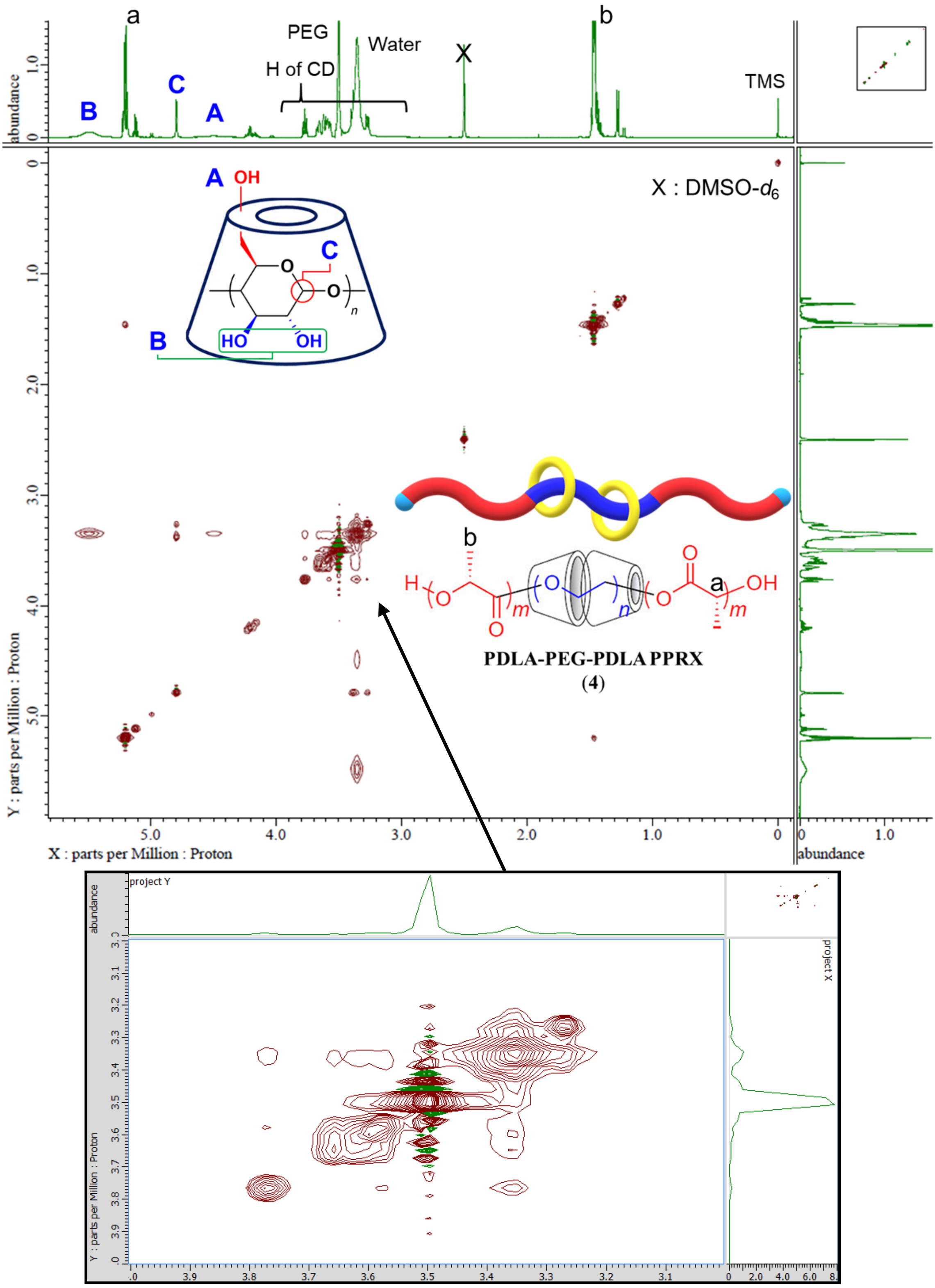


Figure S18. NOESY NMR spectrum of α-CD type PPRX (PDLA-PEG-PDLA PPRX (**4**)) (600 MHz, DMSO-d_6, 298 K).

5.3. NOESY NMR spectrum of β-CD type PPRX (PLLA-PEG-PLLA PPRX (5))

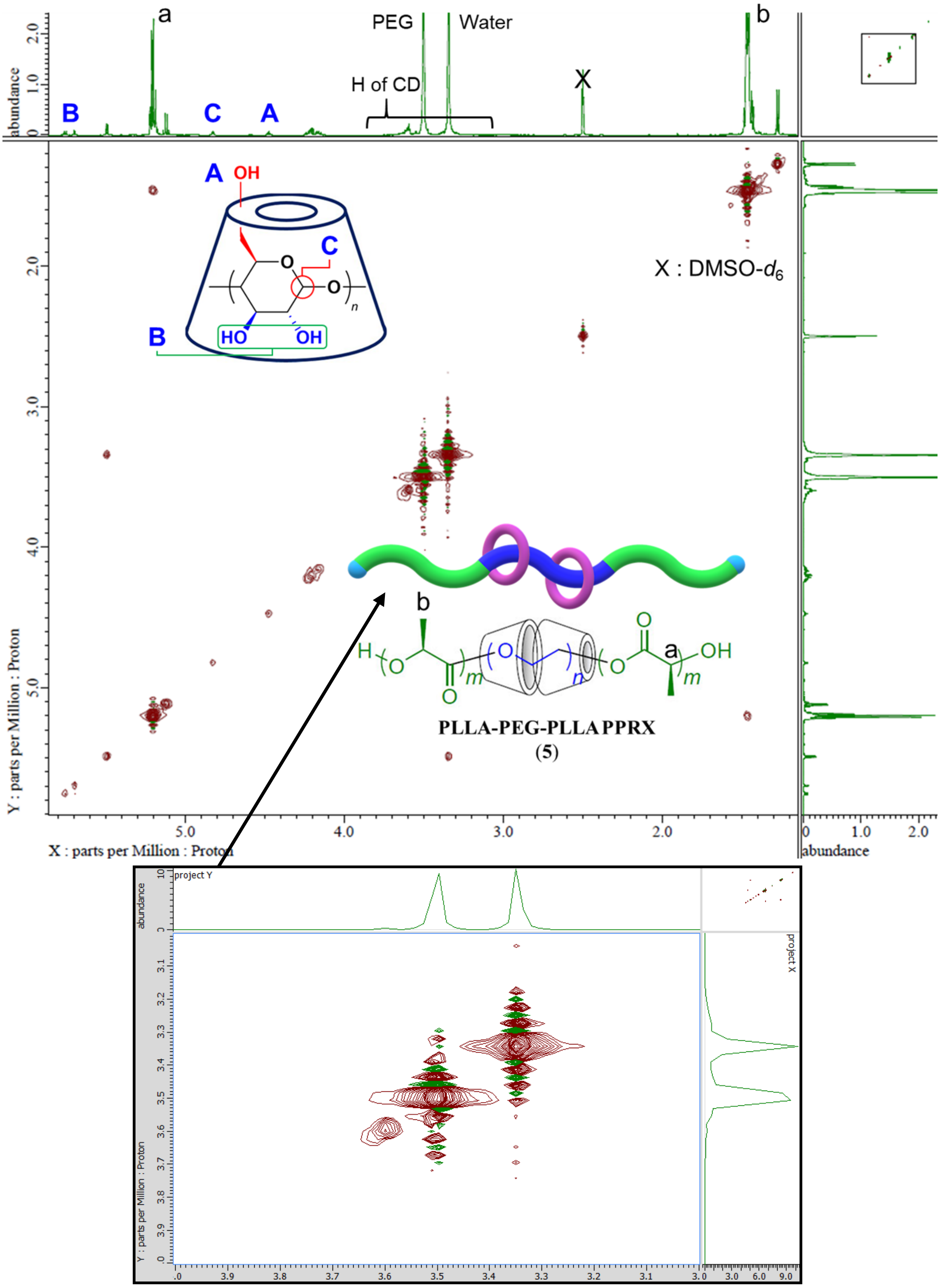


Figure S19. NOESY NMR spectrum of β-CD type PPRX (PLLA-PEG-PLLA PPRX (**5**)) (600 MHz, DMSO-d_6, 298 K).

5.4. NOESY NMR spectrum of β-CD type PPRX (PDLA-PEG-PDLA PPRX (6))

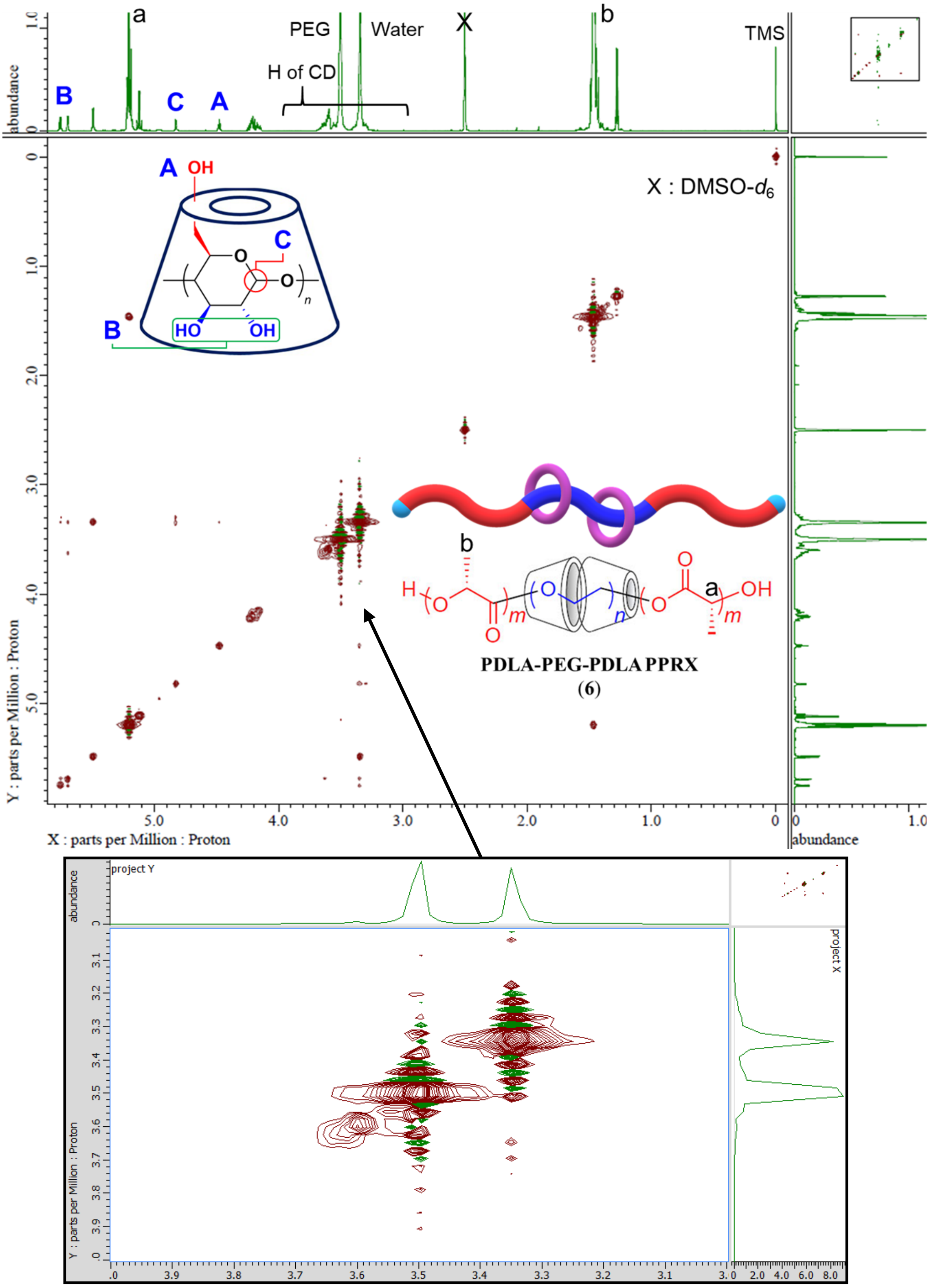


Figure S20. NOESY NMR spectrum of β-CD type PPRX (PDLA-PEG-PDLA PPRX (**6**)) (600 MHz, DMSO-d_6, 298 K).

5.5. NOESY NMR spectrum of γ-CD type PPRX (PLLA-PEG-PLLA PPRX (7))

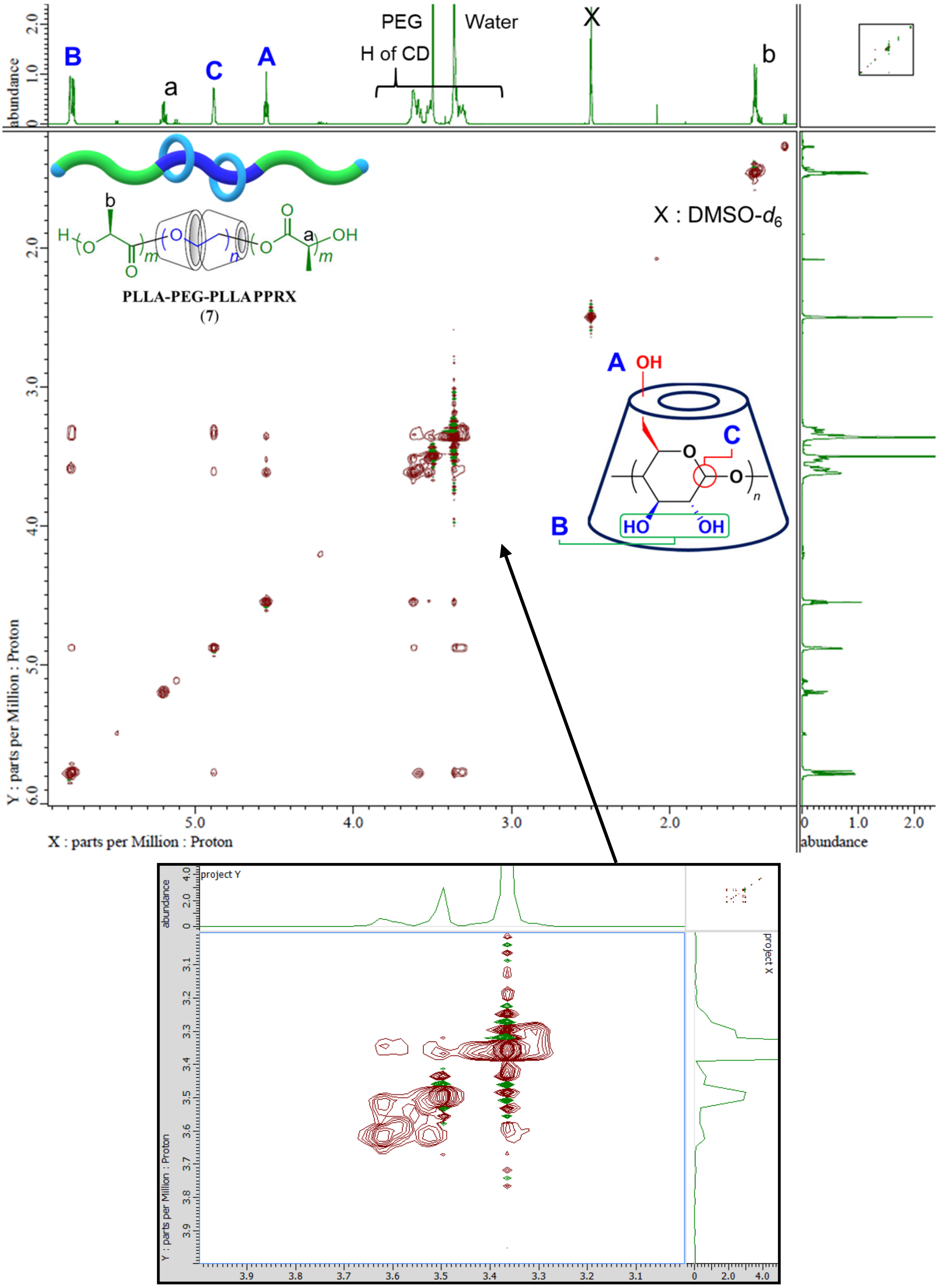


Figure S21. NOESY NMR spectrum of γ-CD type PPRX (PLLA-PEG-PLLA PPRX (7)) (600 MHz, DMSO-d_6, 298 K).

5.6. NOESY NMR spectrum of γ-CD type PPRX (PDLA-PEG-PDLA PPRX (8))

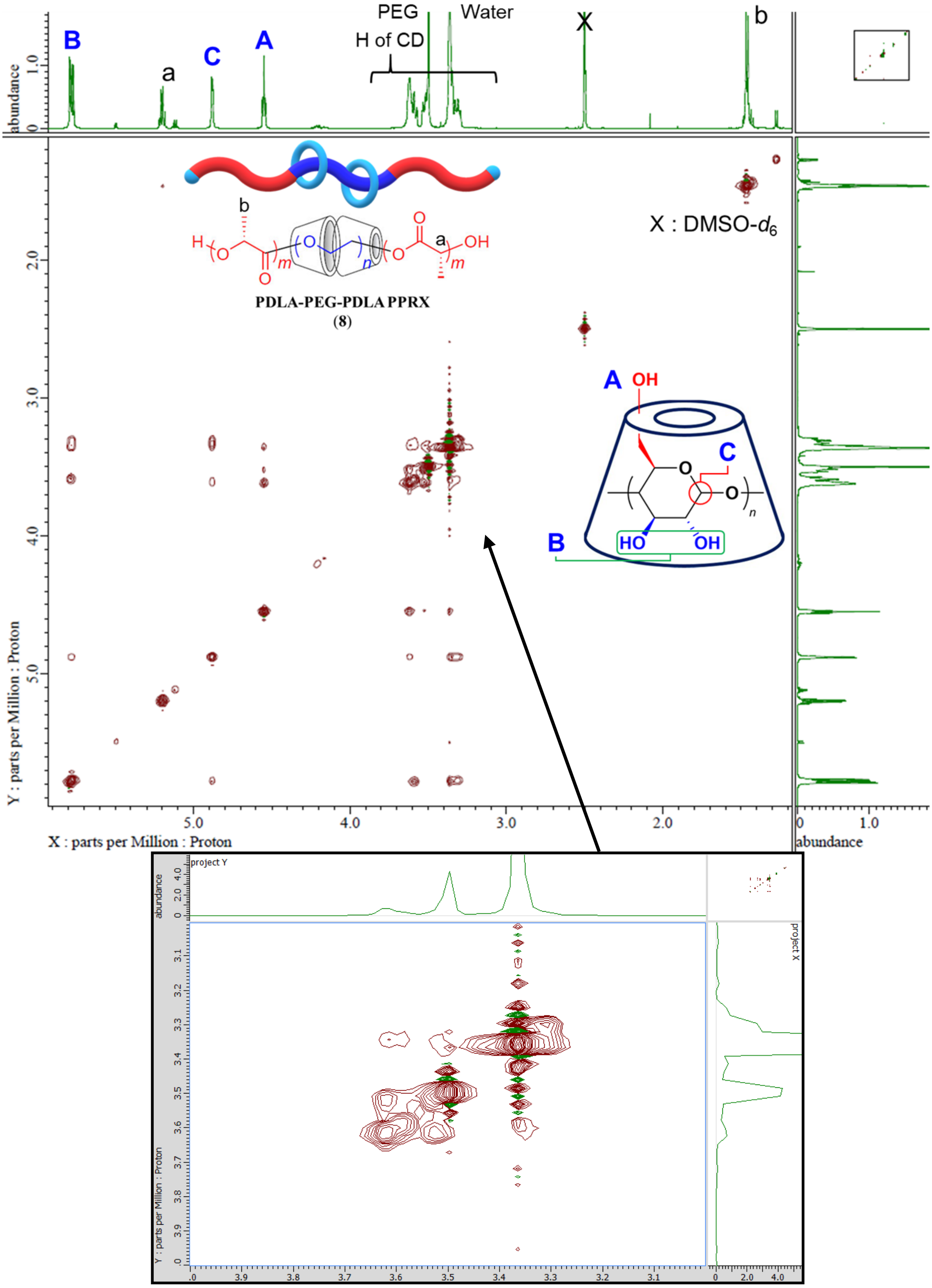


Figure S22. NOESY NMR spectrum of γ-CD type PPRX (PDLA-PEG-PDLA PPRX (**8**)) (600 MHz, DMSO-d_6, 298 K).

