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New type polyrotaxanes based on polyethyleneimine and α-cyclodextrin

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Materials and methods

The synthesis of poly-2-ethyl-2-oxazoline was carried out in a Discover LabMate single-mode microwave reactor (CEM Corporation, United States) at a magnetron frequency of 2.45 GHz and a maximum generator power of 150 W during 2 h. The reaction temperature (100 °C) was controlled by an IR thermometer on the retort outer surface. The NMR spectra were measured on the Bruker AC400 (400 MHz) spectrometer using chloroform and dimethyl sulfoxide solutions. For the purification of the synthesized polymers, Zellu Trans dialysis tubes (Scienova GmbH, Germany, cellulose, regenerated, with MWCO 3500 Da) were used. Chromatographic analysis was performed on the Shimadzu LC-20AD chromatograph equipped with the refractive detector. Samples were studied with Waters Styragel HT4 column (10 μm, 7.8×300 mm) in DMF at 60 °C. Polyethylene oxide standards were chosen for calibration curve. The absolute values of molar masses are determined by static light scattering (SLS) in dilute solutions in 2-nitropropane. The experiments were performed on a Photocor Complex instrument (Photocor Instruments Inc.), which is equipped with a Photocor DL a diode laser (wavelength λ = 632.8 nm and power 5–30 mW).

Synthetic procedures

Poly-2-ethyl-2-oxazoline. A solution of 2-ethyl-2-oxazoline (Aldrich, 10 g) and methyl tosylate (12 mg) in acetonitrile (10 ml) was heated in a microwave oven for 30 min. The polymer was precipitated to cold diethyl ether, dialyzed against water and dried. Yield 9.4 g (94%). M_w 19000 (SLS), M_w/M_n=1.12.

Polyethyleneimine PEI. Poly-2-ethyl-2-oxazoline from the previous step (5 g) was dissolved in a mixture of distilled water (25 ml) and concentrated hydrochloric acid (40 ml), and this mixture was refluxed for 12 h. Sodium hydroxide was added to the mixture at 0 °C until the solution became strongly basic. The resulting precipitates were collected by filtration and washed with ice-cold water. The residue was dried *in vacuo* at 60 °C for 48 h. Yield 2.2 g (94%). M_w 9500 (SLS). ^{1}H NMR ($CDCl_3$): δ 2.70 (s, CH_2-CH_2-NH).

Poly(*N*-propionylethyleneimine)@per-propionyl-α-cyclodextrin 2a. Solutions of α-cyclodextrin (0.55 g) in water (3.8 ml) and PEI (0.03 g) in water (1 ml) were mixed together, and pH value was adjusted to 12 by addition of 5M NaOH. The mixture was sonicated at 60 °C for 20 min. Propionic anhydride (2 ml) was added to thus obtained solution of polypseudopolyrotaxane **1** cooled to 3-5 °C with vigorous stirring. After 60 min, the precipitated polyrotaxane **2a** was separated, washed with saturated sodium bicarbonate solution and dialyzed against water for 24 h. Yield 0.340 g (84%) ^{1}H NMR (DMSO-d_6, δ, ppm) 5.52 (H-1, s); 5.30-3.44 (m) (cyclodextrin moieties), 3.36 (CH_2-CH_2-N,); 2.28 (CO-CH_2-CH_3); 0.96 (CO-CH_2-CH_3). ^{13}C NMR (DMSO-d_6, δ, ppm), propionyl groupse: 174.43 (COO), 173.78 (CON), 27.14 (CO-$\mathit{C}H_2$-CH_3), 9.45 (NCO-CH_2-$\mathit{C}H_3$); CD ring: 99.1 (C^1); 73.7 (C^4); 72.4 (C^2); 72.3 (C^3); 69.4 (C^5); 63.4 (C^6).

