Supporting Information

Exploring the Long-Term Hydrolytic Behavior of Zwitterionic Polymethacrylates and Polymethacrylamides

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1. Detailed 1H- and 13C-NMR spectroscopic characterization of the monomers

2-(N-(2-(methacryloyloxy)ethyl)-N,N-dimethylammonio)ethyl sulfate (M-1)

Figure S1  
a) $^1$H NMR (in D$_2$O) and b) $^{13}$C (APT) NMR spectra (in D$_2$O) of M-1.
Figure S 2 a) $^1$H-$^1$H-COSY and b) $^1$H-$^{13}$C-HMQC NMR spectra (in D$_2$O) of M-1.
3-(N-(2-(methacryloyloxy)ethyl)-N,N-dimethylammonio)propyl sulfate (M-2)

Figure S 3  a) $^1$H NMR (in D$_2$O) and b) $^{13}$C (APT) NMR spectra (in D$_2$O) of M-2.
Figure S 4 a) $^1$H-$^1$H-COSY and b) $^1$H-$^{13}$C-HMQC NMR spectra (in D$_2$O) of M-2.
2-(N-(3-methacrylamidopropyl)-N,N-dimethylammonio)ethyl sulfate (M-3)

Figure S 5  a) $^1$H NMR (in D$_2$O) and b) $^{13}$C (APT) NMR spectra (in D$_2$O) of M-3.
Figure S 6  a) $^1$H-$^1$H-COSY and b) $^1$H-$^{13}$C-HMQC NMR spectra (in D$_2$O) of M-3.
3-(N-(3-methacrylamidopropyl)-N,N-dimethylammonio)propyl sulfate (M-4)

Figure S7  a) $^1$H NMR (in D$_2$O) and b) $^{13}$C (APT) NMR spectra (in D$_2$O) of M-4.
Figure S 8  a) $^1$H-$^1$H-COSY and b) $^1$H-$^{13}$C-HMQC NMR spectra (in D$_2$O) of **M-4**.
2-(N,N-dimethyl-N-(4-vinylbenzyl)ammonio)ethyl sulfate (M-5)

Figure S 9  
a) $^1$H NMR (in D$_2$O) and b) $^{13}$C (APT) NMR spectra (in D$_2$O) of M-5
Figure S 10 a) $^1$H-$^1$H-COSY and b) $^1$H-$^{13}$C-HMQC NMR spectra (in D$_2$O) of M-5.
3-N,N-(dimethyl-N-(4-vinylbenzyl)ammonio)propyl sulfate (M-6)

Figure S11  a) $^1$H NMR (in D$_2$O) and b) $^{13}$C (APT) NMR spectra (in D$_2$O) of M-6
Figure S 12  a) $^1$H-$^1$H-COSY and b) $^1$H-$^{13}$C-HMQC NMR spectra (in D$_2$O) of M-6.
2. Detailed 1H- and 13C-NMR spectroscopic characterization of the polymers

*Polymer P-OEGMA*

![NMR Spectrum](image)

Figure S 13  a) $^1$H NMR (in D$_2$O) of P-OEGMA.
Polymer P-SPE

Figure S 14  a) $^1$H NMR (in dilute aqueous NaCl (9.0 g·L$^{-1}$) in D$_2$O) and b) $^1$H-$^1$H-COSY (in dilute aqueous NaCl (9.0 g·L$^{-1}$) in D$_2$O) of P-SPE.
Figure S 15  a) $^1$H NMR (in dilute aqueous NaCl (9.0 g·L$^{-1}$) in D$_2$O) and b) $^1$H-$^1$H-COSY (in dilute aqueous NaCl (9.0 g·L$^{-1}$) in D$_2$O) of P-SPP.
Polymer P-1

Figure S 16  a) $^1$H NMR (in saturated NaCl solution in D$_2$O) and  
b) $^1$H-$^1$H-COSY (in saturated NaCl solution in D$_2$O) of P-1.
Polymer P-2