5.7. NOESY NMR spectrum of α-CD type PEG PPRX (α-CD type PEG PPRX (9))

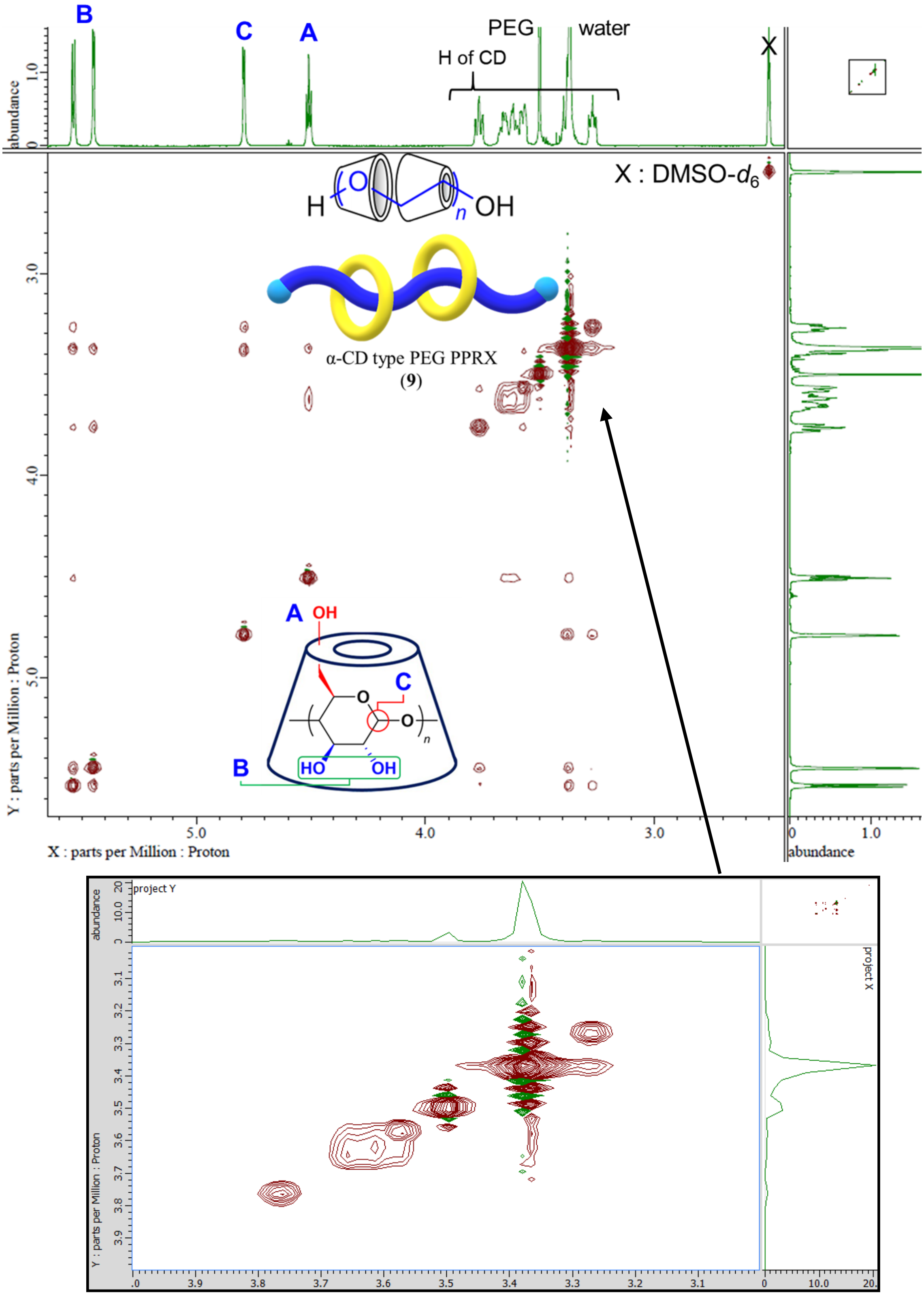


Figure S23. NOESY NMR spectrum of α-CD type PEG PPRX (**9**) (600 MHz, DMSO-d_6, 298 K).

5.8. NOESY NMR spectrum of β-CD type PEG PPRX (β-CD type PEG PPRX (10))

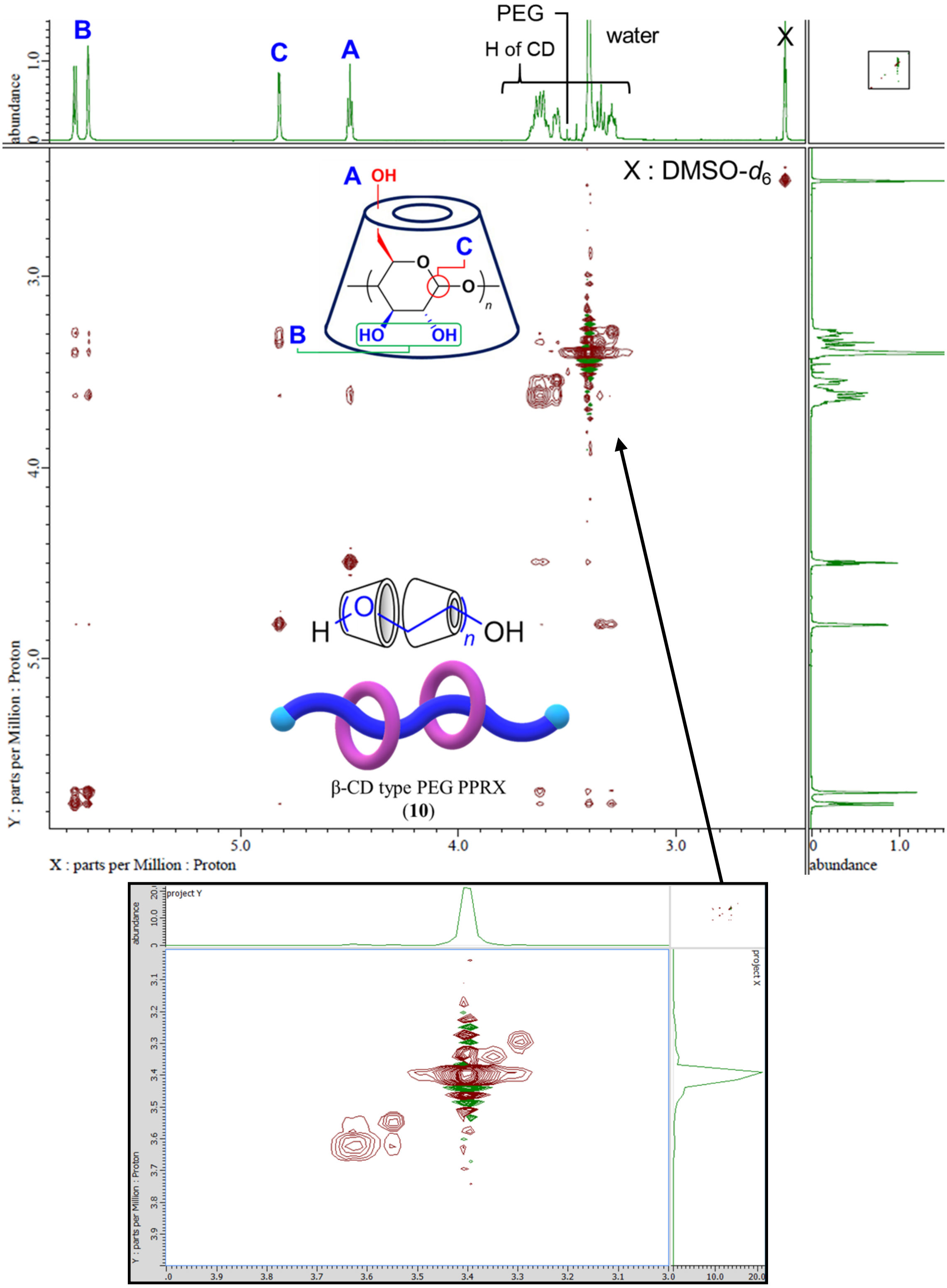


Figure S24. NOESY NMR spectrum of β-CD type PEG PPRX (**10**) (600 MHz, DMSO-d_6, 298 K).

5.9. NOESY NMR spectrum of γ-CD type PEG PPRX (γ-CD type PEG PPRX (11))

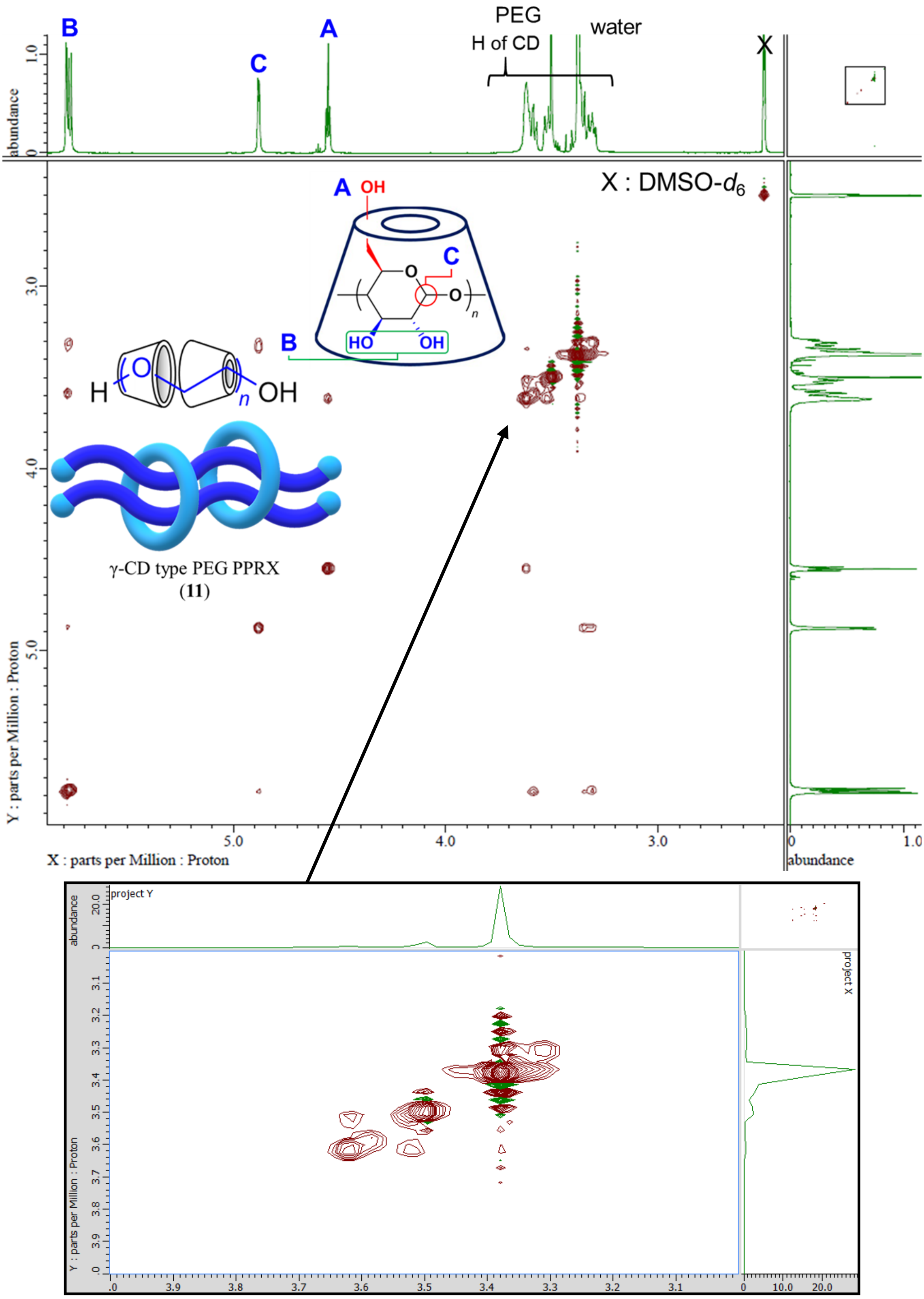


Figure S25. NOESY NMR spectrum of γ-CD type PEG PPRX (**11**) (600 MHz, DMSO-d_6, 298 K).

6. FT-IR

6.1. FT-IR of ABA type BCPs (1 and 2) and ABA type BCP SC (12)

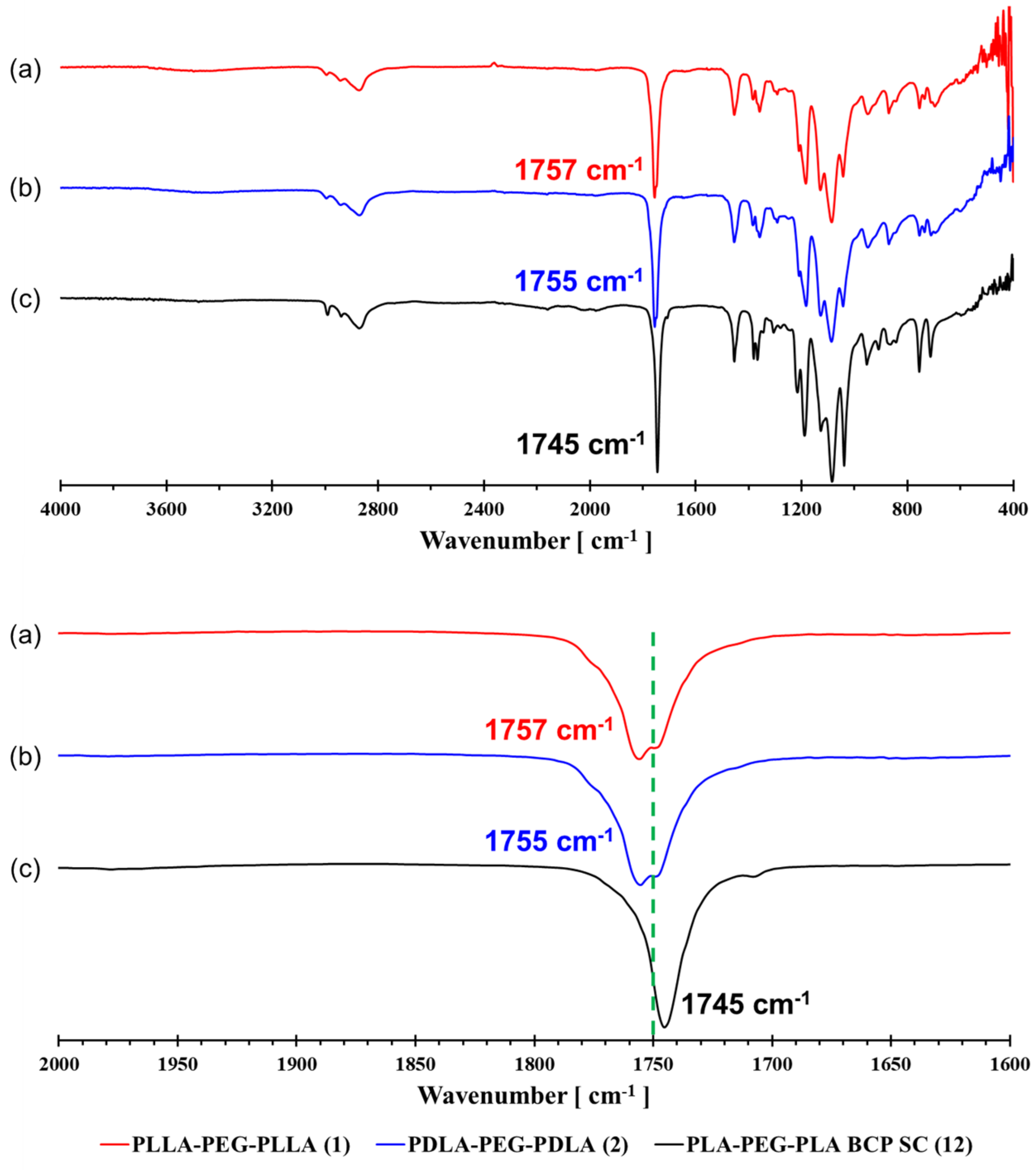


Figure S26. FT-IR spectra of BCPs: PLLA-PEG-PLLA (**1**) (a), PDLA-PEG-PDLA (**2**) (b) and PLA-PEG-PLA BCP SC (**12**) (c).

