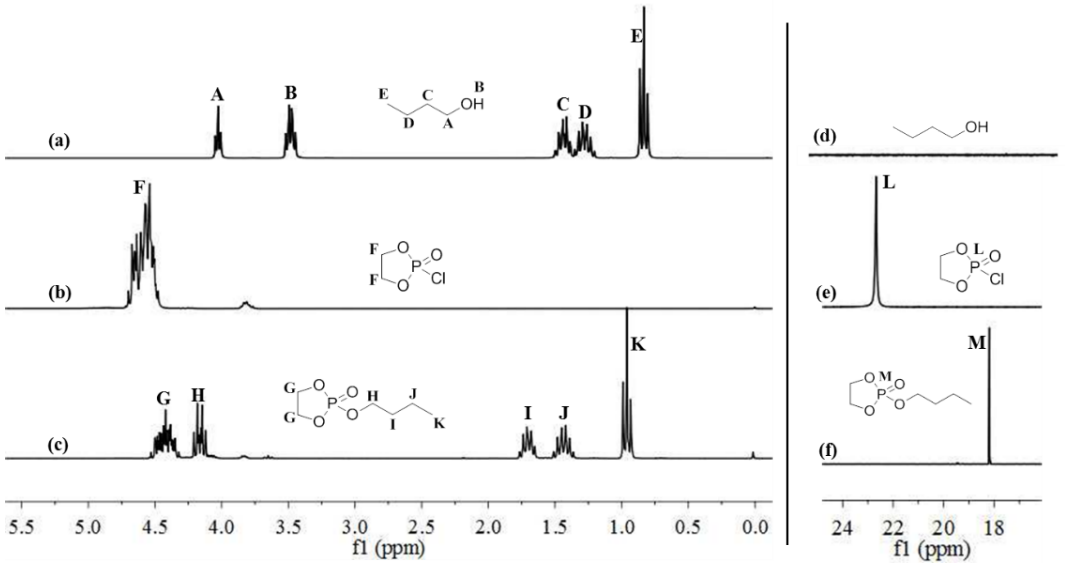
Monomer synthesis

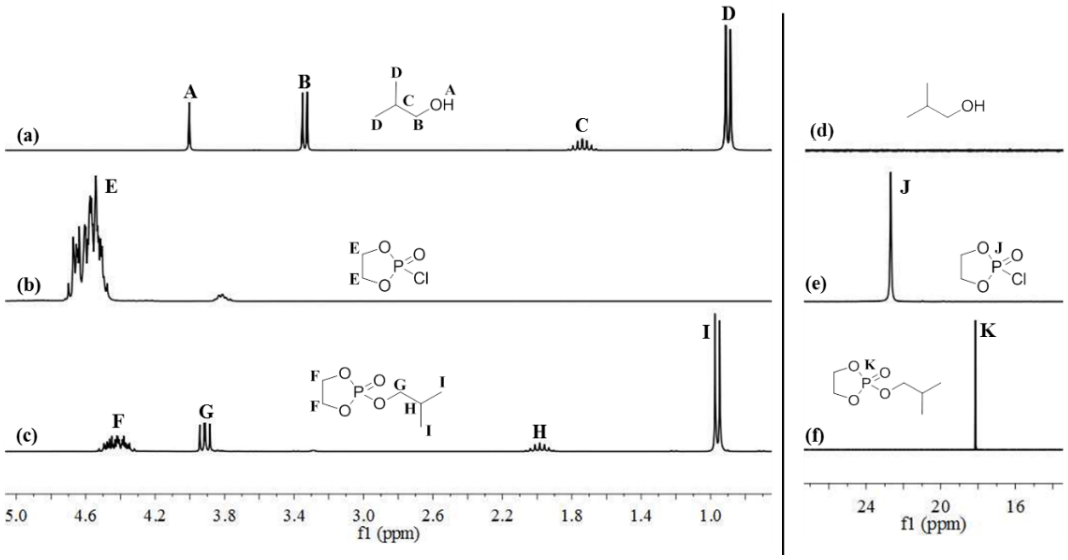
nBP monomer



^{1}H NMR spectra of (a) 1-butanol, (b) COP and (c) nBP monomer and ^{1}H-decoupled ^{31}P NMR spectra of (d) 1-butanol, (e) COP and (f) nBP monomer