Figure S 17  a) $^1$H NMR (in saturated NaCl solution in D$_2$O) and b) $^1$H-$^1$H-COSY (in saturated NaCl solution in D$_2$O of P-2.)
Figure S 18  a) $^1$H NMR (in saturated NaCl solution in D$_2$O) and b) $^1$H-$^1$H-COSY (in saturated NaCl solution in D$_2$O of P-3.
Figure S 19  
a) $^1$H NMR (in saturated NaCl solution in D$_2$O) and  
b) $^1$H-$^1$H-COSY (in saturated NaCl solution in D$_2$O of P-4.
Figure S 20  a) $^1$H NMR (in saturated NaCl solution in D$_2$O) and b) $^1$H-$^1$H-COSY (in saturated NaCl solution in D$_2$O of P-6.)
3. Preparation of buffer solution

1. Monomer/phosphate buffered saline (PBS) pH=7.4
48 mg of a PBS tablet (provider Sigma Aldrich) were dissolved in 5.0 mL of D$_2$O, resulting in a 0.01 M phosphate buffer, 0.0027 M KCl and 0.137 M NaCl solution with a pH value of 7.4 at 25 °C. 0.6 mL of the prepared buffer solution was added to 0.06 mmol monomer shortly before the first NMR measurement. 3-(Trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt was added as inner standard. Monomers M-5 and M-6 dissolved only partially in the buffer solution.

2. Monomer/deuterium chloride pH=0
0.8 mL of deuterium chloride (38 wt% in D$_2$O) and 12.5 of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt (12.5 mM) were dissolved in 4.2 mL of D$_2$O, resulting in a deuterium chloride solution with a pH-value of 0. 0.3 mL of the so prepared solution was added to a 0.3 mL/0.06 mmol of monomer solution shortly before the first NMR measurement. Monomers M-5 and M-6 dissolved only partially in the buffer solution.

3. Monomer/carbonate buffer pH=10
302.4 mg of NaHCO$_3$, 148.4 mg of Na$_2$CO$_3$ and 12.5 mg of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt (12.5 mM) were dissolved in 5.0 mL of D$_2$O, resulting in a 1 molar carbonate buffer solution with a pH-value of 10. 0.6 mL of the prepared buffer solution was added to 0.06 mmol of monomer shortly before the first NMR measurement. Monomers M-5 and M-6 dissolved only partially in the buffer solution.

4. Monomer/sodium hydroxide pH=14
400 mg of NaOH and 12.5 of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt (12.5 mM) were dissolved in 5.0 mL of D$_2$O, resulting in a sodium hydroxide solution with a pH-value of 14. 0.3 mL of the prepared solution was added to 0.06 mmol monomer in 0.3 mL D$_2$O shortly before the first NMR measurement. Monomers M-5 and M-6 dissolved only partially in the buffer solution.

5. Polymer/phosphate buffered saline (PBS) pH=7.4
48 mg of a PBS pill (provider Sigma Aldrich) and 12.5 mg of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt (12.5 mM) were dissolved in 5.0 mL of D$_2$O, resulting in a 0.01 M phosphate buffer, 0.0027 M KCl and 0.137 M NaCl solution with a pH value of 7.4 at 25 °C. The prepared buffer solution was added to the equivalent weight of 0.06 mmol repeating units of the polymer before the first NMR measurement. In case of P-1 to P-6 the prepared phosphate buffer solution was additionally saturated with sodium chloride. Polymer P-5 did not dissolve in the sodium chloride saturated phosphate buffer solution.

6. Monomer/deuterium chloride pH=0
0.8 mL of deuterium chloride (38 wt% in D$_2$O) and 12.5 of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid sodium salt (12.5 mM) were dissolved in 4.2 mL of D$_2$O, resulting in a deuterium chloride solution with a pH-value of 0. 0.3 mL of the prepared solution was added to a polymer solution in pure D$_2$O (in case of P-OEGMA, P-SPE and P-SPP), or in a saturated NaCl in D$_2$O (in case of P-1 to P-6) before the first NMR measurement. For P-1 to P-6, the DCl solution was additionally saturated with sodium chloride, before
added to the polymer solution. **P-5** did not dissolve in the sodium chloride saturated deuterium chloride solution.