6.2. FT-IR of α-CD type PPRXs (3 and 4) and α-CD type PPRX SC (13)

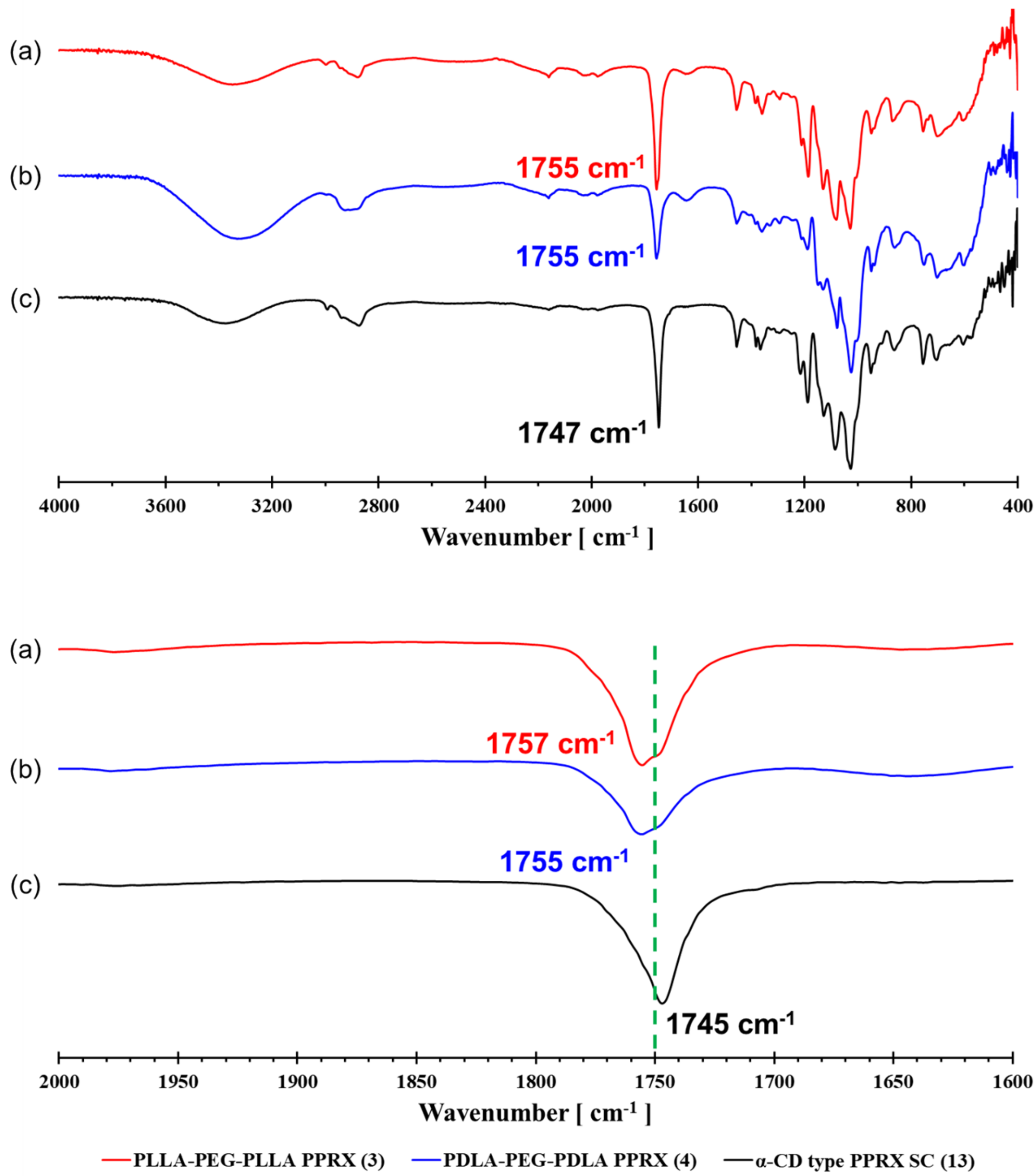


Figure S27. FT-IR spectra of α-CD type PPRXs: PLLA-PEG-PLLA PPRX (**3**) (a), PDLA-PEG-PDLA PPRX (**4**) (b) and α-CD type PPRX SC (**13**) (c).

6.3. FT-IR of β-CD type PPRXs (5 and 6) and β-CD type PPRX SC (14)

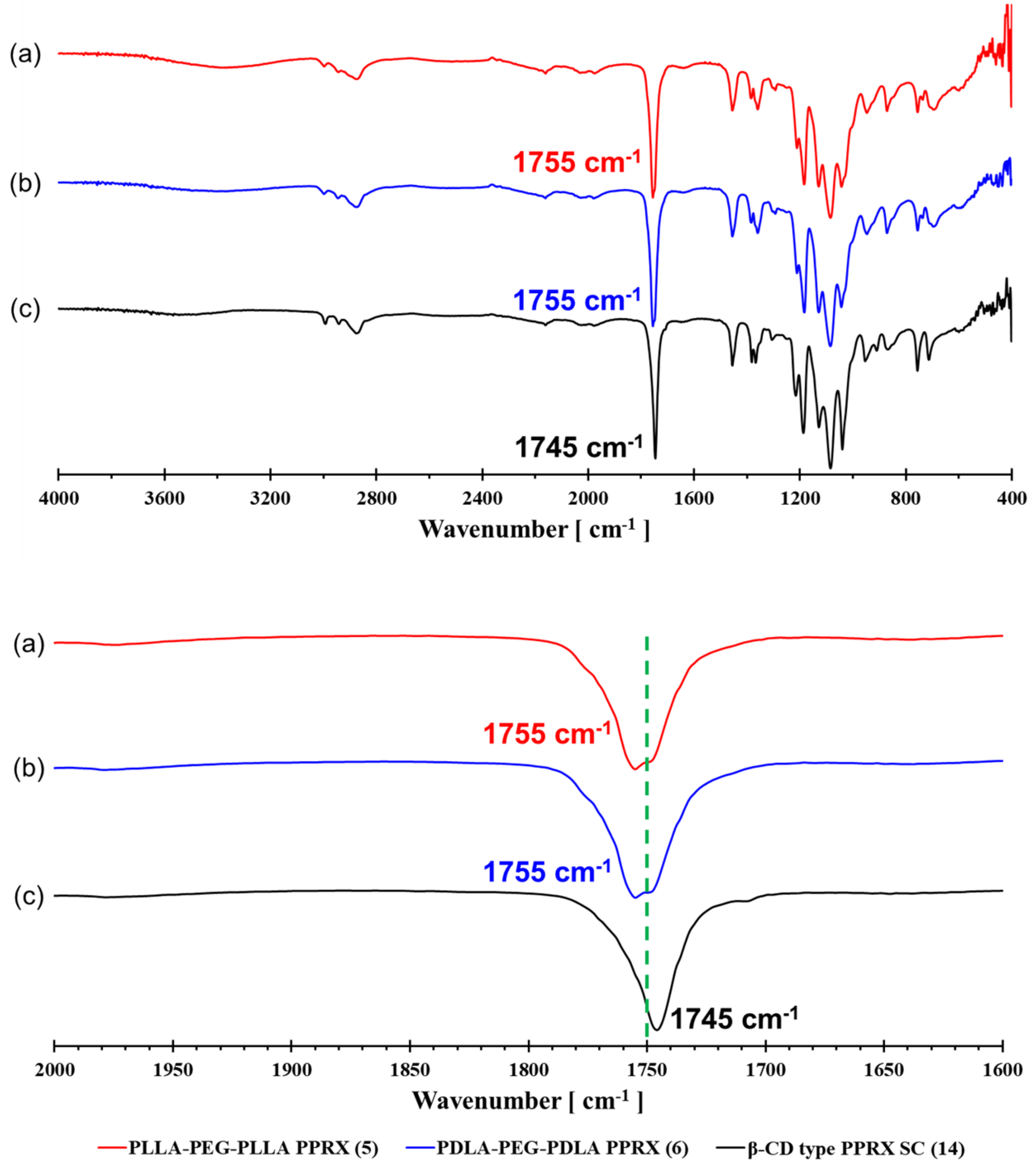


Figure S28. FT-IR spectra of β-CD type PPRXs: PLLA-PEG-PLLA PPRX (**5**) (a), PDLA-PEG-PDLA PPRX (**6**) (b) and β-CD type PPRX SC (**14**) (c).

6.4. FT-IR of γ-CD type PPRXs (7 and 8) and γ-CD type PPRX SC (15)

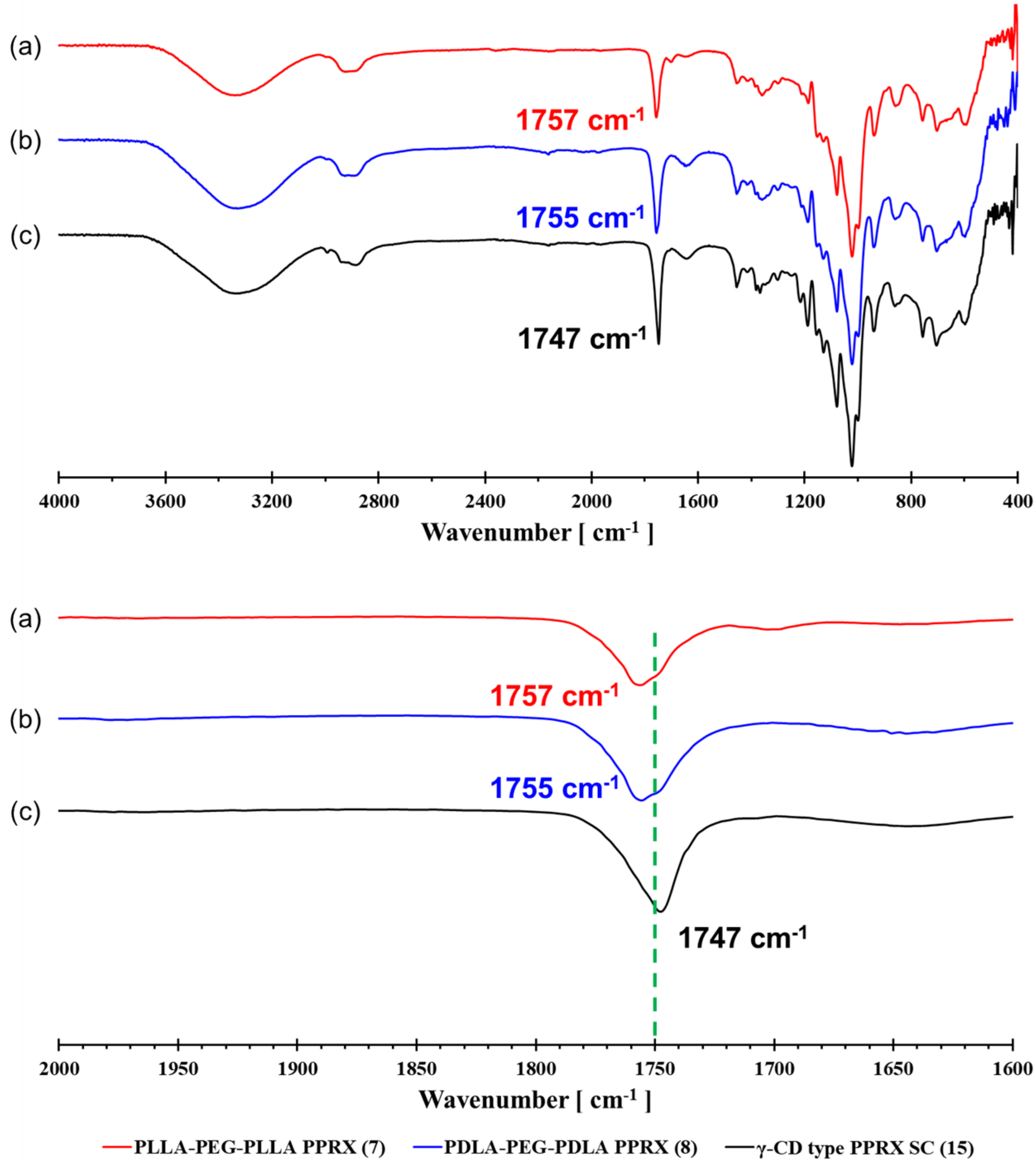


Figure S29. FT-IR spectra of γ-CD type PPRXs: PLLA-PEG-PLLA PPRX (**7**) (a), PDLA-PEG-PDLA PPRX (**8**) (b) and γ-CD type PPRX SC (**15**) (c).

6.5. FT-IR of PEG PPRXs (9, 10 and 11)

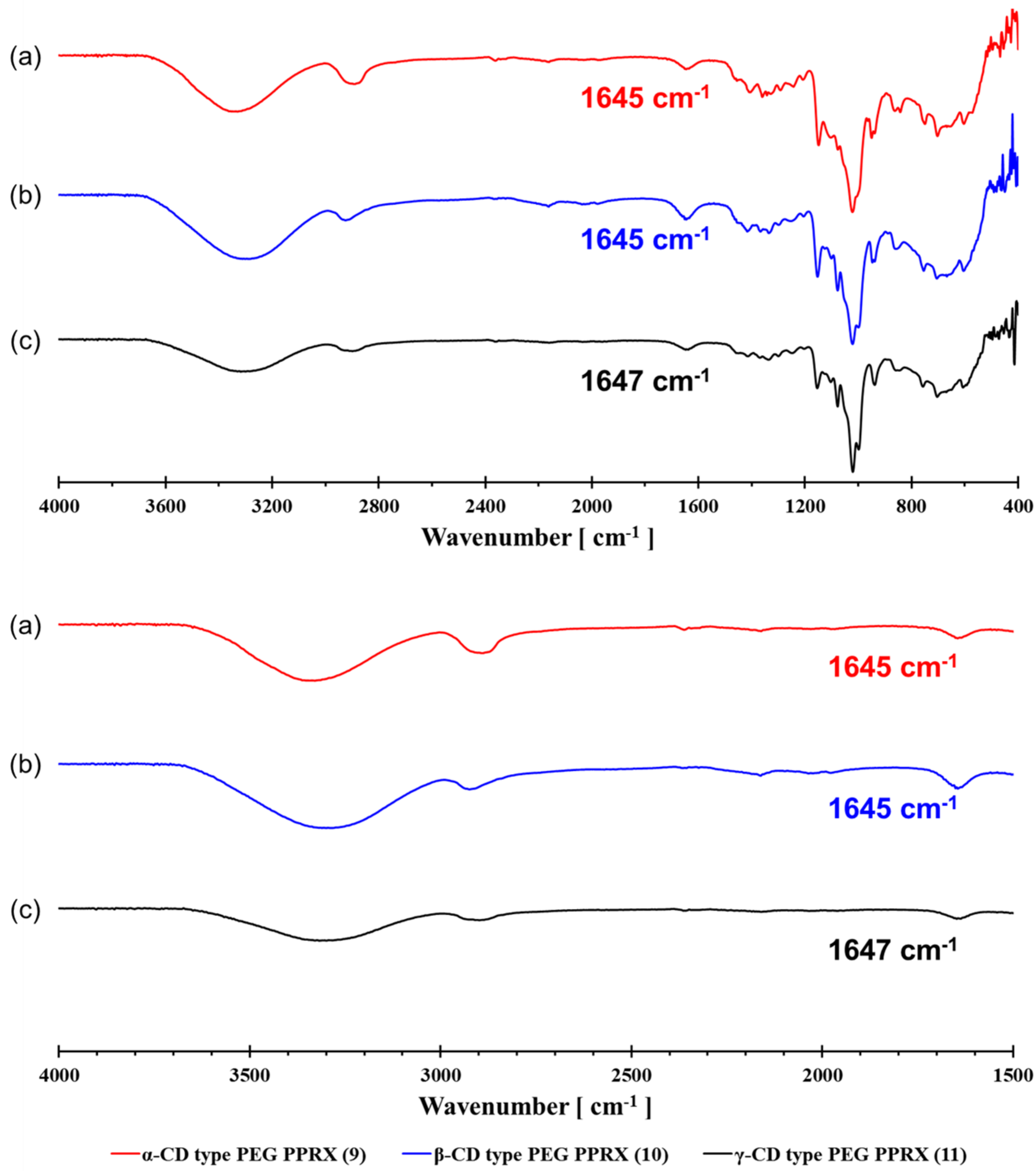


Figure S30. FT-IR spectra of PEG PPRXs: α-CD type PEG PPRX (**9**) (a), β-CD type PEG PPRX (**10**) (b) and γ-CD type PEG PPRX (**11**) (c).

6.6. FT-IR of α-, β- and γ-CD

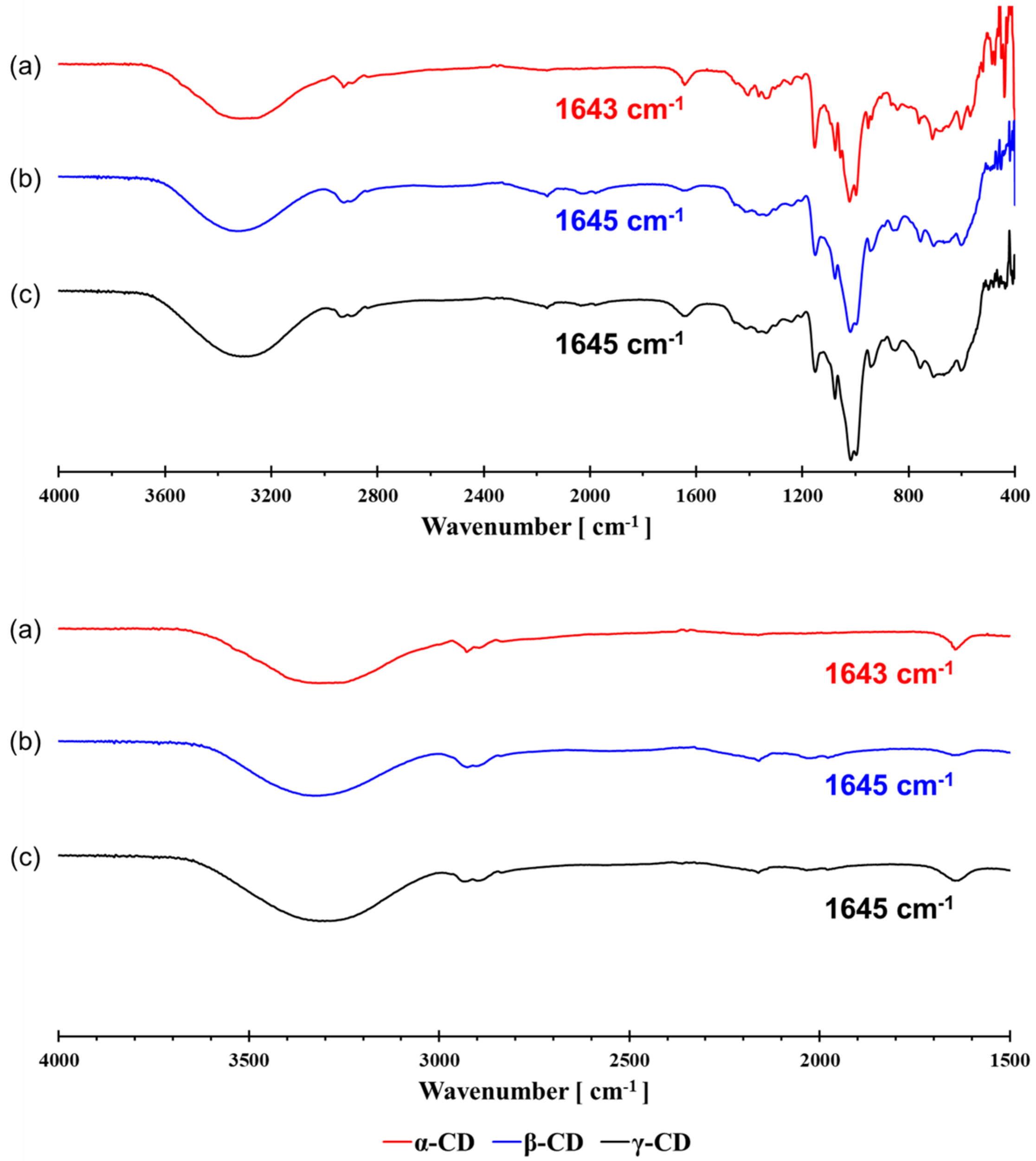


Figure S31. FT-IR spectra of CDs: α-CD (a), β-CD (b) and γ-CD (c).