^{1}H NMR (250 MHz, $CDCl_3$,) of nBP: 0.95 ppm (t, 3H, $–CH_2–C\underline{\mathbf{H}}_3$), 1.4 ppm (m, 2H, $–C\underline{\mathbf{H}}_2–CH_3$), 1.7 ppm (m, 2H, $–C\underline{\mathbf{H}}_2–CH_2–CH_3$), 4.15 ppm (dt, $^{2}J_{HH}$ = 6.5 Hz and $^{3}J_{PH}$ = 8.7 Hz, 2H, $–O–C\underline{\mathbf{H}}_2–CH_2–CH_2–CH_3$), 4.4 ppm (m, 4H, $–O–C\underline{\mathbf{H}}_2–C\underline{\mathbf{H}}_2–O–$). ^{1}H-decoupled ^{31}P NMR ($CDCl_3$, 101 mHz): 18.2 ppm.

iBP monomer

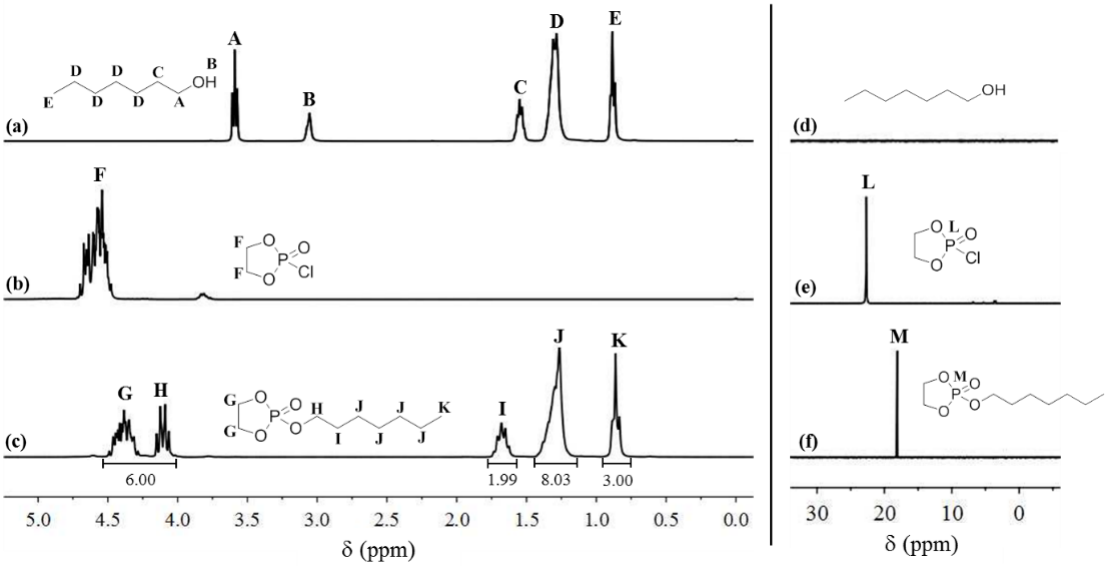


^{1}H NMR spectra of (a) 2-methylpropan-1-ol, (b) COP and (c) iBP monomer and ^{1}H-decoupled ^{31}P NMR spectra of (d) 2-methylpropan-1-ol, (e) COP and (f) iBP monomer