7. **Polymer/carbonate buffer pH=10**

302.4 mg of NaHCO₃, 148.4 mg of Na₂CO₃ and 12.5 mg of 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (12.5 mM) were dissolved in 5 mL of D₂O, resulting in a carbonate buffer solution with a pH-value of 10. 0.3 mL of the prepared buffer solution was added in a polymer solution in pure D₂O (in case of P-OEGMA, P-SPE and P-SPP), or in saturated NaCl in D₂O (in case of **P-1** to **P-6**) before the first NMR measurement. **P-5** did not dissolve in the sodium chloride saturated carbonate buffer solution.

8. **Polymer/sodium hydroxide pH=14**

400 mg of NaOH and 12.5 of 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (12.5 mM) were dissolved in 5.0 mL of D₂O, resulting in a sodium hydroxide solution with a pH-value of 14. 0.3 mL of the prepared solution was added to a polymer solution in pure D₂O (in case of **P-OEGMA, P-SPE and P-SPP**), or in a saturated NaCl in D₂O (in case of **P-1** to **P-6**) before the first NMR measurement. For **P-1** and **P-6**, the NaOH solution was additionally saturated with sodium chloride, before added to the polymer solution. **P-5** did not dissolve in the sodium chloride saturated sodium hydroxide solution.
4. Evolution of the monomer and polymer 1H-NMR spectra upon storage in aqueous media at 22 °C at various pH values.

4.1. Monomer hydrolysis in phosphate buffered saline (pH = 7.4)

Figure S 21  Evolution of ester and amid hydrolysis of monomers in phosphate buffered saline (PBS) in D$_2$O (undiluted PBS contains yields in 0.137 mol*L$^{-1}$ of NaCl, 0.0027 mol*L$^{-1}$ of KCl and 0.01 mol*L$^{-1}$ phosphate buffer, pH 7.4 at 25 °C): (□) = OEGMA, (□) = SPE, (•) = SPP, (□) = M-1, (□) = M-2, (•) = M-3, (X) = M-4.

Calculation of hydrolysis in mol %:

\[
\text{Hydrolyse}_{M-1} \text{ [mol %]} = \frac{I_{a_2'}*100}{I_{a'}+I_{a_2'}} + \frac{I_{a_2''}*100}{I_{a''}+I_{a_2''}} \div 2
\]

\[
\text{Hydrolyse}_{M-2} \text{ [mol %]} = \frac{I_{a_2'}*100}{I_{a'}+I_{a_2'}} + \frac{I_{a_2''}*100}{I_{a''}+I_{a_2''}} \div 2
\]

\[
\text{Hydrolyse}_{M-3} \text{ [mol %]} = \frac{I_{a_2'}*100}{I_{a'}+I_{a_2'}} + \frac{I_{a_2''}*100}{I_{a''}+I_{a_2''}} \div 2
\]

\[
\text{Hydrolyse}_{M-4} \text{ [mol %]} = \frac{I_{a_2'}*100}{I_{a'}+I_{a_2'}} + \frac{I_{a_2''}*100}{I_{a''}+I_{a_2''}} \div 2
\]
\[
\text{Hydrolyse}_{\text{OEGMA}} \text{ [mol %]} = \left( \frac{I_{a''} \cdot 100}{I_{a'+I_{a''}}} + \frac{I_{a'''} \cdot 100}{I_{a'''+I_{a'''}}} \right) / 2 \\
\text{Hydrolyse}_{\text{SPE}} \text{ [mol %]} = \left( \frac{I_{a''} \cdot 100}{I_{a'+I_{a''}}} + \frac{I_{a'''} \cdot 100}{I_{a'''+I_{a'''}}} \right) / 2 \\
\text{Hydrolyse}_{\text{SPP}} \text{ [mol %]} = \left( \frac{I_{a''} \cdot 100}{I_{a'+I_{a''}}} + \frac{I_{a'''} \cdot 100}{I_{a'''+I_{a'''}}} \right) / 2 
\]

The Index 2 in e.g. \( I_{e_2} \) indicates the hydrolysis product of the ester/amid product, while no index e.g. \( I_{a''} \) determines the unchanged molecule without hydrolysis.