7. XRD

7.1. XRD of ABA type BCPs (1 and 2) and ABA type BCP SC (12)

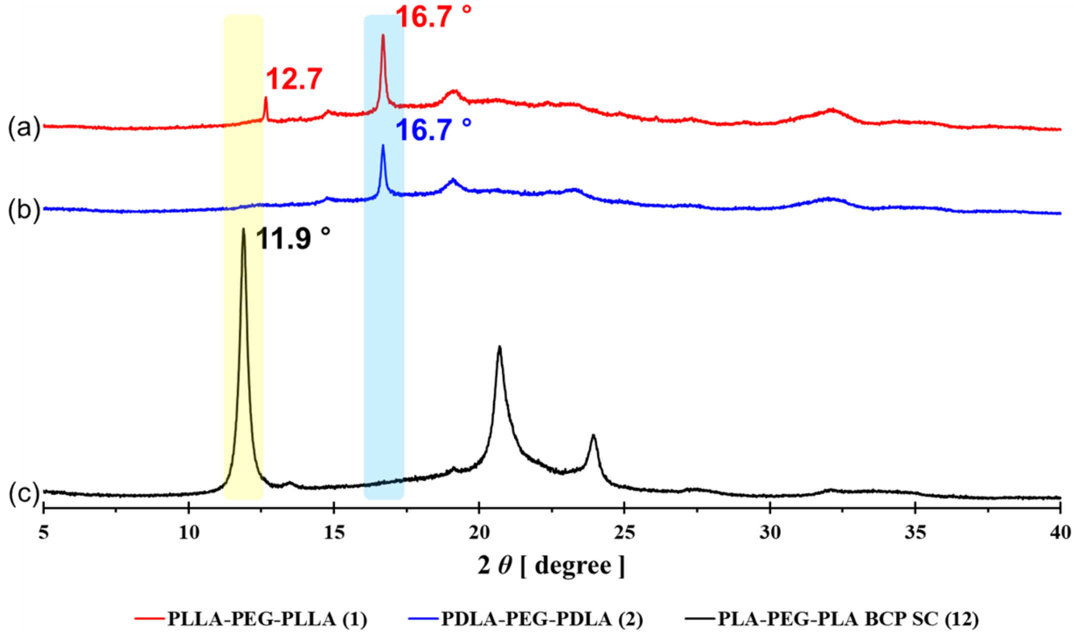


Figure S32. XRD spectra of BCP types: PLLA-PEG-PLLA (**1**) (a), PDLA-PEG-PDLA (**2**) (b) and PLA-PEG-PLA BCP SC (**12**) (c).

7.2. XRD of α-CD type PPRXs (3 and 4) and α-CD type PPRX SC (13)

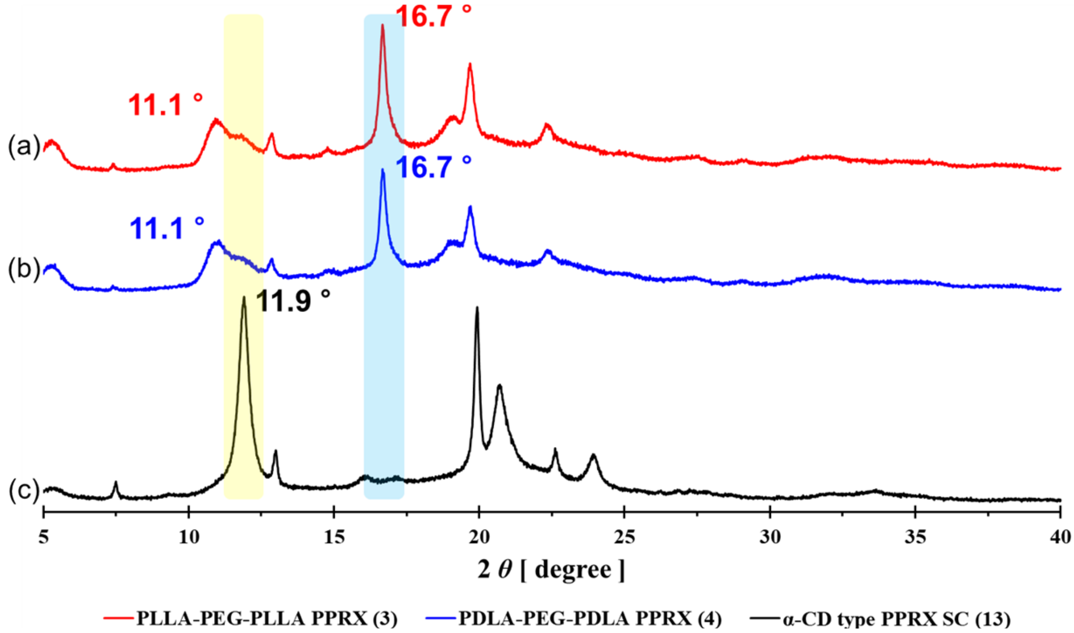


Figure S33. XRD spectra of α-CD type PPRXs: PLLA-PEG-PLLA PPRX (**3**) (a), PDLA-PEG-PDLA PPRX (**4**) (b) and α-CD type PPRX SC (**13**) (c).

7.3. XRD of β-CD type PPRXs (5 and 6) and β-CD type PPRX SC (14)

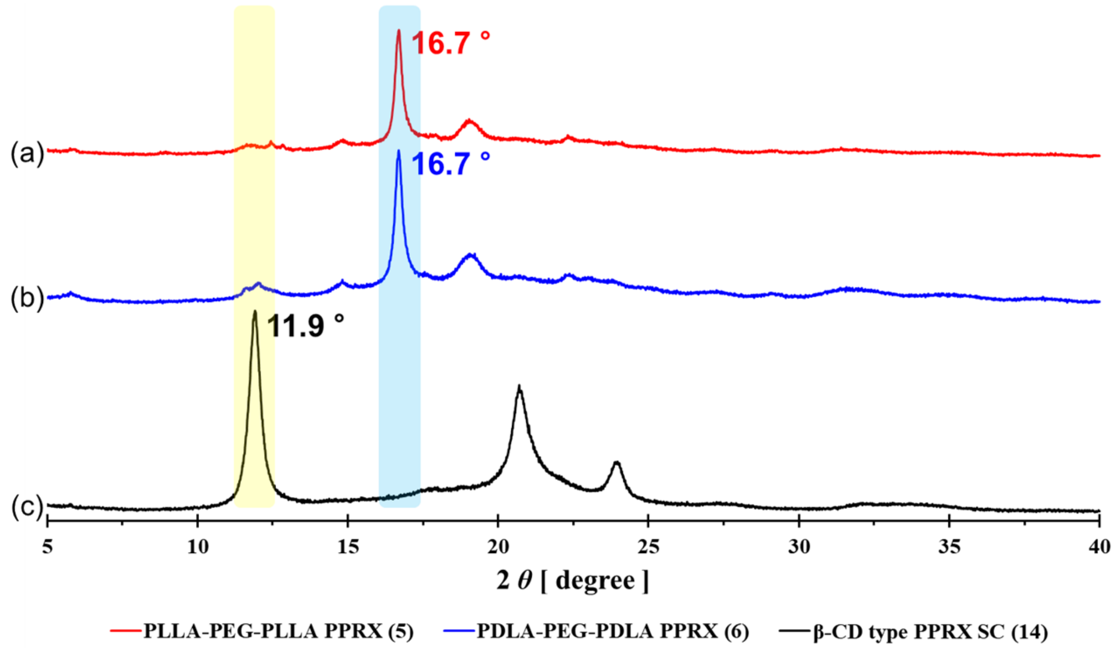


Figure S34. XRD spectra of β-CD type PPRXs: PLLA-PEG-PLLA PPRX (**5**) (a), PDLA-PEG-PDLA PPRX (**6**) (b) and β-CD type PPRX SC (**14**) (c).

7.4. XRD of γ-CD type PPRXs (7 and 8) and γ-CD type PPRX SC (15)

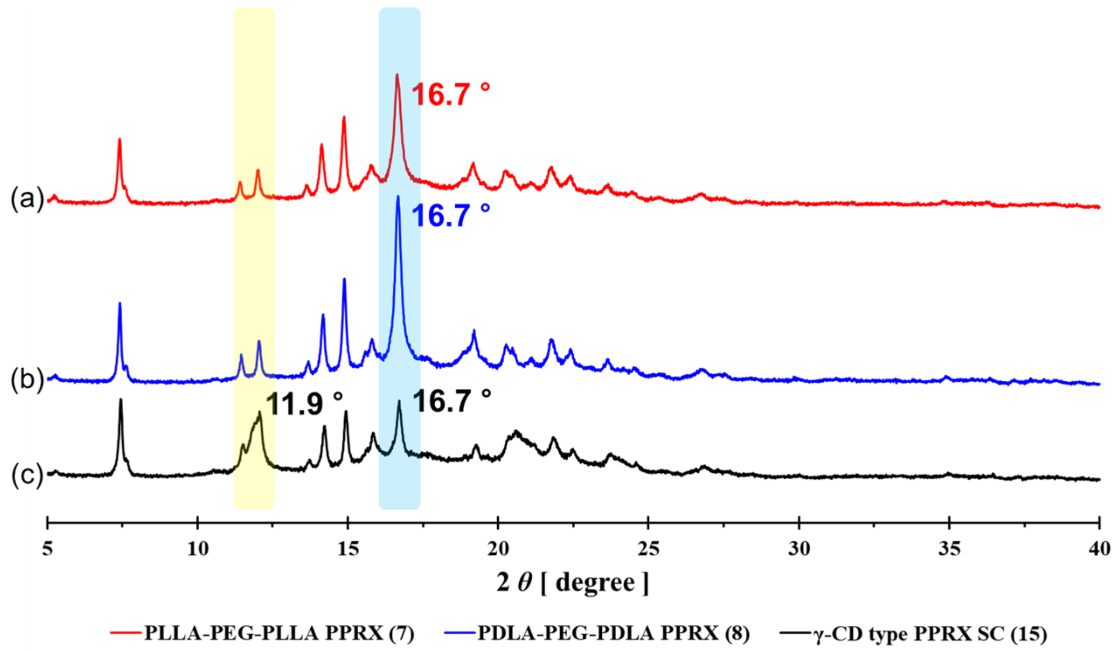


Figure S35. XRD spectra of γ-CD type PPRXs: PLLA-PEG-PLLA PPRX (**7**) (a), PDLA-PEG-PDLA PPRX (**8**) (b) and γ-CD type PPRX SC (**15**) (c).

7.5. XRD of PEG PPRXs (9, 10 and 11)

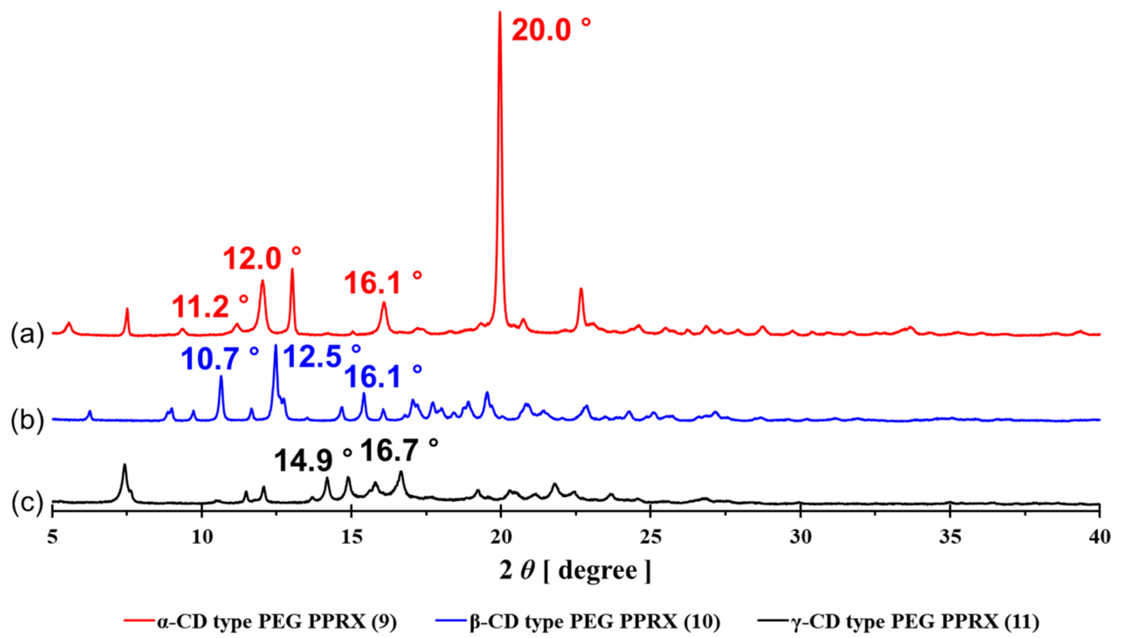


Figure S36. XRD spectra of PEG PPRXs: α-CD type PEG PPRX (**9**) (a), β-CD type PEG PPRX (**10**) (b) and γ-CD type PEG PPRX (**11**).

7.6. XRD of α-, β- and γ-CD

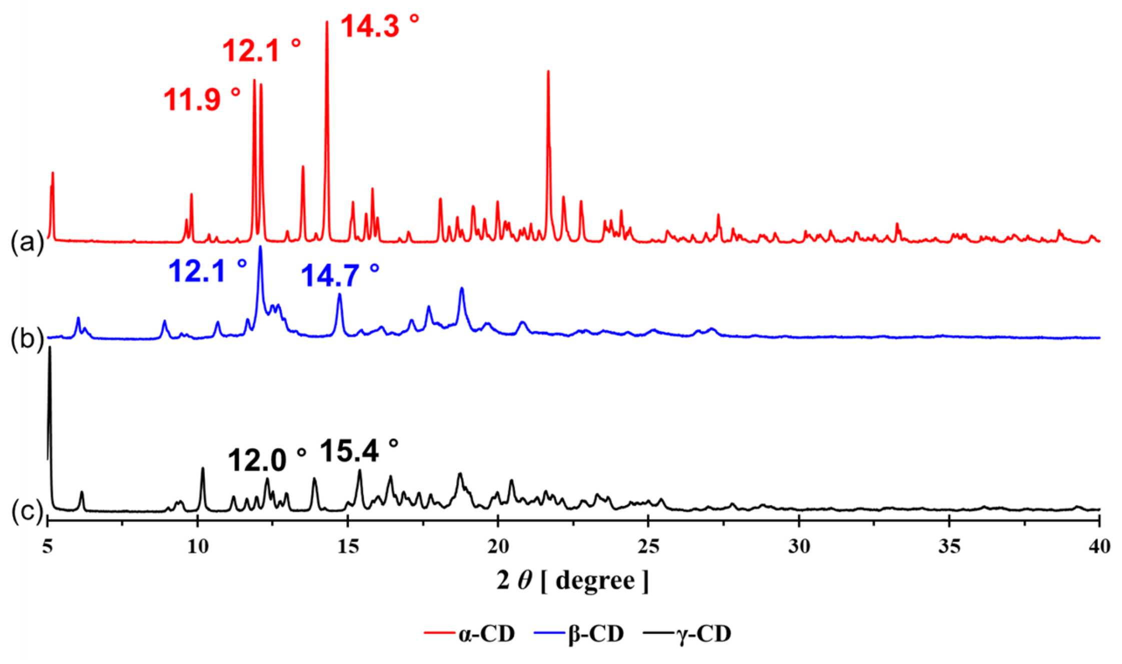


Figure S37. XRD spectra of CDs: α-CD (a), β-CD (b) and γ-CD (c).

8. DSC

8.1. DSC of ABA type BCPs (1 and 2) and ABA type BCP SC (12)

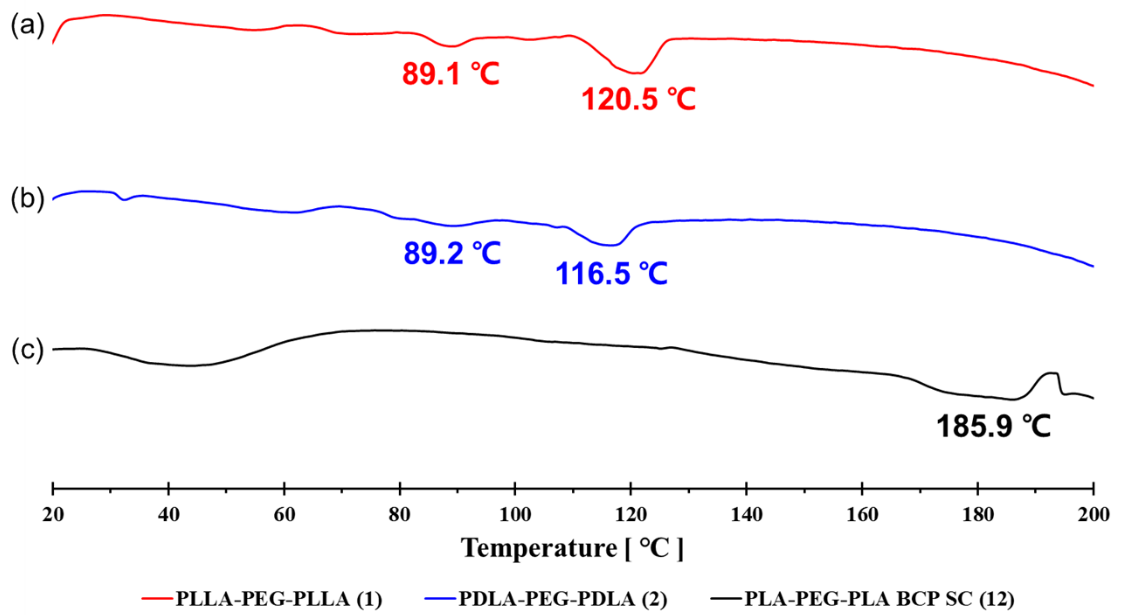


Figure S38. DSC analyses of BCP types: PLLA-PEG-PLLA (**1**) (a), PDLA-PEG-PDLA (**2**) (b) and PLA-PEG-PLA BCP SC (**12**) (c).