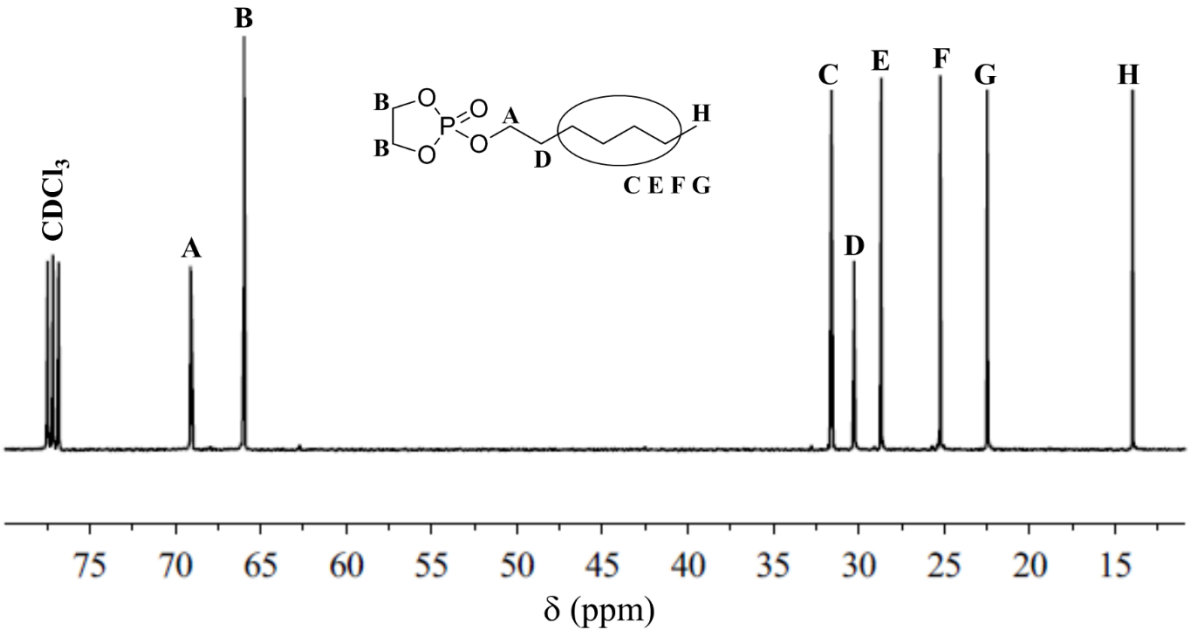
^{1}H NMR ($CDCl_3$, 250 MHz) of iBP: 0.96 ppm (d, J_{HH} = 6.7 Hz, 3H, $–CH_2–C\underline{\mathbf{H}}_3$), 2.0 ppm (m, 1H, $–C\underline{\mathbf{H}}–(CH_3)_2$), 3.9 ppm (dd, J_{HH} = 6.6 Hz and J_{PH} = 8.1 Hz, 2H,

–O–C**H**$_2$–CH–(CH$_3$)$_2$), 4.4 ppm (m, 4H, –O–C**H**$_2$–C**H**$_2$–O–). ^{1}H-decoupled ^{31}P NMR ($CDCl_3$, 101 mHz): 18.1 ppm.

nHP monomer



^{1}H NMR spectra in $CDCl_3$ of (a) 1-heptanol, (b) COP and (c) nHP monomer and ^{1}H-decoupled ^{31}P NMR in $CDCl_3$ spectra of (d) 1-heptanol, (e) COP and (f) nHP monomer