Poly(*N*-butyroylethyleneimine)@per-butyroyl-α-cyclodextrin 2b was prepared similarly, yield 78%. ^{1}H NMR (DMSO-d_6, δ, ppm) 5.52 -3.44 (m) (cyclodextrin moieties), 3.39 (CH_2-CH_2-N,); 2.32 (CO-CH_2-CH_2-CH_3); 1.68(CO-CH_2-CH_2-CH_3) 0.96 (CO-CH_2-CH_2-CH_3).

Poly(*N*-isobutyroylethyleneimine)@per-isobutyroyl-α-cyclodextrin 2c was prepared similarly, yield 71%. ^{1}H NMR (DMSO-d_6, δ, ppm) 5.52 -3.44 (m) (cyclodextrin moieties), 3.39 (CH_2-CH_2-N,); 2.56 (CO-$CH(CH_3)_2$); 1.11 (CO-$CH(CH_3)_2$).

^{1}H NMR and ^{13}C NMR spectra and GPC profiles

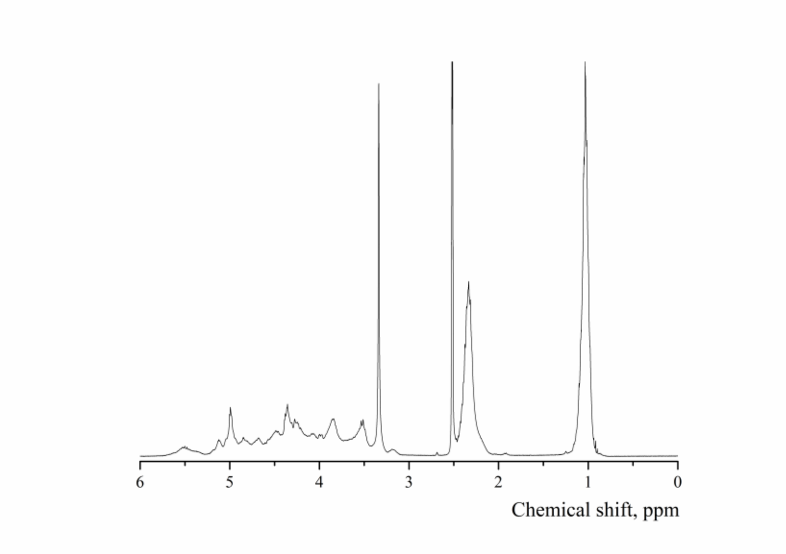

Figure S1 ^{1}H NMR spectrum of poly(*N*-propionylethyleneimine)@per-propionyl-α-cyclodextrin **2a**.

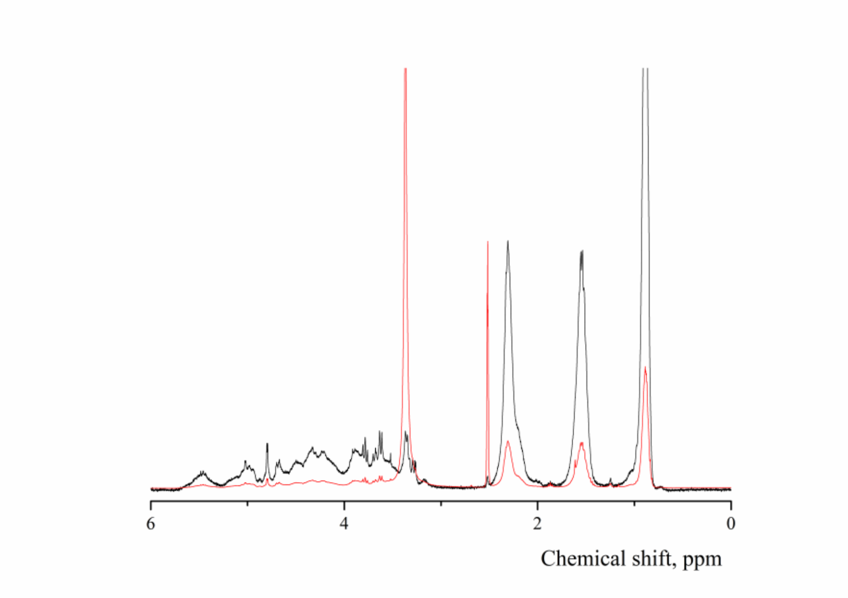

Figure S2 ^{1}H NMR DOSY spectra of poly(*N*-propionylethyleneimine)@per-propionyl-α-cyclodextrin **2a**.