8.2. DSC of α-CD type PPRXs (3 and 4) and α-CD type PPRX SC (13)

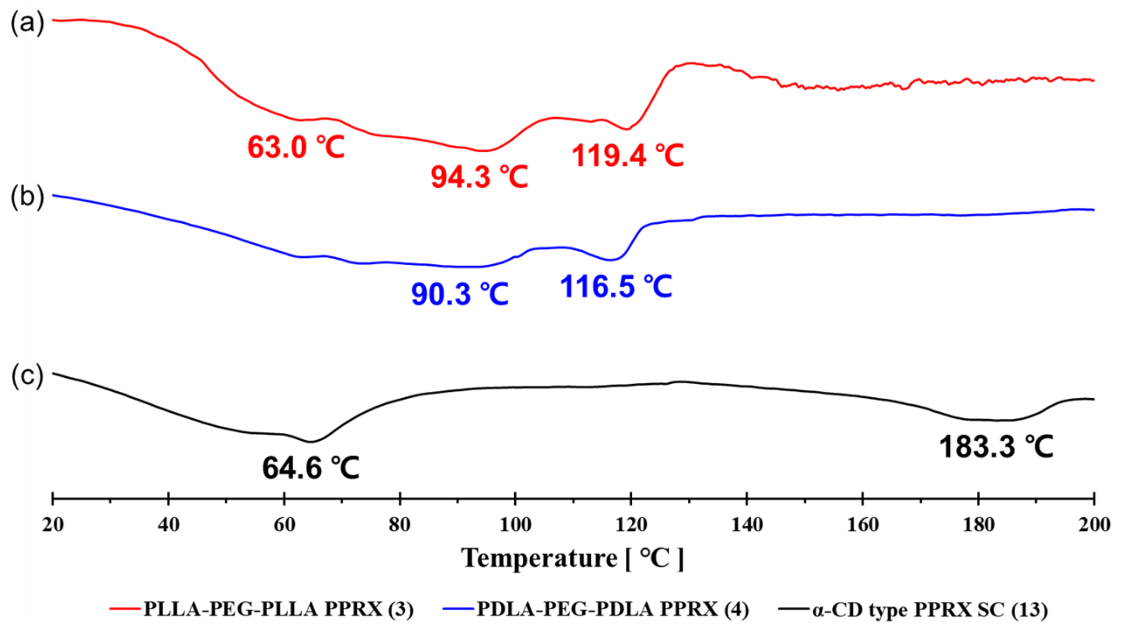


Figure S39. DSC analyses of α-CD type PPRXs: PLLA-PEG-PLLA PPRX (**3**) (a), PDLA-PEG-PDLA PPRX (**4**) (b) and α-CD type PPRX SC (**13**) (c).

8.3. DSC of β-CD type PPRXs (5 and 6) and β-CD type PPRX SC (14)

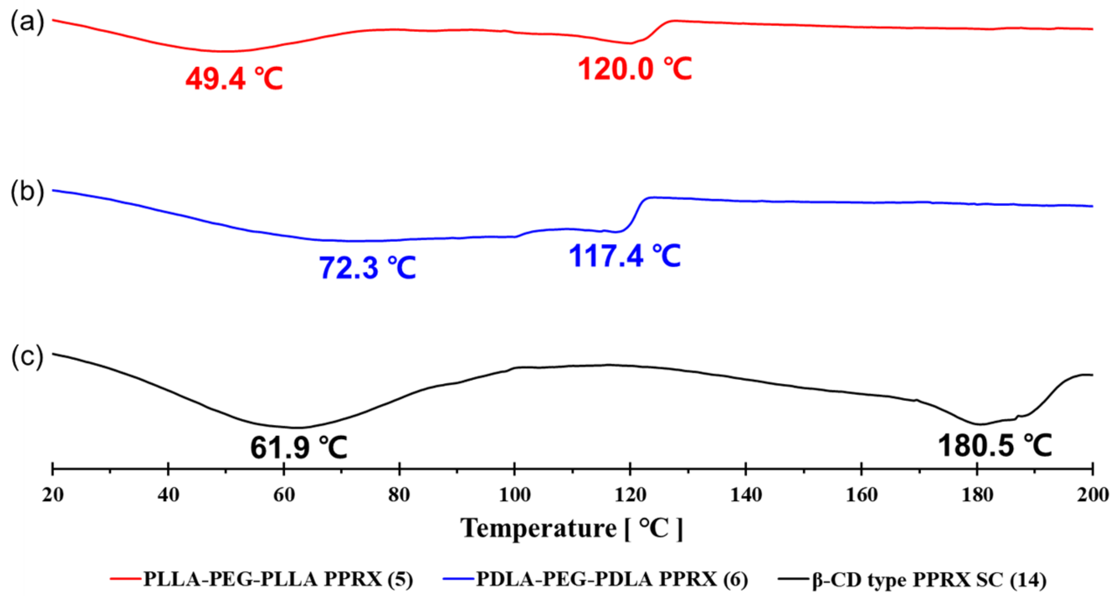


Figure S40. DSC analyses of β-CD type PPRXs: PLLA-PEG-PLLA PPRX (**5**) (a), PDLA-PEG-PDLA PPRX (**6**) (b) and β-CD type PPRX SC (**14**) (c).

8.4. DSC of γ-CD type PPRXs (7 and 8) and γ-CD type PPRX SC (15)

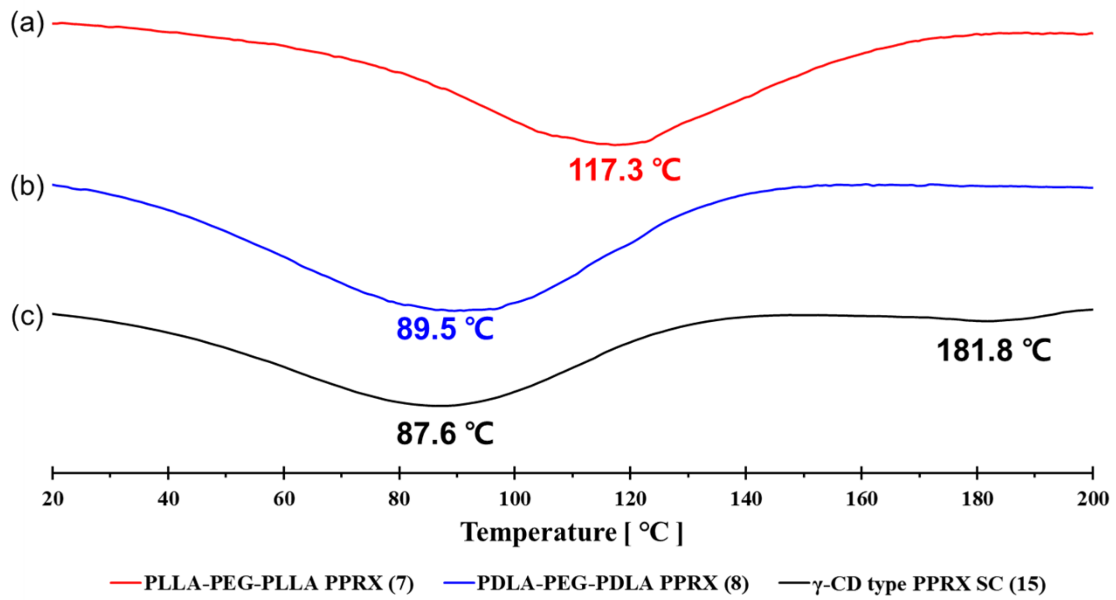


Figure S41. DSC analyses of γ-CD type PPRXs: PLLA-PEG-PLLA PPRX (**7**) (a), PDLA-PEG-PDLA PPRX (**8**) (b) and γ-CD type PPRX SC (**15**) (c).

8.5. DSC of PEG PPRXs (**9**, **10** and **11**)

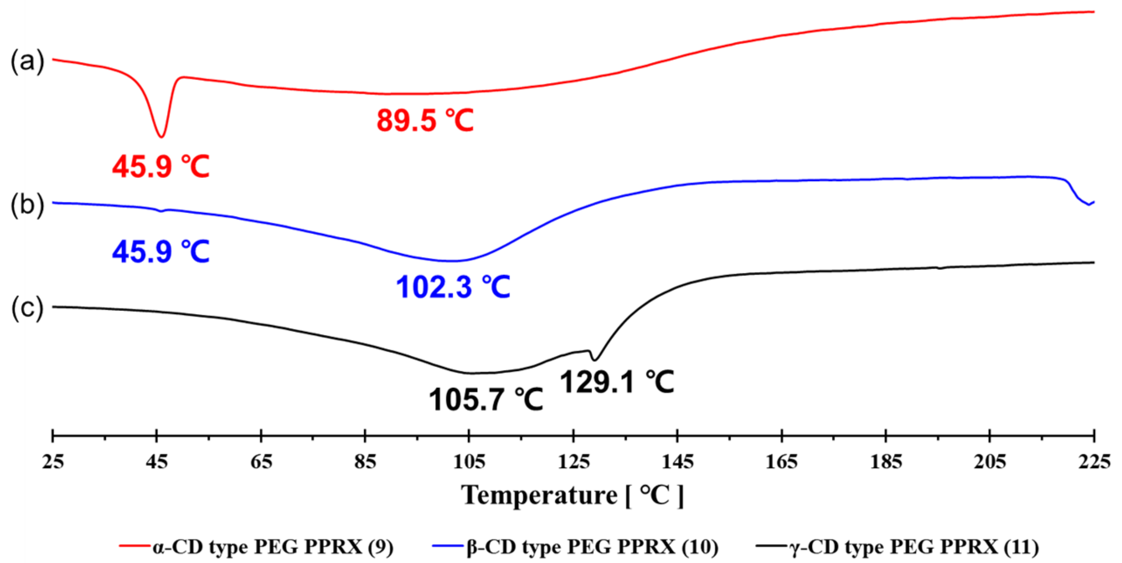


Figure S42. DSC analyses PEG PPRXs: α-CD type PEG PPRX (**9**) (a), β-CD type PEG PPRX (**10**) (b) and γ-CD type PEG PPRX (**11**).

8.6. DSC of α-, β- and γ-CD

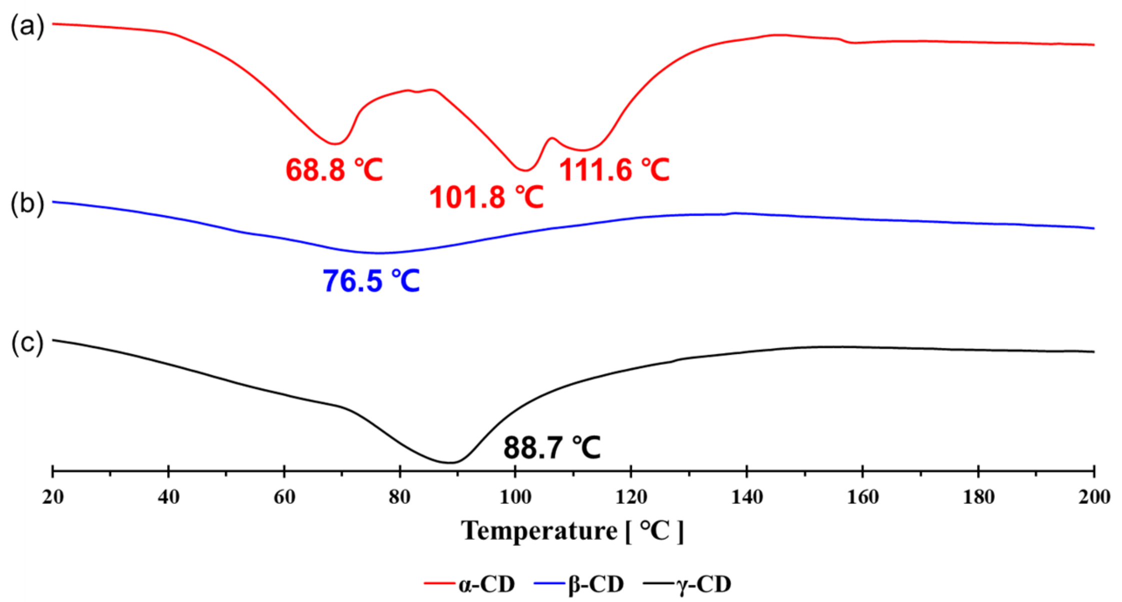


Figure S43. DSC analyses of CDs: α-CD (a), β-CD (b) and γ-CD (c).

9. TGA

9.1. TGA of ABA type BCPs (1 and 2) and ABA type BCP SC (12)

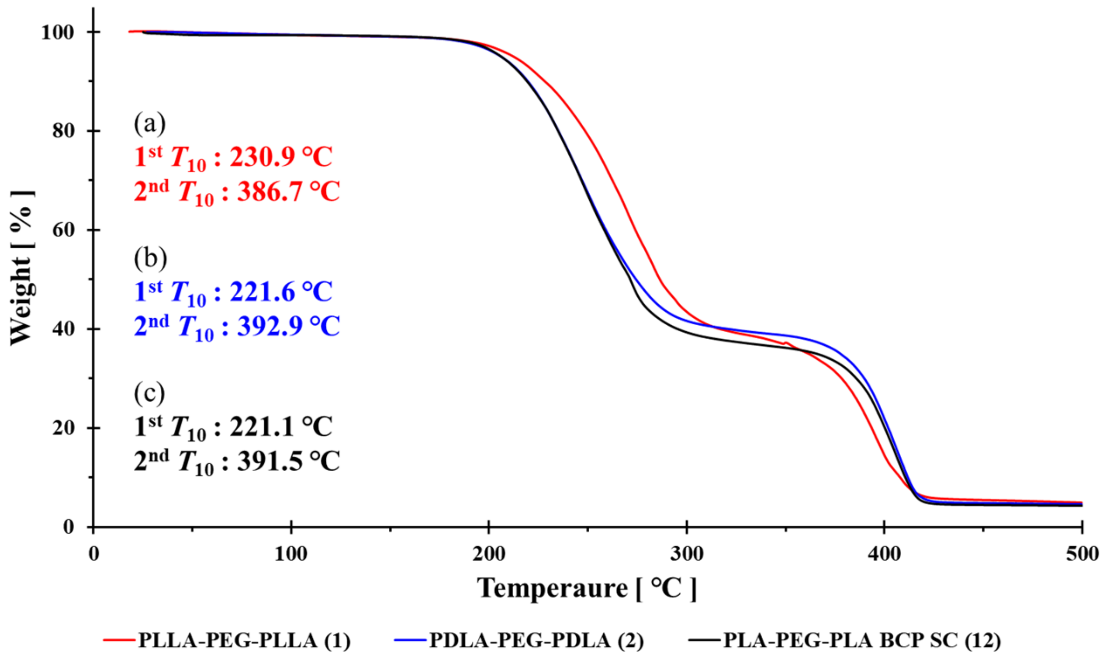


Figure S44. TGA of BCP types: PLLA-PEG-PLLA (**1**) (a), PDLA-PEG-PDLA (**2**) (b) and PLA-PEG-PLA BCP SC (**12**) (c).

9.2. TGA of α-CD type PPRXs (3 and 4) and α-CD type PPRX SC (13)

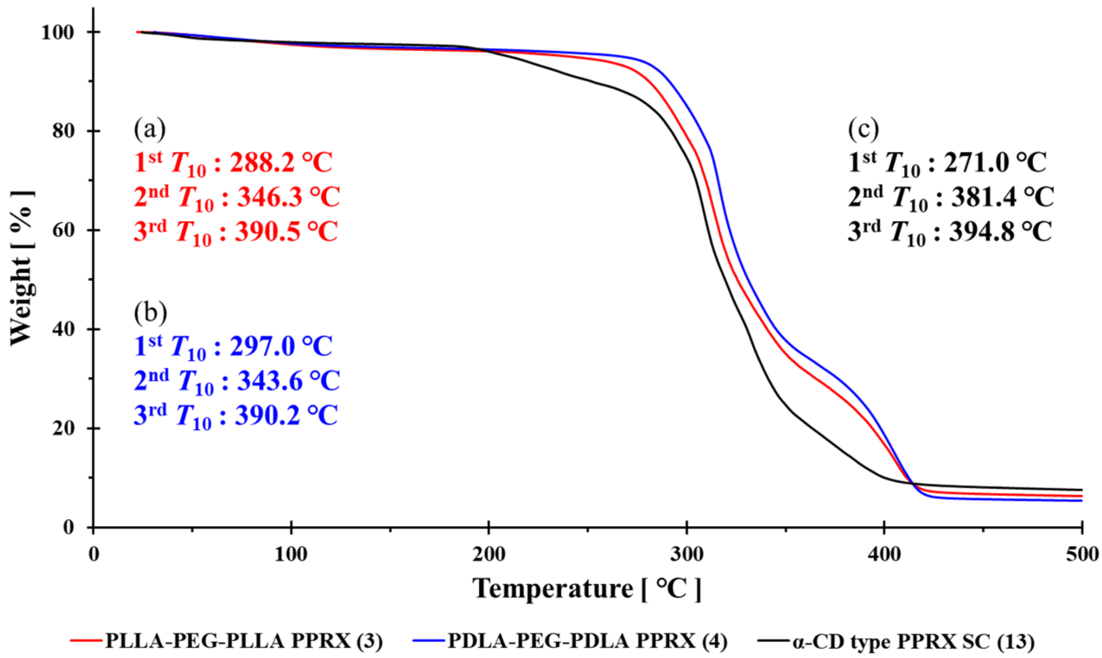


Figure S45. TGA of α-CD type PPRXs: PLLA-PEG-PLLA PPRX (**3**) (a), PDLA-PEG-PDLA

PPRX (**4**) (b) and α-CD type PPRX SC (**13**) (c).

9.3. TGA of β-CD type PPRXs (5 and 6) and β-CD type PPRX SC (14)

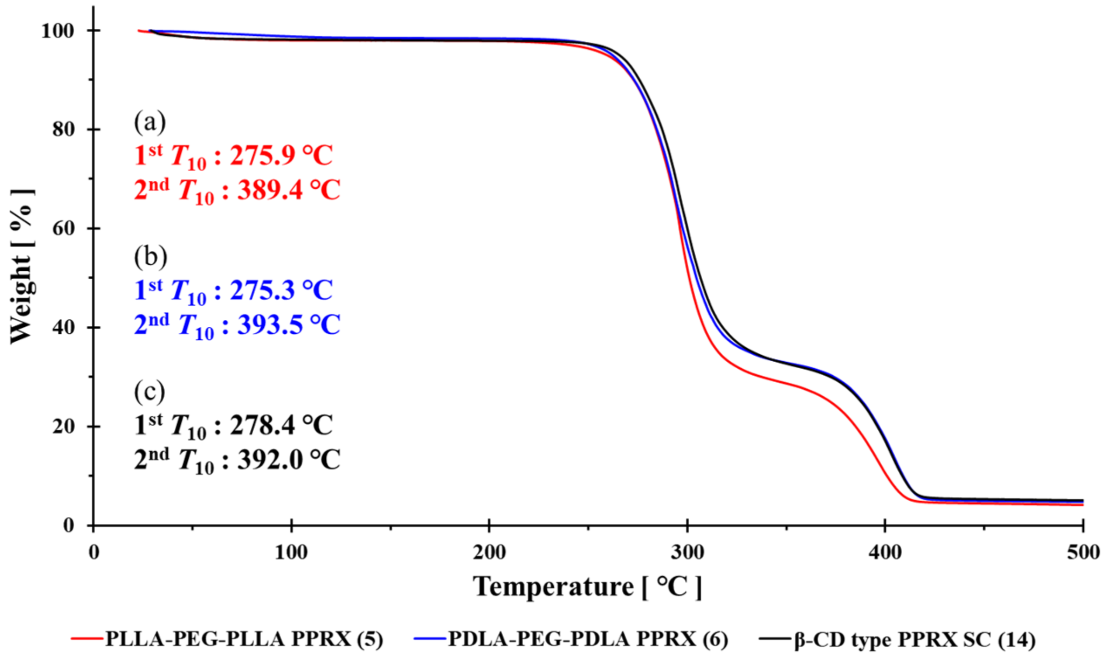


Figure S46. TGA of β-CD type PPRXs: PLLA-PEG-PLLA PPRX (**5**) (a), PDLA-PEG-PDLA PPRX (**6**) (b) and β-CD type PPRX SC (**14**) (c).