^{13}C NMR spectra in $CDCl_3$ of nHP monomer

Synthesis of polyphosphate homopolymer

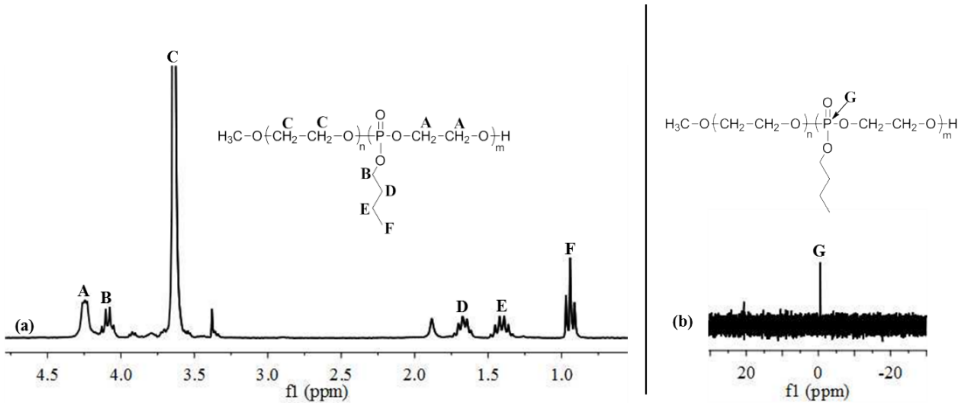
The homopolymerization of nHP was performed in CH_2Cl_2 at 0°C with benzyl alcohol as an initiator, DBU as a catalyst and TU as a co-catalyst with a ratio $[Bz\text{-}OH]_0/[Monomer]_0/[DBU]_0/[TU]_0$= 1/50/5/5. In a glass reactor, TU (370 mg, 1 mmol) and the cyclic phosphate monomer (20 mmol) were dried by three successive azeotropic distillations with toluene and dissolved in CH_2Cl_2 ($[Monomer]_0$ = 1 mol L^{-1}) before the successive addition under inert atmosphere of a dichloromethane stock solution of BzOH (0.35 mL, 0.2 mmol), and a dichloromethane stock solution of DBU (0.15, 1 mmol) under nitrogen atmosphere. After 60 minutes of polymerization, the solution was concentrated under vacuum and the polymer was precipitated in cold diethyl ether and filtrated. Residual DBU was eliminated overnight by dialysis against MeOH (Spectrum, membrane porosity= 1000 g mol^{-1}). After elimination of MeOH under vacuum, the residue was dissolved in THF and the homopolymer was recovered by precipitation in cold diethyl ether before being dried under vacuum.

Contact angle of polyphosphate homopolymers

Polyphosphate homopolymer solutions were prepared by dissolving 40 mg of polymer in 1 mL of chloroform. Glass slides were coated with polyphosphate using the spin-coating method with a spin speed of 1000 rpm at room temperature. Residual chloroform was evaporated in a heat chamber at 50°C overnight. The contact angle was measured by depositing a 15 µL drop of water on the polyphosphate homopolymer surfaces by using a Digidrop GBX New Technologies Development (DGD Fast/60) and a Windrop software.