\( I_{a'}(M-1, \text{ range in ppm}) = 6.3-6.1 \)
\( I_{a_2'}(M-1, \text{ range in ppm}) = 5.7-5.6 \)
\( I_{a''}(M-1, \text{ range in ppm}) = 5.9-5.7 \)
\( I_{a_2''}(M-1, \text{ range in ppm}) = 5.4-5.3 \)
\( I_{a'}(M-2, \text{ range in ppm}) = 6.3-6.1 \)
\( I_{a_2'}(M-2, \text{ range in ppm}) = 5.7-5.6 \)
\( I_{a''}(M-2, \text{ range in ppm}) = 5.9-5.7 \)
\( I_{a_2''}(M-2, \text{ range in ppm}) = 5.4-5.3 \)
\( I_{a'}(M-3, \text{ range in ppm}) = 5.9-5.6 \)
\( I_{a_2'}(M-3, \text{ range in ppm}) = \) no signal
\( I_{a''}(M-3, \text{ range in ppm}) = 5.6-5.4 \)
\( I_{a_2''}(M-3, \text{ range in ppm}) = \) no signal
\( I_{a'}(M-4, \text{ range in ppm}) = 5.9-5.6 \)
\( I_{a_2'}(M-4, \text{ range in ppm}) = \) no signal
\( I_{a''}(M-4, \text{ range in ppm}) = 5.6-5.4 \)
\( I_{a_2''}(M-4, \text{ range in ppm}) = \) no signal
\( I_{a'}(\text{OEGMA}, \text{ range in ppm}) = 6.3-6.0 \)
\( I_{a''}(\text{OEGMA}, \text{ range in ppm}) = 5.8-5.5 \)
\( I_{a_2''}(\text{OEGMA}, \text{ range in ppm}) = 5.4-5.3 \)
\( I_{a'}(\text{SPE}, \text{ range in ppm}) = 6.4-6.1 \)
\( I_{a''}(\text{SPE}, \text{ range in ppm}) = 5.9-5.7 \)
\( I_{a_2''}(\text{SPE}, \text{ range in ppm}) = 5.5-5.3 \)
\( I_{a'}(\text{SPP}, \text{ range in ppm}) = 5.9-5.6 \)
\( I_{a_2'}(\text{SPP}, \text{ range in ppm}) = \) no signal
\( I_{a''}(\text{SPP}, \text{ range in ppm}) = 5.6-5.4 \)
\( I_{a_2''}(\text{SPP}, \text{ range in ppm}) = \) no signal

S26
$^{1}$H-NMR spectrum showing the degradation of 0.1 M solution of OEGMA in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.

Figure S 22
Figure S 23  

\( ^1\text{H-NMR} \) spectrum showing the degradation of 0.1 M solution of SPE in phosphate buffered saline (PBS) in D\(_2\)O (pH = 7.4) at room temperature over time.
Figure S 24  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of SPP in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 25  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-1 in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 26 $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-2 in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 27  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-3 in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 28  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-4 in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 29  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-5 in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 30  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-6 in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
4.2. Monomer hydrolysis in 1 M hydrochloric acid pH=0

**Figure S 31.** Evolution of ester and amid hydrolysis of monomers in 1 M hydrochloric acid in D$_2$O (pH=0): (□) = OEGMA, (◮) = SPE, (★) = SPP, (□) = M-1, (◮) = M-2, (＋) = M-3, (X) = M-4.

Calculation of hydrolysis in mol %:

\[
Hydrolyse_{M-1} \text{ [mol %]} = \frac{I_{a_2} \times 100}{I_{a_2} + I_{a_2''}} + \frac{I_{a_2''} \times 100}{I_{a_2''} + I_{a_2'}}/2
\]

\[
Hydrolyse_{M-2} \text{ [mol %]} = \frac{I_{a_2} \times 100}{I_{a_2} + I_{a_2'}} + \frac{I_{a_2'} \times 100}{I_{a_2'} + I_{a_2''}}/2
\]

\[
Hydrolyse_{M-3} \text{ [mol %]} = \frac{I_{f_2} \times 100}{I_{f_2} + I_{f_2} + I_{f_2'}}
\]

\[
Hydrolyse_{M-4} \text{ [mol %]} = \frac{I_{c_2} \times 100}{I_{c_2} + I_{c_2} + I_{c_2'}}
\]

\[
Hydrolyse_{OEGMA} \text{ [mol %]} = \frac{I_{c_2} \times 100}{I_{c_2} + I_{c_2} + I_{c_2'}}
\]

\[
Hydrolyse_{SPE} \text{ [mol %]} = \frac{I_{a_2'} \times 100}{I_{a_2'} + I_{a_2''}} + \frac{I_{a_2''} \times 100}{I_{a_2''} + I_{a_2'}}/2
\]

\[
Hydrolyse_{SPP} \text{ [mol %]} = \frac{I_{c_2} \times 100}{I_{c_2} + I_{c_2} + I_{c_2'}}
\]