9.4. TGA of γ-CD type PPRXs (7 and 8) and γ-CD type PPRX SC (15)

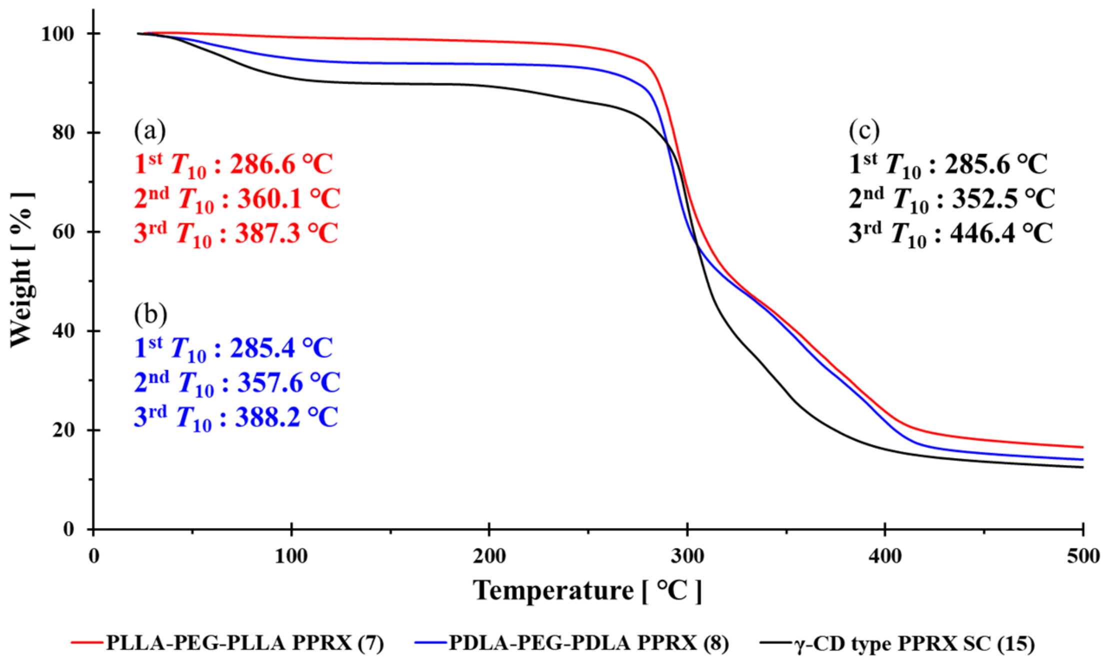


Figure S47. TGA of γ-CD type PPRXs: PLLA-PEG-PLLA PPRX (**7**) (a), PDLA-PEG-PDLA

PPRX (**8**) (b) and γ-CD type PPRX SC (**15**) (c).

9.5. TGA of PEG PPRXs (9, 10 and 11)

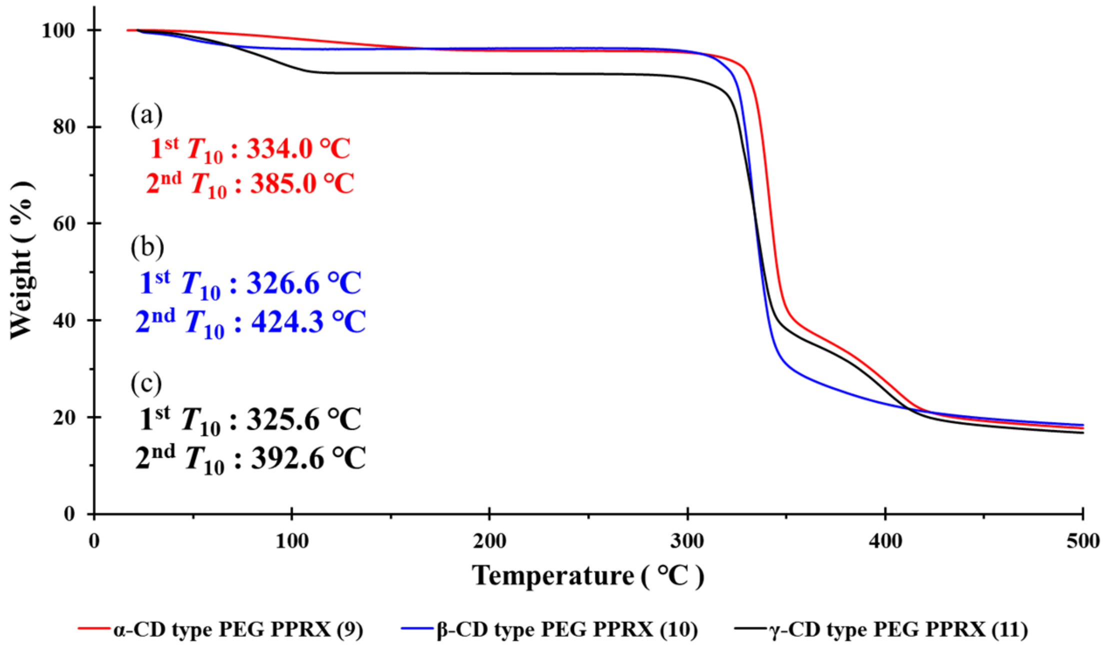


Figure S48. TGA of PEG PPRXs: α-CD type PEG PPRX (**9**) (a), β-CD type PEG PPRX (**10**) (b) and γ-CD type PEG PPRX (**11**).

9.6. TGA of α-, β- and γ-CD

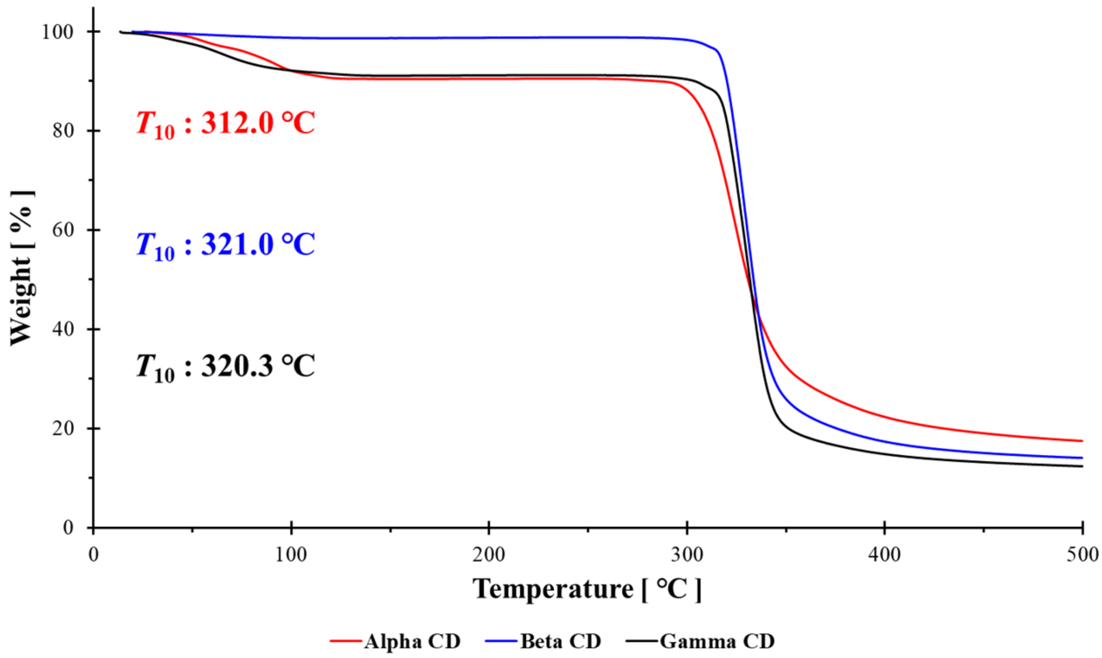


Figure S49. TGA of CDs: α-CD (a), β-CD (b) and γ-CD (c).

Table S4. TGA table of each BCP and PPRX samples

Entry	Sample name	Sample type	1st T_{10} (°C)	2nd T_{10} (°C)	3rd T_{10} (°C)
1	PLLA-PEG-PLLA (**1**)	BCP	230.9 [a]	386.7 [b]	-
2	PDLA-PEG-PDLA (**2**)	BCP	221.6 [a]	392.9 [b]	-
3	PLLA-PEG-PLLA PPRX (**3**)	PPRX	288.2 [a]	346.3 [b]	390.5 [d]
4	PDLA-PEG-PDLA PPRX (**4**)	PPRX	297.0 [a]	343.6 [b]	390.2 [d]
5	PLLA-PEG-PLLA PPRX (**5**)	PPRX	275.9 [a]	389.4 [c]	-
6	PDLA-PEG-PDLA PPRX (**6**)	PPRX	275.3 [a]	393.5 [c]	-
7	PLLA-PEG-PLLA PPRX (**7**)	PPRX	286.6 [a]	360.1 [b]	387.3 [d]
8	PDLA-PEG-PDLA PPRX (**8**)	PPRX	285.4 [a]	357.6 [b]	388.2 [d]
9	PEG 1500	Polymer	336.6 [a]	-	-
10	α-CD type PEG PPRX (**9**)	PPRX	334.0 [a]	385.0 [c]	-
11	β-CD type PEG PPRX (**10**)	PPRX	326.6 [a]	424.3 [c]	-
12	γ-CD type PEG PPRX (**11**)	PPRX	325.6 [a]	392.6 [c]	-
13	α-CD	CD	312.0 [a]	-	-
14	β-CD	CD	321.0 [a]	-	-
15	γ-CD	CD	320.3 [a]	-	-
16	PLA-PEG-PLA BCP SC (**12**)	BCP SC	221.1 [a]	391.5 [b]	-
17	α-CD type PPRX SC (**13**)	PPRX SC	271.0 [a]	381.4 [b]	394.8 [d]
18	β-CD type PPRX SC (**14**)	PPRX SC	278.4 [a]	392.0 [c]	-
19	γ-CD type PPRX SC (**15**)	PPRX SC	285.6 [a]	352.5 [b]	446.4 [d]

[a] Measured the temperature at which weight has decreased by 10% based on 150 °C. [b] Measured the temperature at which weight has decreased by 10% based on 330 °C. [c] Measured the temperature at which weight has decreased by 10% based on 350 °C. [d] Measured the temperature at which weight has decreased by 10% based on 360 °C.

Table S5. Sample information related each types of BCP and PPRX.

Entry	Sample name	H_2O (%) [a]	PLA (%)	CD (%)	PEG (%)	Remain (%) [g]
1	PLLA-PEG-PLLA (**1**)	1.0	61.7 [b]	-	31.8 [e]	5.5
2	PDLA-PEG-PDLA (**2**)	0.9	60.4 [b]	-	33.8 [e]	4.9
3	PLLA-PEG-PLLA PPRX (**3**)	3.4	11.2 [c]	50.4 [d]	28.3 [e]	6.7
4	PDLA-PEG-PDLA PPRX (**4**)	3.1	6.4 [c]	52.7 [d]	32.1 [e]	5.7
5	PLLA-PEG-PLLA PPRX (**5**)	2.0	26.3 [c]	43.0 [d]	24.2 [e]	4.5
6	PDLA-PEG-PDLA PPRX (**6**)	1.5	25.9 [c]	39.8 [d]	27.9 [e]	4.9
7	PLLA-PEG-PLLA PPRX (**7**)	1.1	14.3 [c]	43.0 [d]	23.6 [e]	18.0
8	PDLA-PEG-PDLA PPRX (**8**)	6.0	16.7 [c]	36.8 [d]	25.1 [e]	15.4
9	PEG 1500	0.2	-	-	98.7 [f]	1.1
10	α-CD type PEG PPRX (**9**)	3.4	-	54.3 [b]	23.1 [e]	19.2
11	β-CD type PEG PPRX (**10**)	3.9	-	65.2 [b]	11.1 [e]	19.8
12	γ-CD type PEG PPRX (**11**)	8.9	-	52.9 [b]	19.9 [e]	18.3
13	α-CD	9.6	-	71.4 [f]	-	19.0
14	β-CD	1.3	-	83.7 [f]	-	15.0
15	γ-CD	8.9	-	77.8 [f]	-	13.3

[a] Measured the change in weight from room temperature to 150 ℃. [b] Measured the change in weight from 150 ℃ to 350 ℃. [c] Measured the change in weight from 150 ℃ to 290 ℃. [d] Measured the change in weight from 290 ℃ to 350 ℃. [e] Measured the change in weight from 350 ℃ to 450 ℃. [f] Measured the change in weight from 150 ℃ to 450 ℃. [g] Measured the remaining weight after 450 ℃.

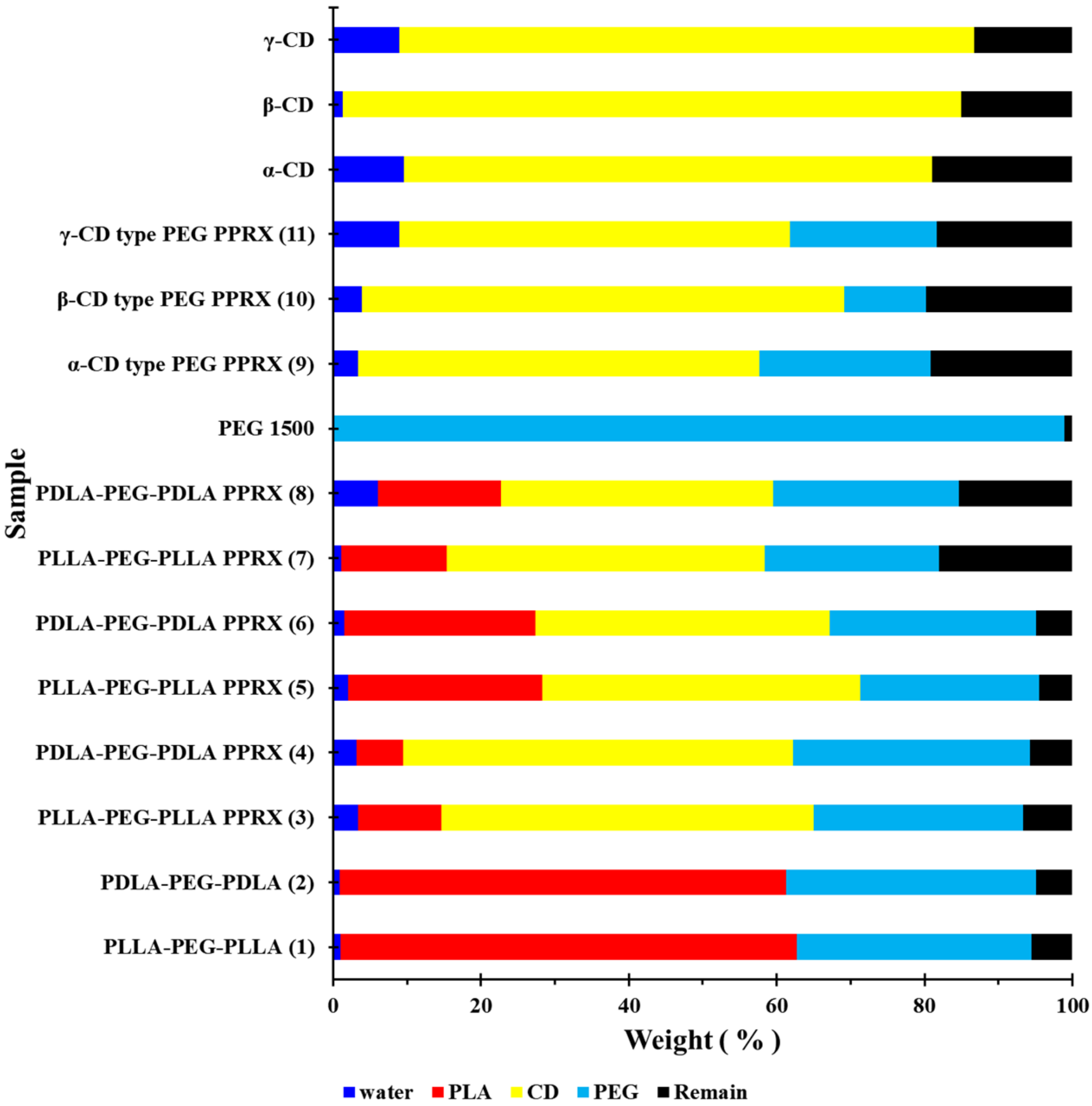


Figure S50. The weight ratio of BCPs, PPRXs, PEG 1500, PEG PPRXs and each CDs via TGA.

Table S6. Sample information related each BCP SC and PPRX SC samples

Entry	Sample name	H_2O (%) [a]	PLA (%)	CD (%)	PEG (%) [e]	Remain (%) [f]
1	PLA-PEG-PLA BCP SC (**12**)	0.8	63.0 [b]	-	31.7	4.5
2	α-CD type PPRX SC (**13**)	2.5	16.3 [c]	56.6 [d]	19.7	4.9
3	β-CD type PPRX SC (**14**)	2.0	21.7 [c]	43.6 [d]	26.0	6.7
4	γ-CD type PPRX SC (**15**)	10.1	12.3 [c]	50.0 [d]	13.9	13.7

[a] Measured the change in weight from room temperature to 150 °C. [b] Measured the change in weight from 150 °C to 350 °C. [c] Measured the change in weight from 150 °C to 290 °C. [d] Measured the change in weight from 290 °C to 350 °C. [e] Measured the change in weight from 350 °C to 450 °C. [f] Measured the remaining weight after 450 °C.