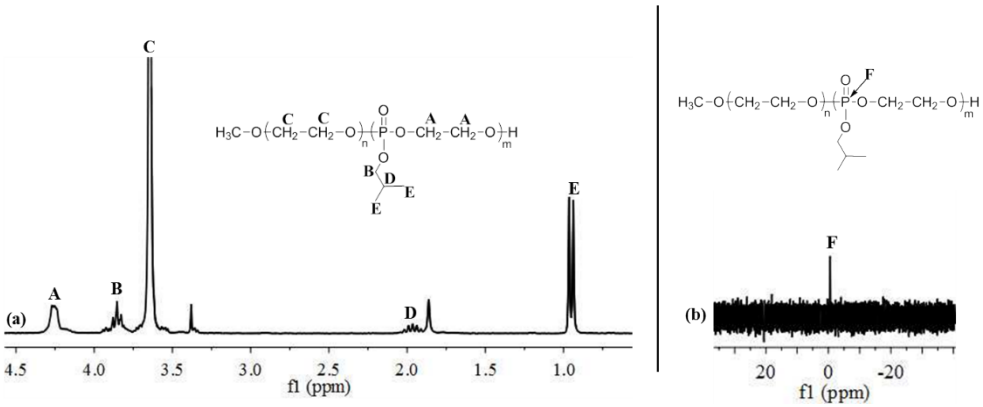
NMR of PEO-*b*-polyphosphate copolymers

PEO-b-PnBP copolymer



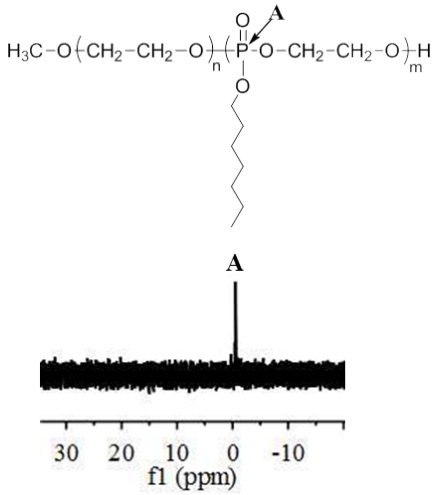
(a)[1]H NMR and (b) [1]H-decoupled [31]P NMR spectra of PEO-b-PnBP

PEO-b-PiBP copolymer



(a) [1]H NMR and (b) [1]H-decoupled [31]P NMR spectra of PEO-b-PiBP

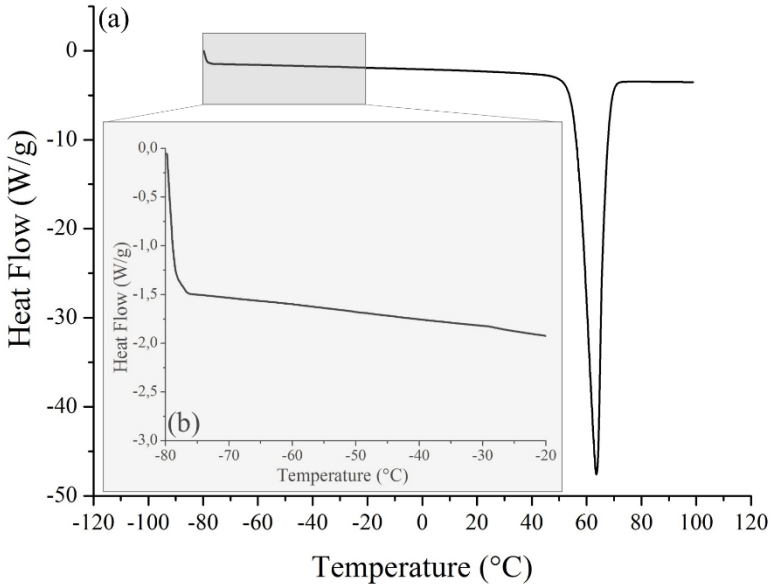
PEO-b-PnHP copolymer



[1]H-decoupled [31]P NMR spectrum of PEO-b-PnHP amphiphilic copolymer

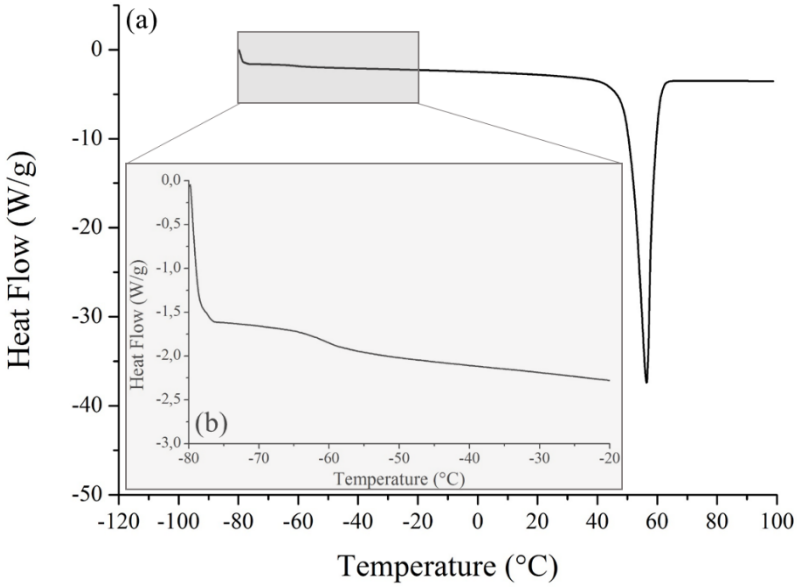
DSC curves of PEO-*b*-polyphosphate copolymers