The Index 2 in e.g. $I_{a_2}$ indicates the hydrolysis product of the ester/amid product, while no index e.g. $I_{a_2'}$ determines the unchanged molecule without hydrolysis.
I_{a'}(M-1, \text{ range in ppm}) = 6.2-6.1
I_{a_2}(M-1, \text{ range in ppm}) = 6.1-6.0
I_{a''}(M-1, \text{ range in ppm}) = 5.9-5.8
I_{a_2''}(M-1, \text{ range in ppm}) = 5.8-5.7
I_{a'}(M-2, \text{ range in ppm}) = 6.4-6.2
I_{a_2}(M-2, \text{ range in ppm}) = 6.2-6.0
I_{a''}(M-2, \text{ range in ppm}) = 6.0-5.9
I_{a_2''}(M-2, \text{ range in ppm}) = 5.9-5.6
I_{f+f_6}(M-3, \text{ range in ppm}) = 2.4-2.2
I_{f_3}(M-3, \text{ range in ppm}) = 2.2-2.0
I_{c+c_3}(M-4, \text{ range in ppm}) = 2.0-1.9
I_{c_2}(M-4, \text{ range in ppm}) = 1.9-1.8
I_{c+c_3}(OEGMA, \text{ range in ppm}) = 2.1-2.0
I_{c_2}(OEGMA, \text{ range in ppm}) = 2.1-1.9
I_{a'}(SPE, \text{ range in ppm}) = 6.3-6.1
I_{a_2}(SPE, \text{ range in ppm}) = 6.1-6.0
I_{a''}(SPE, \text{ range in ppm}) = 5.8-5.7
I_{a_2''}(SPE, \text{ range in ppm}) = 5.7-5.6
I_{c+c_3}(SPP, \text{ range in ppm}) = 2.0-1.9
I_{c_2}(SPP, \text{ range in ppm}) = 1.9-1.8
Figure S 32. Evolution of sulfate and sulfonate hydrolysis of monomers in 1 M hydrochloric acid in D$_2$O (pH=0): (□) = SPE, (■) = SPP, (△) = M1, (□) = M2, (+) = M3, (X) = M4, (□) = M5, (□) = M6.

Calculation of hydrolysis in mol %:

$Hydrolyse_{M-1}$ [mol %] = \( \frac{[I_{k3+e3} - 2 \times I_{a2}]}{[I_{g+i} - 2 \times I_{a2}]/2 + [I_{k3+e3} - 2 \times I_{a2}]/2} \times 100 \)

$Hydrolyse_{M-2}$ [mol %] = \( \frac{I_{j3} \times 100}{I_{j2} + I_{j3}} \)

$Hydrolyse_{M-3}$ [mol %] = \( \frac{I_{k3} \times 100}{I_k + I_{k5}} \)

$Hydrolyse_{M-4}$ [mol %] = \( \frac{I_{k3} \times 100}{I_i + I_{k5}} \)

$Hydrolyse_{M-5}$ [mol %] = \( \frac{I_{i3} \times 100}{I_i + I_{i3}} \)

$Hydrolyse_{M-6}$ [mol %] = \( \frac{I_{j3} \times 100}{I_{j2} + I_{j3}} \)

$Hydrolyse_{SPE}$ [mol %] = \( \frac{I_{k+k2} + I_{k5}}{I_k + I_{k5}} \)

$Hydrolyse_{SPP}$ [mol %] = \( \frac{I_{k3} \times 100}{I_k + I_{k3}} \)