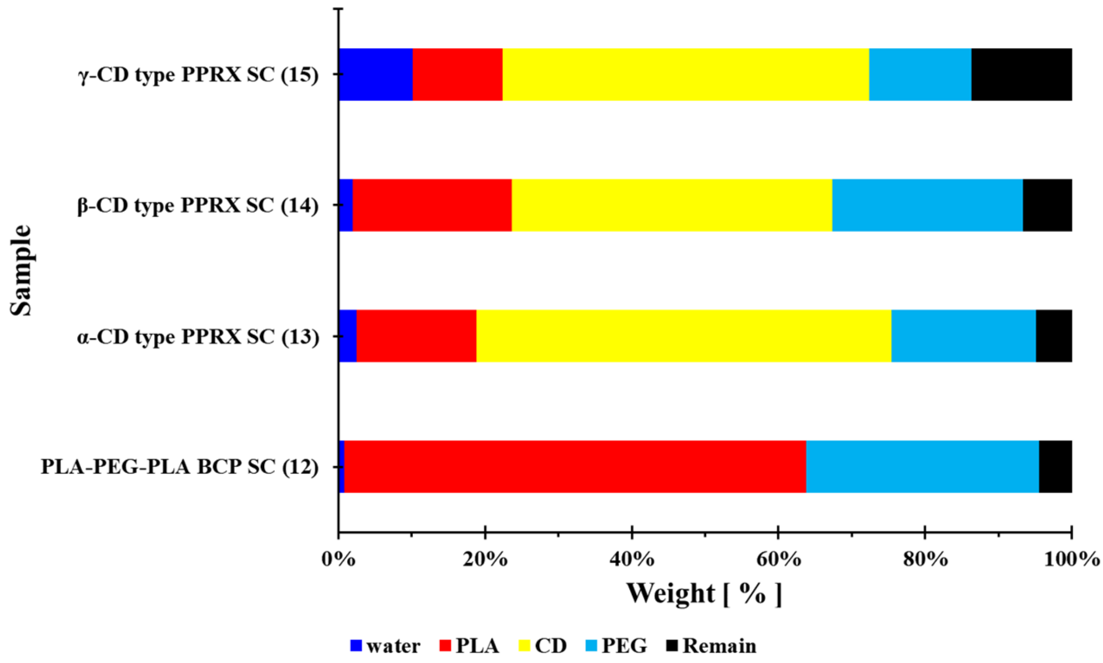


Figure S51. The weight ratio of SC samples via TGA.

10. Analysis of SC samples

10.1. ^{1}H NMR spectrum of ABA type BCP SC (12)

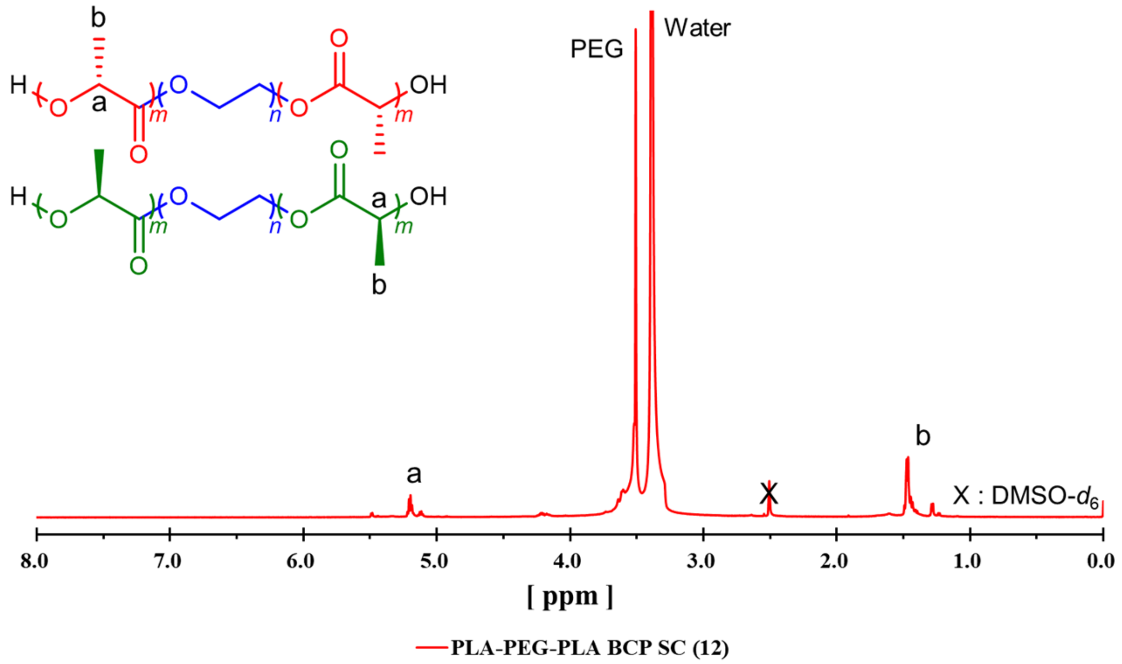


Figure S52. ^{1}H NMR spectrum of PLA-PEG-PLA BCP SC (**12**). (600 MHz, 298 K, DMSO-d_6)

10.2. ^{1}H NMR spectrum of α-CD type PPRX SC (13)

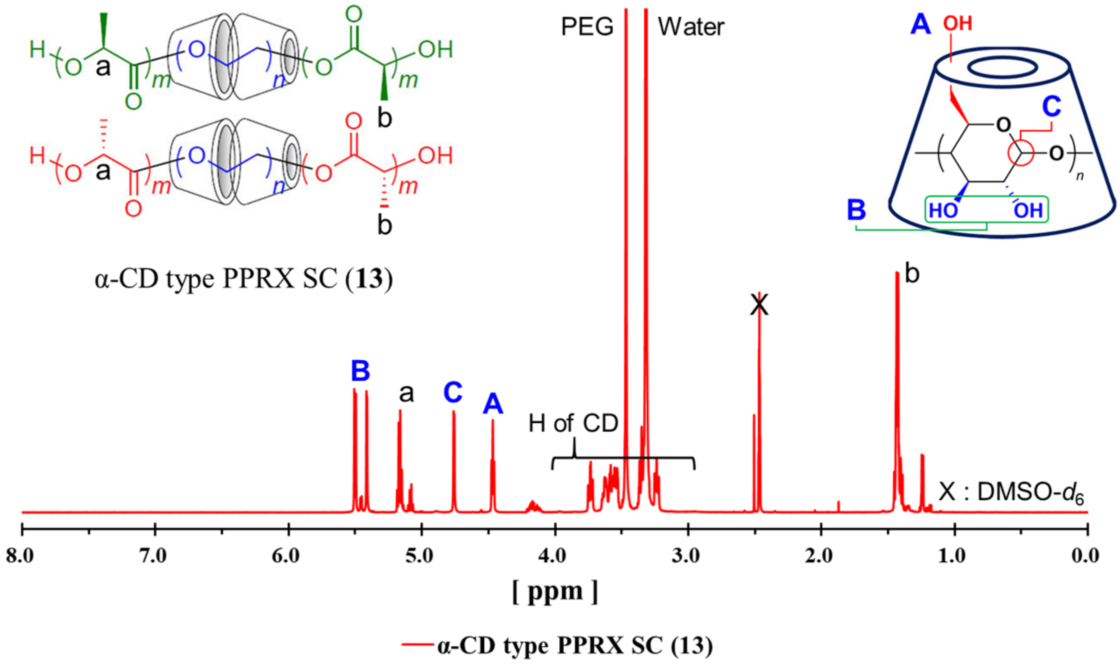


Figure S53. ^{1}H NMR spectrum of α-CD type PPRX SC (**13**). (600 MHz, 298 K, DMSO-d_6)

10.3. ^{1}H NMR spectrum of β-CD type PPRX SC (14)

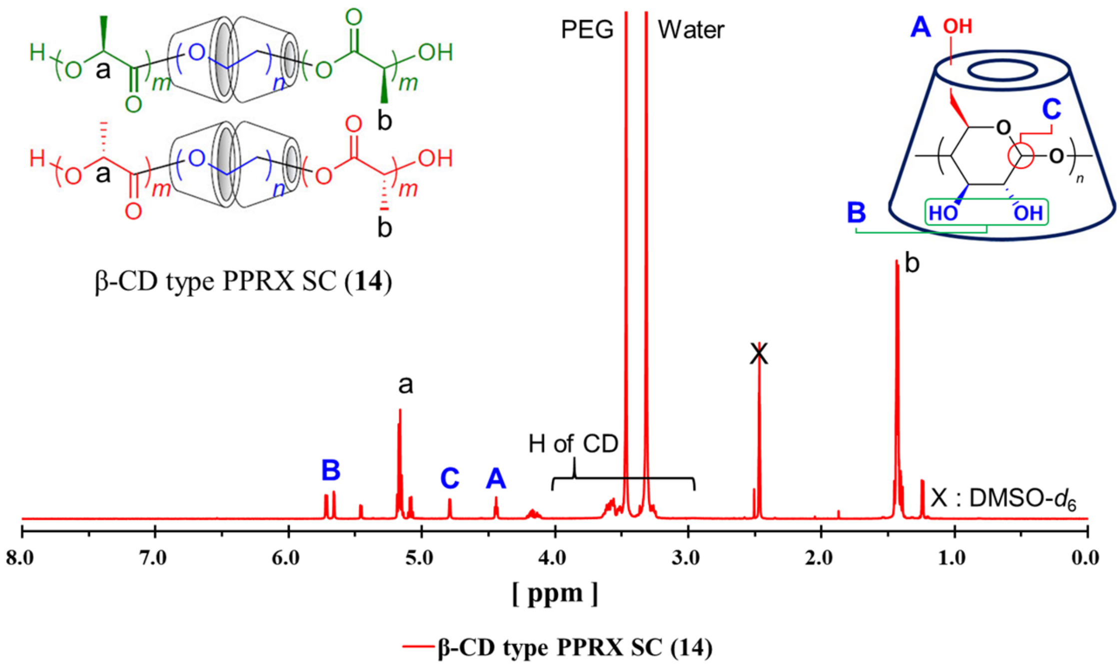


Figure S54. ^{1}H NMR spectrum of β-CD type PPRX SC (**14**). (600 MHz, 298 K, DMSO-d_6)

10.4. ¹H NMR spectrum of γ-CD type PPRX SC (15)

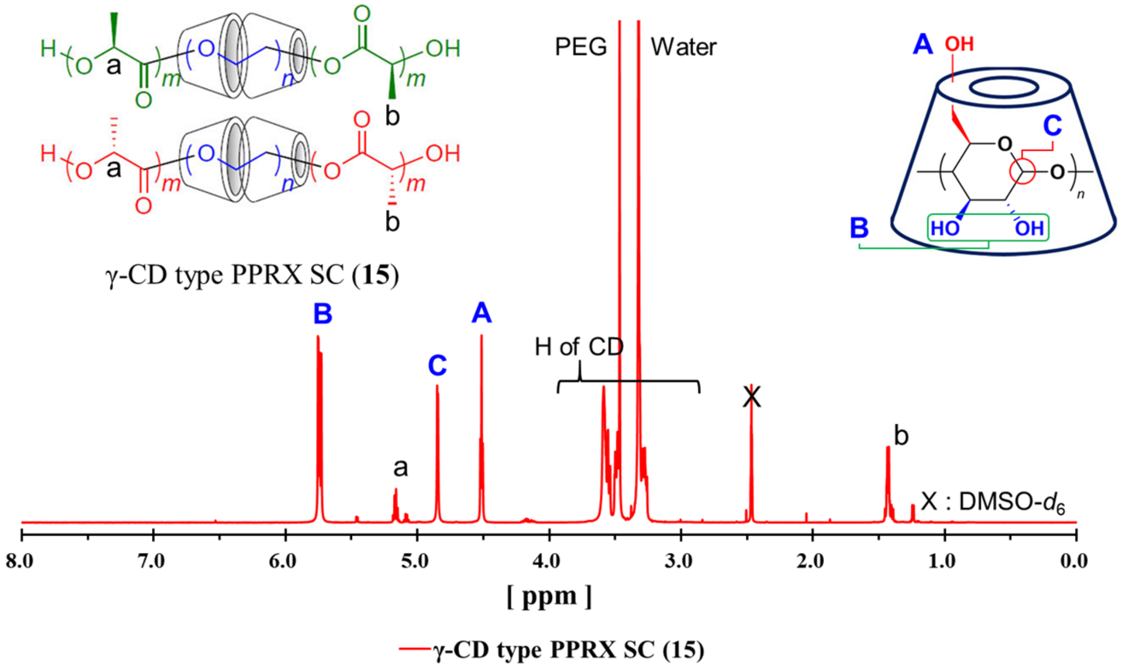


Figure S55. ¹H NMR spectrum of γ-CD type PPRX SC (**15**). (600 MHz, 298 K, DMSO-d_6)

10.5. DOSY NMR spectrum of α-CD type PEG PPRX SC (13)

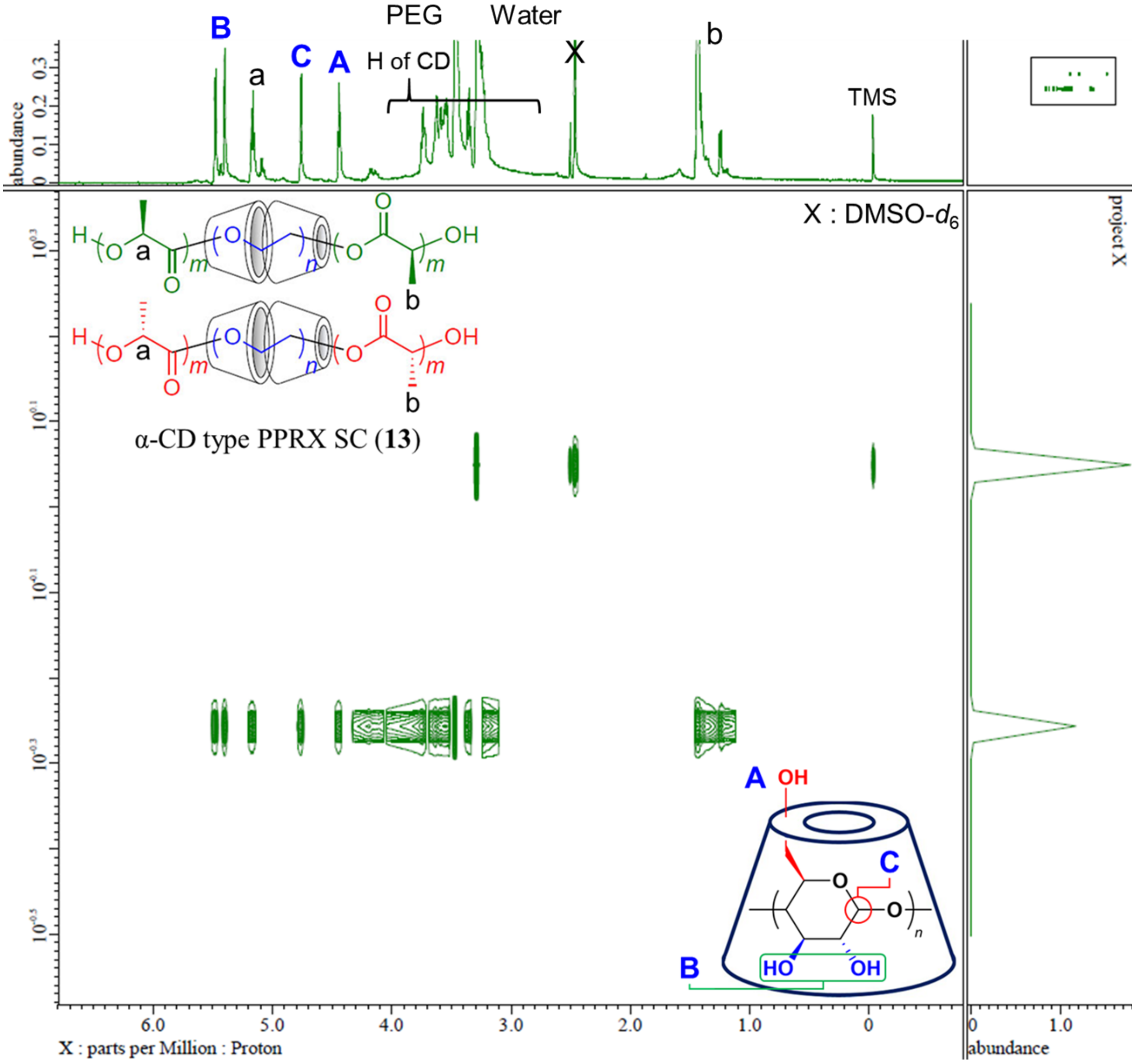


Figure S56. DOSY NMR spectrum of α-CD type PPRX SC (**13**) (600 MHz, DMSO-d_6, 298 K).

In Figure S56, the DOSY spectra of α-CD type SC PPRX (**13**) resulted in same values of diffusion coefficient around 10^0 μm^{2}ms^{-1} at around 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PLA moiety, and around 5.5, 4.8, 4.5, and the peak from 4.0 to 3.0 ppm of outside protons of α-CD moieties. This can suggest as formation of single structure by same diffusion coefficient with PLA-PEG-PLA BCP SC (**12**) as the axle components and α-CD as the wheel components.

10.6. DOSY NMR spectrum of β-CD type PEG PPRX SC (14)

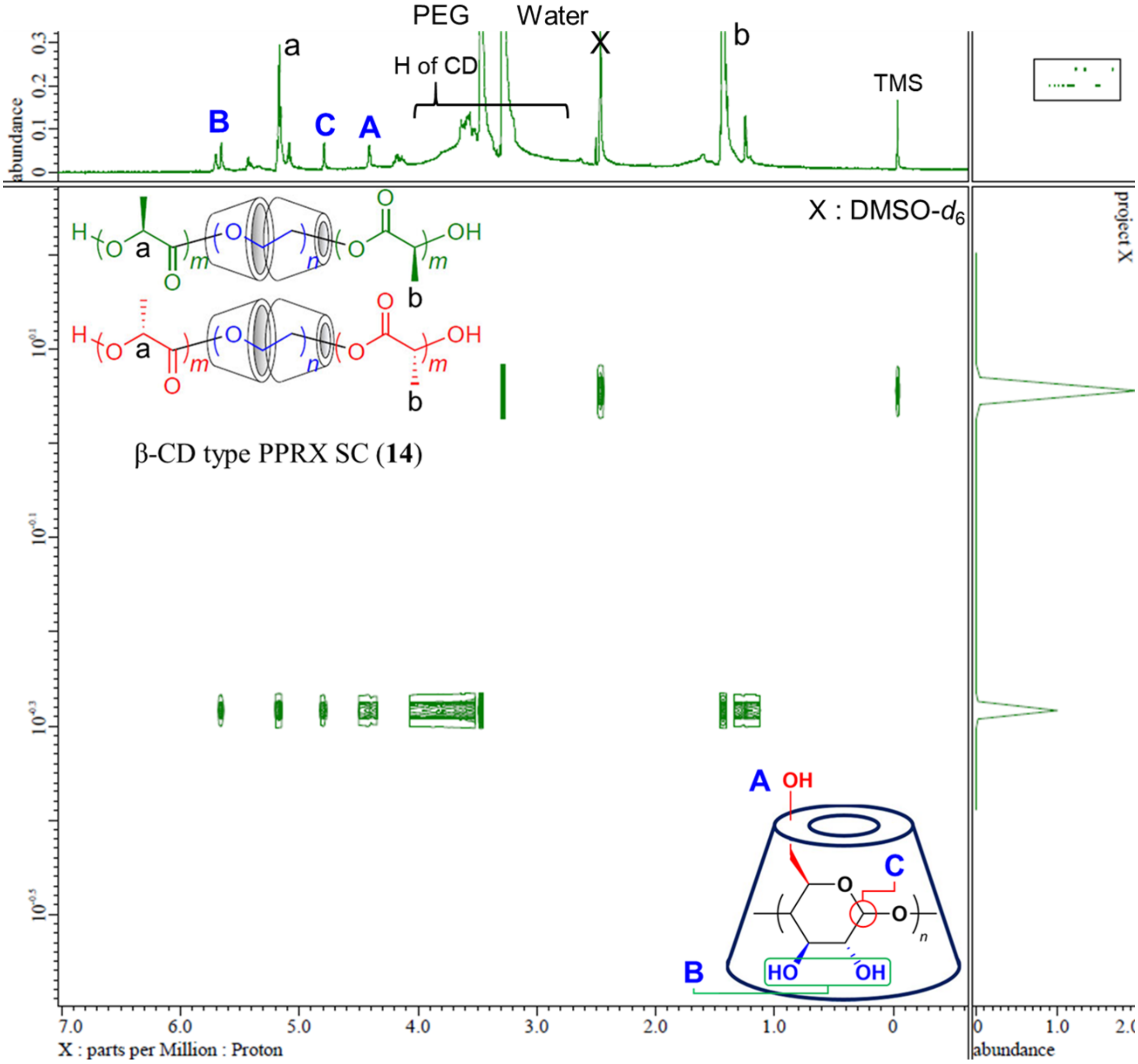


Figure S57. DOSY NMR spectrum of β-CD type PPRX SC (**14**) (600 MHz, DMSO-d_6, 298 K).