For PEO polymer



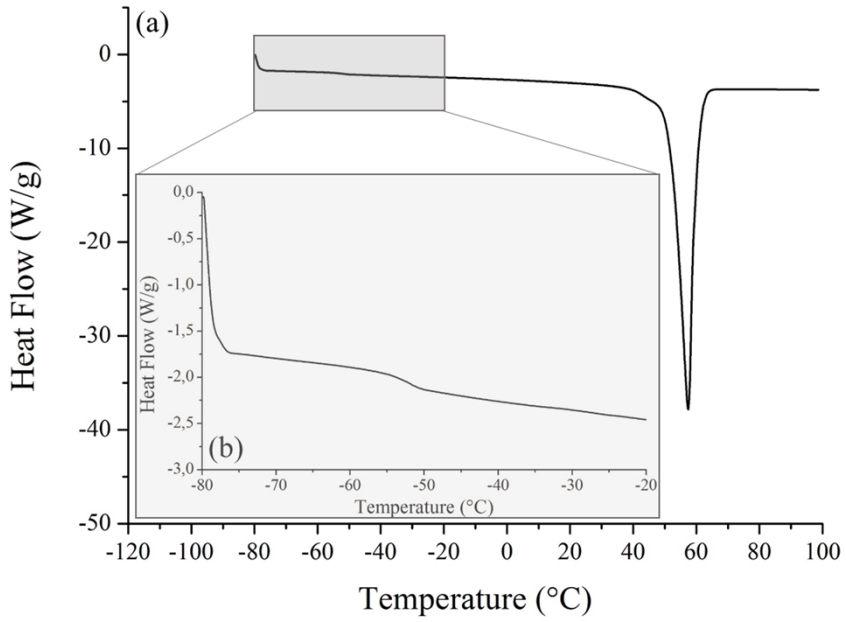
DSC curve for PEO polymer under dynamic nitrogen atmosphere (50 mL min^{-1}) with a temperature ramp of 20°C min^{-1} between (a) -80°C to 100°C and (b) -80°C to -20°C

For PEO-b-PnBP copolymer



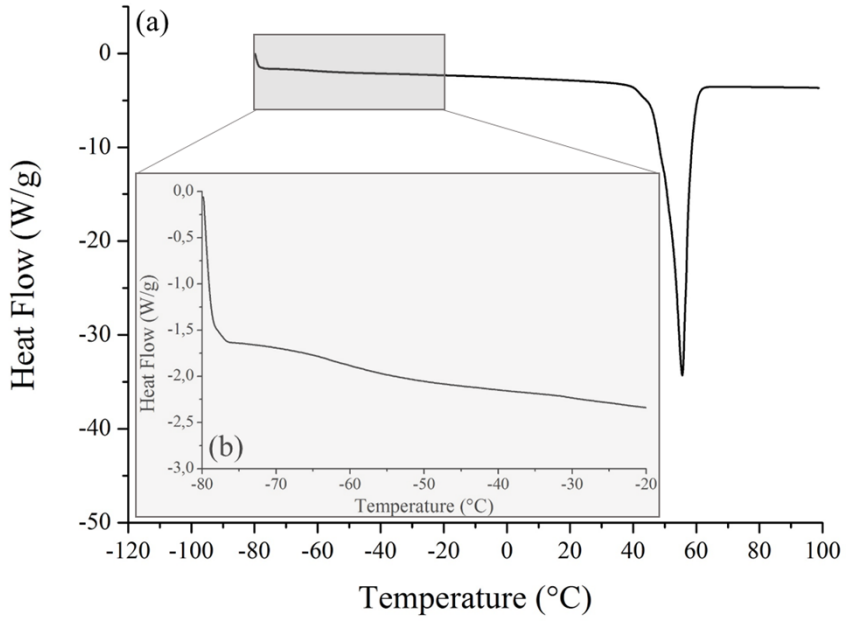
DSC curve for PEO-b-PnBP copolymer under dynamic nitrogen atmosphere (50 mL min^{-1}) with a temperature ramp of 20°C min^{-1} between (a) -80°C to 100°C and (b) -80°C to -20°C