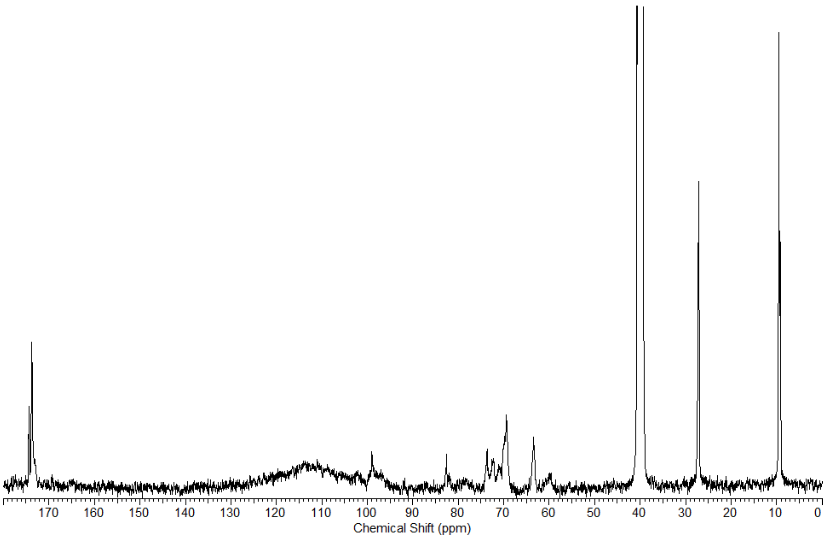

Figure S3 ^{13}C NMR spectrum of poly(*N*-propionylethyleneimine)@per-propionyl-α-cyclodextrin **2a**.

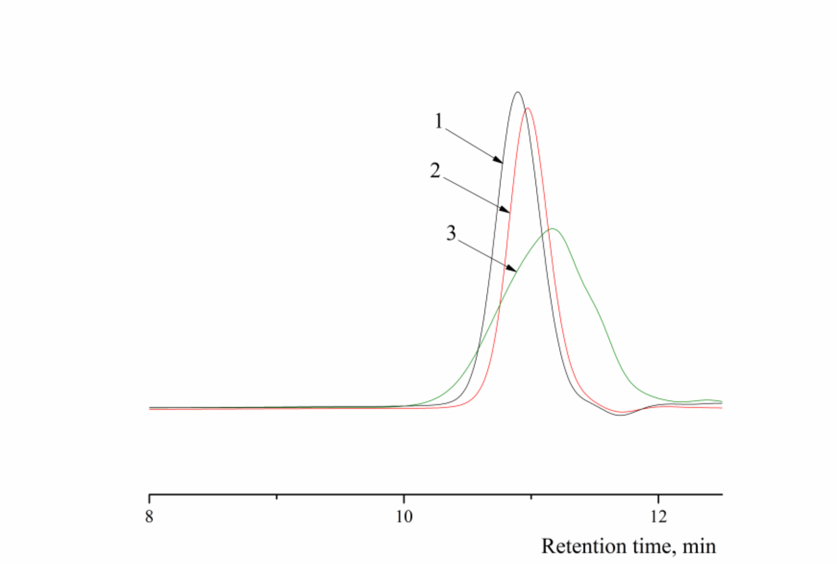

Figure S4 GPC profiles of poly(*N*-alkanoylethyleneimine)@per-alkanoyl-α-cyclodextrins **2a-c**. (*1*) – propionyl **2a**, (*2*) – butyroyl **2b**, (*3*) – isobutyroyl **2c**.