In Figure S57, the DOSY spectra of β-CD type SC PPRX (**14**) is resulted in same values of diffusion coefficient between $10^{-0.1}$ μm^{2}ms^{-1} and 10^0 μm^{2}ms^{-1} at around 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PLA moiety, and around 5.8, 4.8, 4.5, and the peak from 4.0 to 3.0 ppm of outside protons of β-CD moieties. This can imply the formation of single structure by same diffusion coefficient with PLA-PEG-PLA BCP SC (**12**) as the axle components and β-CD as the wheel components.

10.7. DOSY NMR spectrum of γ-CD type PEG PPRX SC (15)

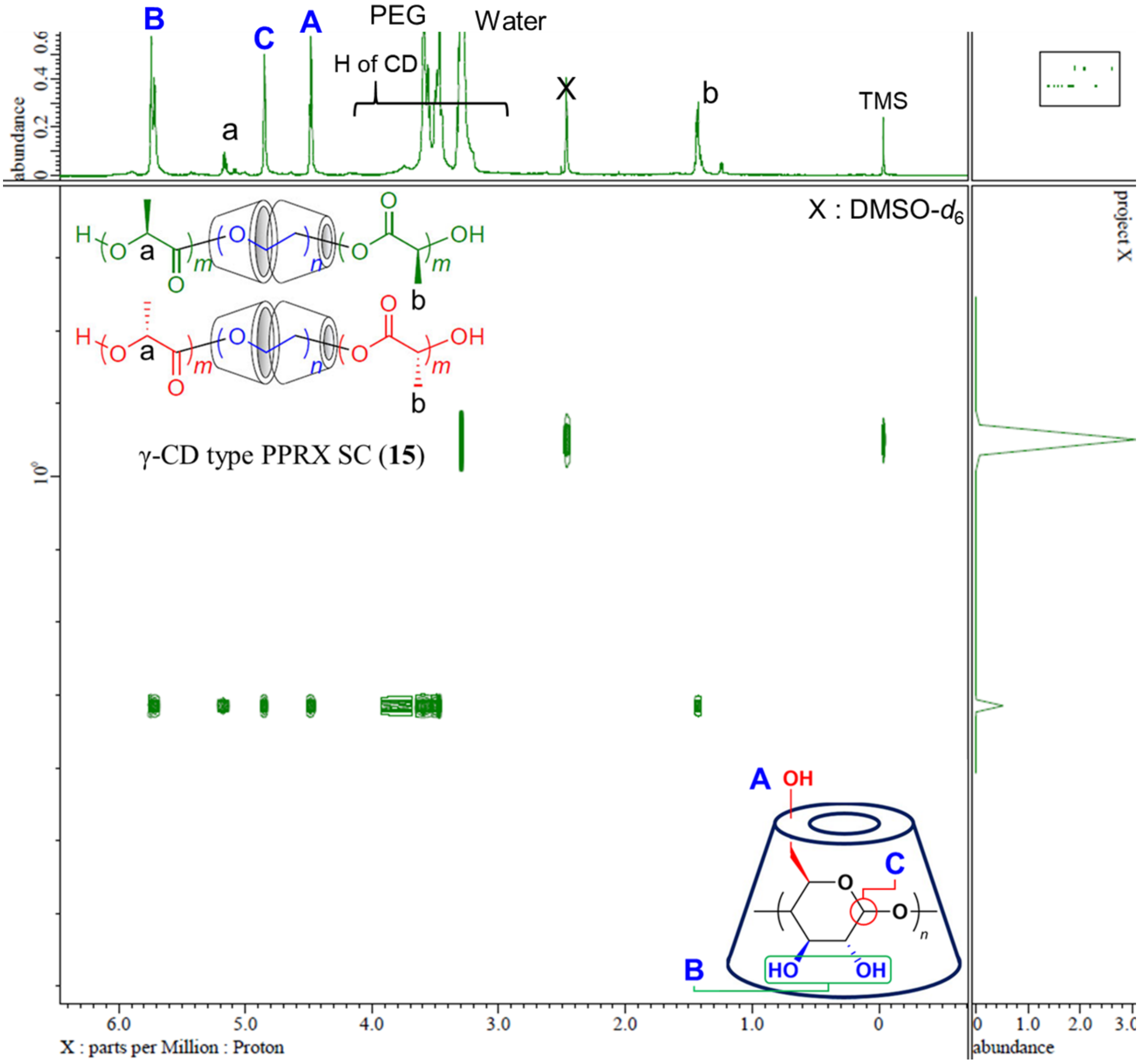


Figure S58. DOSY NMR spectrum of γ-CD type PPRX SC (**15**) (600 MHz, DMSO-d_6, 298 K).

In Figure 58, the DOSY spectra of γ-CD type SC PPRX (**15**) is resulted in same values of diffusion coefficient around $10^{-0.1}$ μm^{2}ms^{-1} at around 3.5 ppm of the PEG moiety, around 5.3 and 1.5 ppm of the PLA moiety, and around 5.8, 4.8, 4.5, and the broad peak from 4.0 to 3.0 ppm of outside protons of γ-CD moieties. This can indicate the formation of single structure by the same diffusion coefficient with PLA-PEG-PLA BCP SC (**12**) as the axle components and γ-CD as the wheel components.

10.8. NOESY NMR spectrum of α-CD type PEG PPRX SC (13)

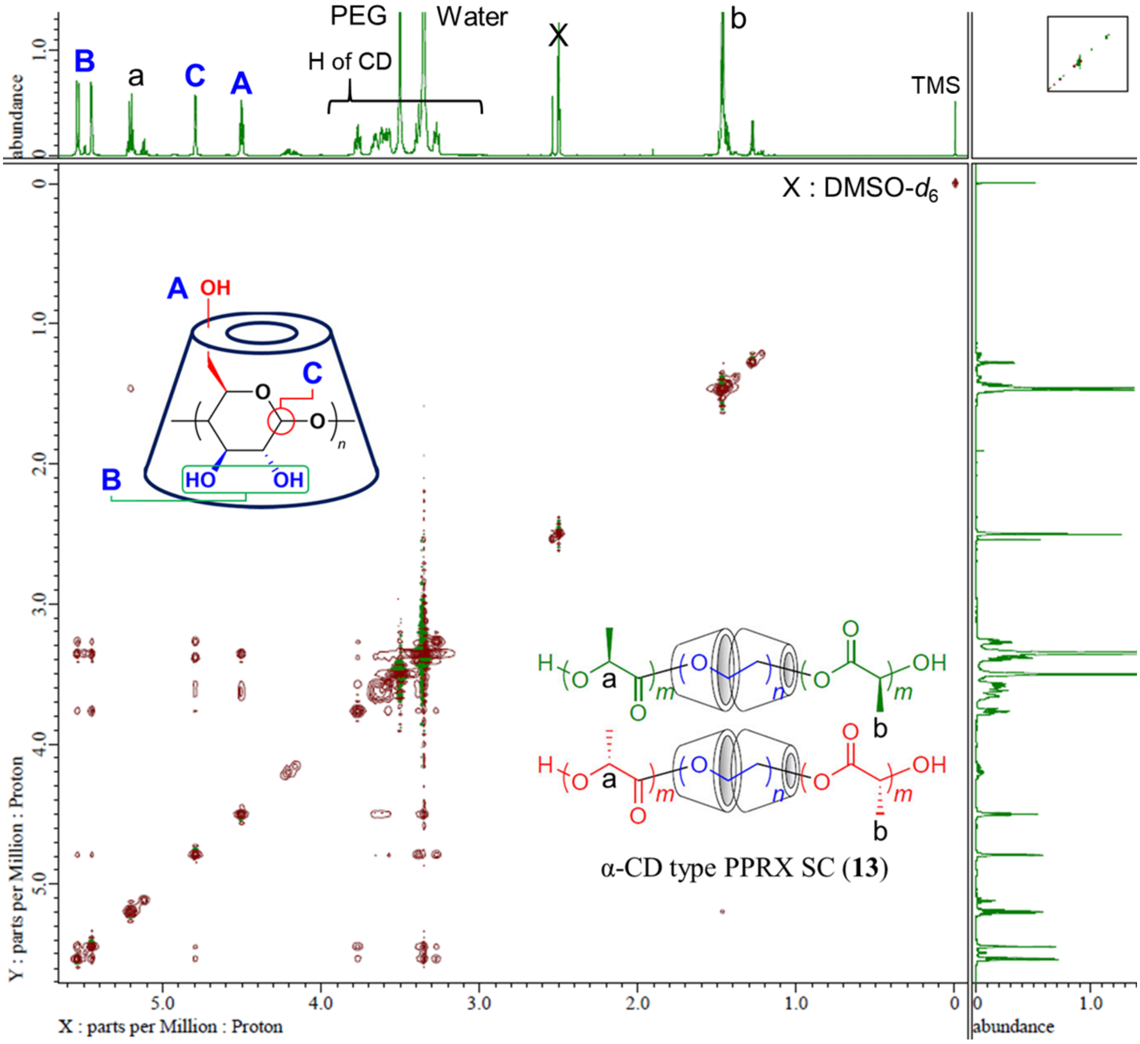


Figure S59. NOESY NMR spectrum of α-CD type PPRX SC (**13**) (600 MHz, DMSO-d_6, 298 K).

10.9. NOESY NMR spectrum of β-CD type PEG PPRX SC (14)

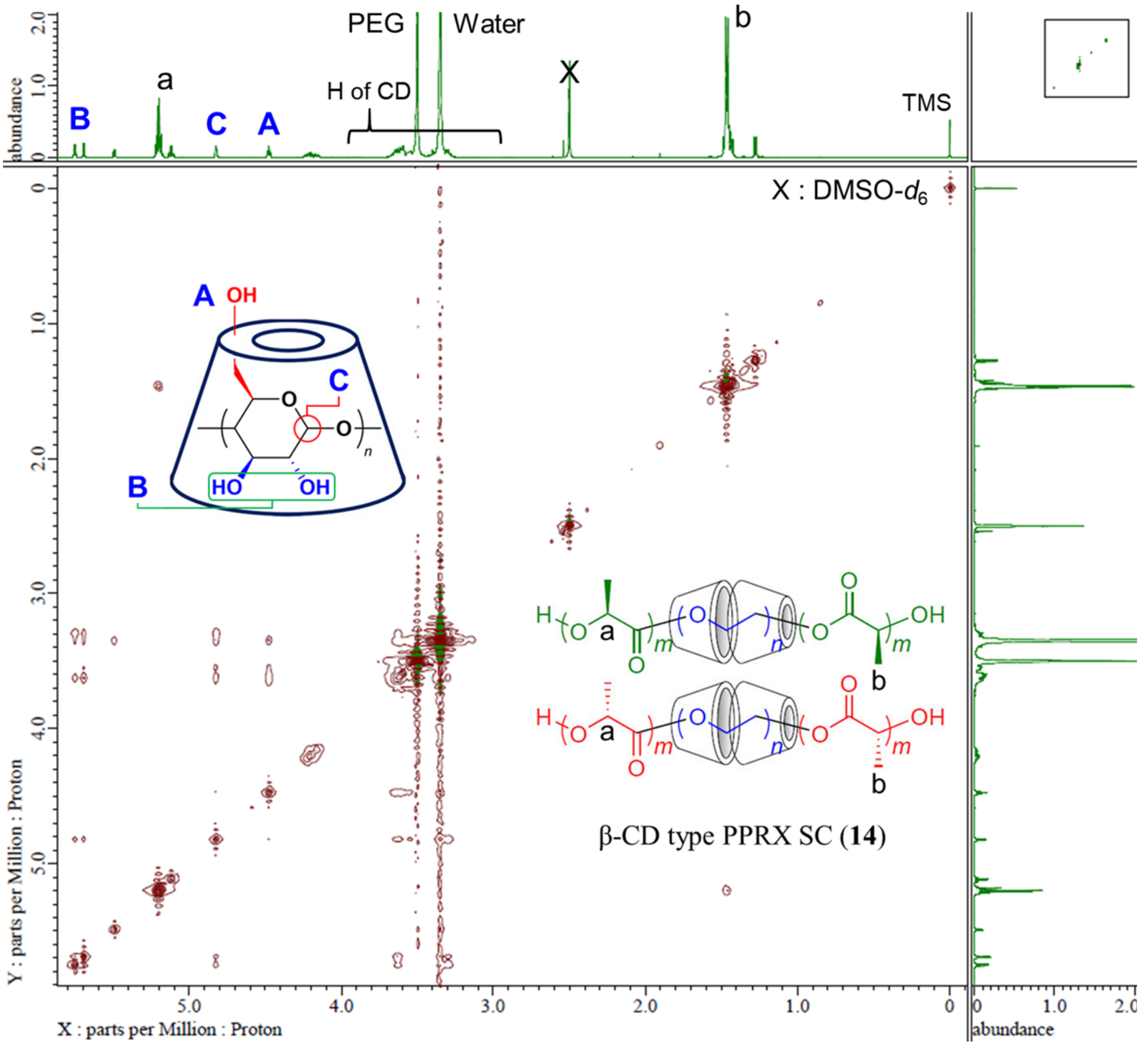


Figure S60. NOESY NMR spectrum of β-CD type PPRX SC (**14**) (600 MHz, DMSO-d_6, 298 K).

10.10. NOESY NMR spectrum of γ-CD type PEG PPRX SC (15)

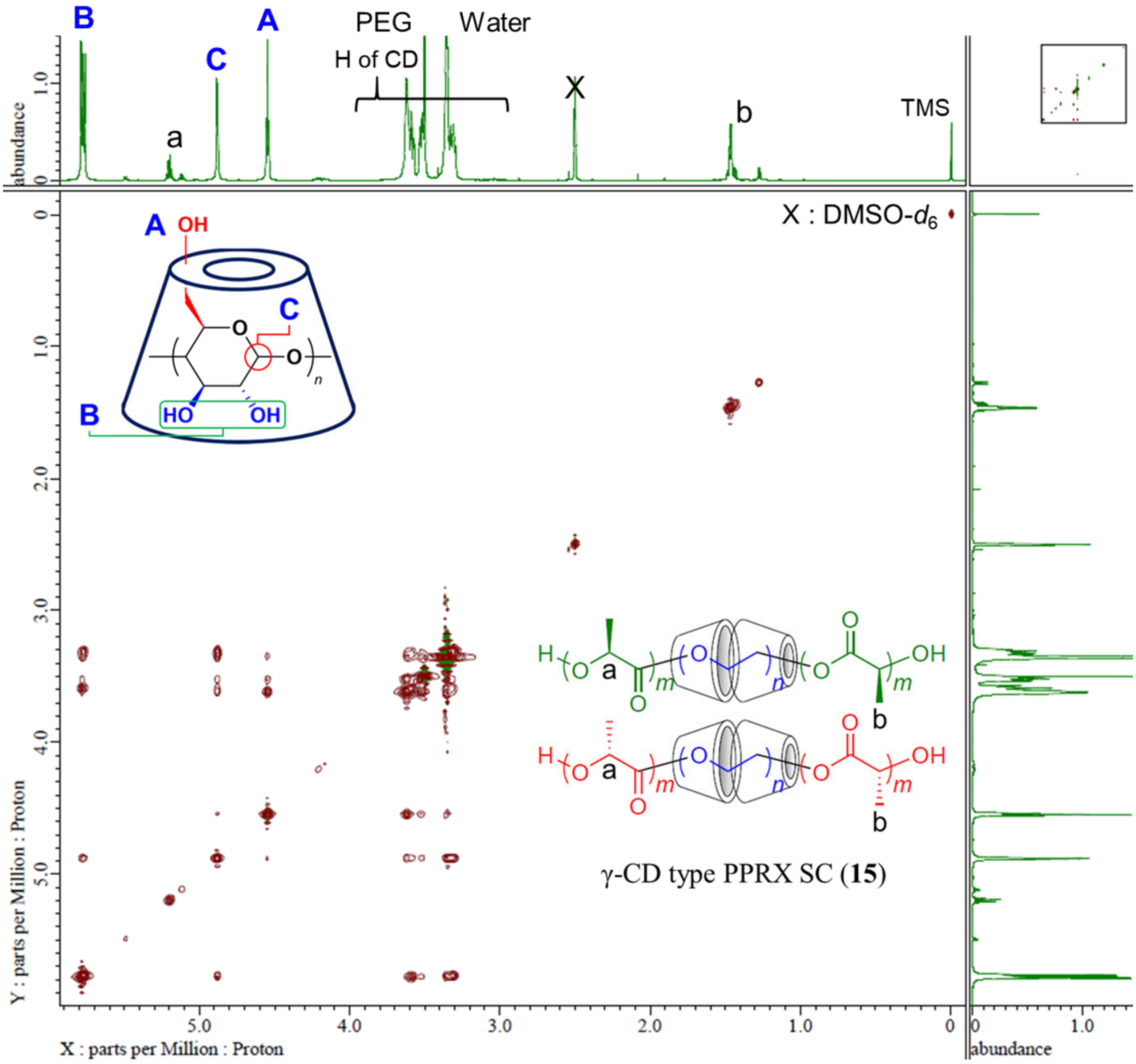


Figure S61. NOESY NMR spectrum of γ-CD type PPRX SC (**15**) (600 MHz, DMSO-d_6, 298 K).