For PEO-b-PiBP copolymer



DSC curve for PEO-b-PiBP copolymer under dynamic nitrogen atmosphere (50 mL min^{-1}) with a temperature ramp of 20°C min^{-1} between (a) -80°C to 100°C and (b) -80°C to -20°C

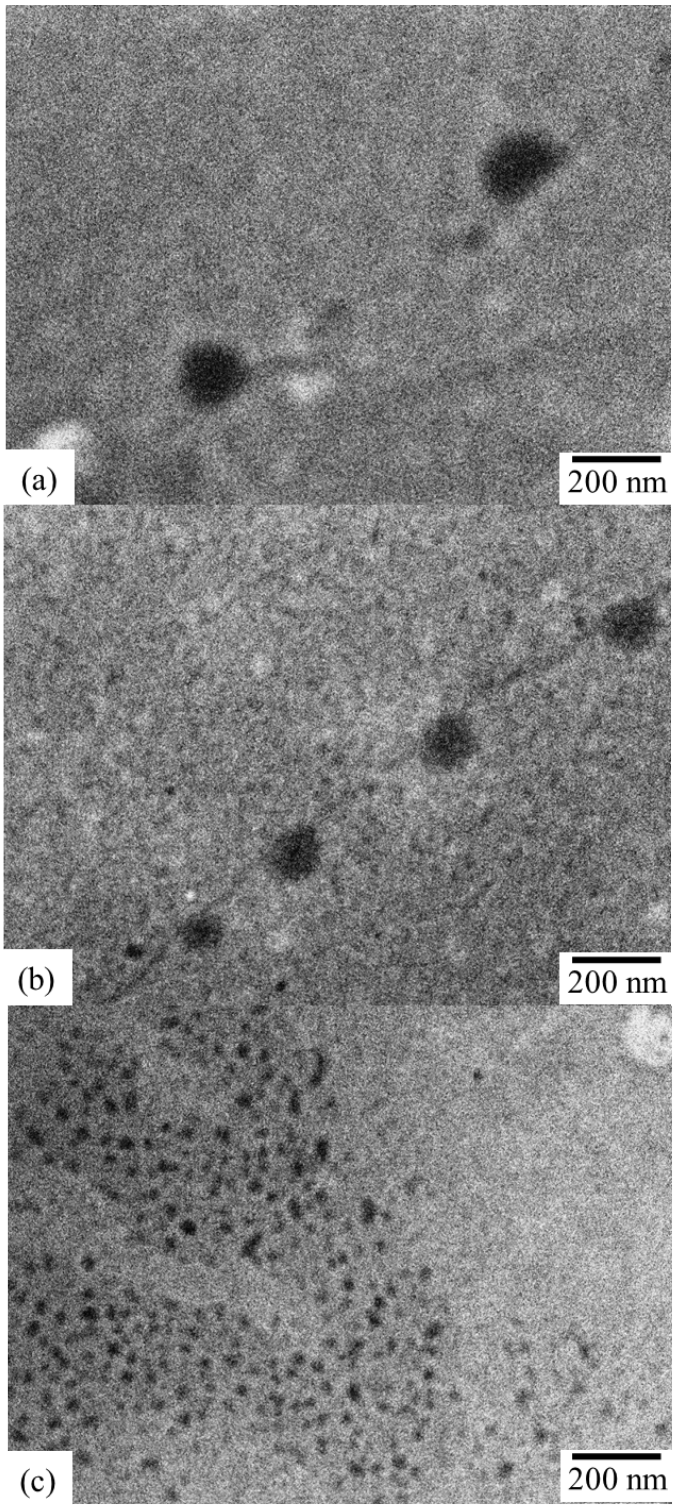
For PEO-b-PnHP copolymer



DSC curve for PEO-b-PnHP copolymer under dynamic nitrogen atmosphere (50 mL min^{-1}) with a temperature ramp of 20°C min^{-1} between (a) -80°C to 100°C and (b) -80°C to -20°C

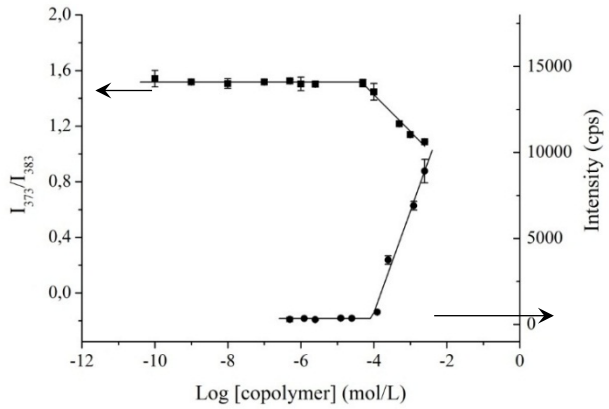
Aqueous behavior of PEO-*b*-polyphosphate diblock copolymers

TEM images of PEO-b-polyphosphate self-assembled nanoparticles



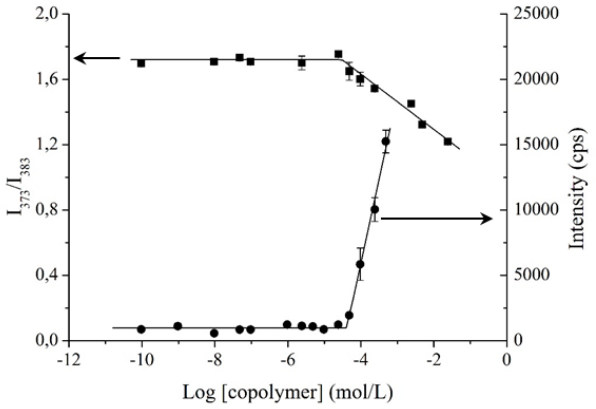
TEM images of self-assembled nanoparticles for PEO-b-polyphosphate amphiphilic copolymers: (a) PEO_{113}-b-$PiBP_8$, (b) PEO_{113}-b-$PnBP_9$ and (c) PEO_{113}-b-$PnHP_8$

PEO-b-PnBP copolymer



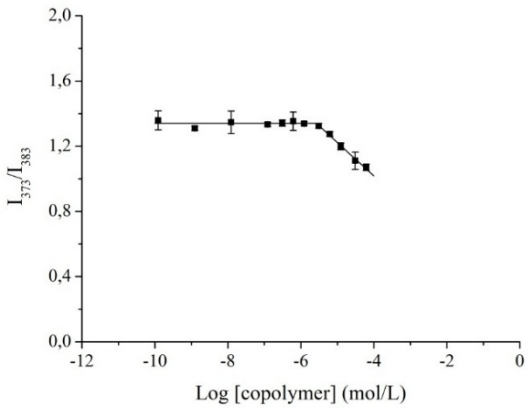
Plots of scattered intensity (from DLS measurements) and I_{373}/I_{383} ratio (from pyrene fluorescence spectra) versus log[copolymer] for the PEO-b-PnBP

PEO-b-PiBP copolymer



Plots of scattered intensity (from DLS measurements) and I_{373}/I_{383} ratio (from pyrene fluorescence spectra) versus log[copolymer] for the PEO-b-PiBP

PEO-b-PnHP copolymer



Plots of I_{373}/I_{383} ratio (from pyrene fluorescence spectra) versus log[copolymer] for the PEO-b-PnHP