The Index 2 in e.g. $I_{e2}$ indicates the hydrolysis product of the ester/amid product, while no index e.g. $I_{a''}$ determines the unchanged molecule without hydrolysis.
\begin{align*}
I_{k_3+e_3}(M-1, \text{ range in ppm}) &= 4.6-4.4 \\
I_{e_2}(M-1, \text{ range in ppm}) &= 6.1-6.2 \\
I_{g+i}(M-1, \text{ range in ppm}) &= 4.2-4.0 \\
I_{j_2}(M-2, \text{ range in ppm}) &= 2.2-2.0 \\
I_{j_2}(M-2, \text{ range in ppm}) &= 2.4-2.2 \\
I_{k_3}(M-3, \text{ range in ppm}) &= 4.2-3.9 \\
I_{k_3}(M-3, \text{ range in ppm}) &= 4.6-4.3 \\
I_{k_3}(M-4, \text{ range in ppm}) &= 3.8-3.6 \\
I_{k_3}(M-4, \text{ range in ppm}) &= 4.3-4.0 \\
I_{l_5}(M-5, \text{ range in ppm}) &= 3.6-3.4 \\
I_{l_5}(M-5, \text{ range in ppm}) &= 3.9-3.6 \\
I_{j_3}(M-6, \text{ range in ppm}) &= 2.2-2.0 \\
I_{j_3}(M-6, \text{ range in ppm}) &= 2.4-2.2 \\
I_{k_3}(SPE, \text{ range in ppm}) &= \text{no signal} \\
I_{k_3+k_3}(SPE, \text{ range in ppm}) &= 3.1-2.9 \\
I_{k_3}(SPP, \text{ range in ppm}) &= \text{no signal} \\
I_{k_3}(SPP, \text{ range in ppm}) &= 3.1-2.9
\end{align*}
Figure S 33  
$^1$H-NMR spectrum showing the degradation of 0.1 M solution of OEGMA in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 34  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of **SPE** in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 35  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of SPP in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 36  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-1 in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 37  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-2 in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 38  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-3 in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 39  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-4 in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 40  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-5 in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 41  

$^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-6 in hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
4.1. 2D-Spektra ($^1$H-$^1$H-COSY) - Monomer hydrolysis pH=0

Figure S 42  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of SPP in hydrochloric acid in D$_2$O, after 291 days.

Figure S 43  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of M-1 in hydrochloric acid in D$_2$O, after 291 days.
Figure S 44  \(^1\)H-\(^1\)H-COSY NMR spectra of 0.1 M solution of M-2 in hydrochloric acid in D\(_2\)O, after 291 days.

Figure S 45  \(^1\)H-\(^1\)H-COSY NMR spectra of 0.1 M solution of M-3 in hydrochloric acid in D\(_2\)O, after 291 days.
Figure S 46  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of M-4 in hydrochloric acid in D$_2$O, after 291 days.

Figure S 47  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of M-5 in hydrochloric acid in D$_2$O, after 291 days.
Figure S 48  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of M-6 in hydrochloric acid in D$_2$O, after 291 days.
4.3. Monomer hydrolysis hydrogen carbonate buffer (pH=10)

Calculation of hydrolysis in mol %:

\[ \text{Hydrolysis}_{M-1} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a''}} + \frac{(I_{a''} * 100)}{I_{a''} + I_{a'_2}} \times \frac{1}{2} \]

\[ \text{Hydrolysis}_{M-2} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a'_2}} + \frac{(I_{a'_2} * 100)}{I_{a'_2} + I_{a''}} \times \frac{1}{2} \]

\[ \text{Hydrolysis}_{M-3} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a'_2}} + \frac{(I_{a'_2} * 100)}{I_{a'_2} + I_{a''}} \times \frac{1}{2} \]

\[ \text{Hydrolysis}_{M-4} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a'_2}} + \frac{(I_{a'_2} * 100)}{I_{a'_2} + I_{a''}} \times \frac{1}{2} \]

\[ \text{Hydrolysis}_{OEGMA} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a'_2}} + \frac{(I_{a''} * 100)}{I_{a''} + I_{a'_2}} \times \frac{1}{2} \]

\[ \text{Hydrolysis}_{SPE} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a'_2}} + \frac{(I_{a''} * 100)}{I_{a''} + I_{a'_2}} \times \frac{1}{2} \]

\[ \text{Hydrolysis}_{SPP} \text{[mol %]} = \frac{(I_{a_2} * 100)}{I_{a'} + I_{a'_2}} + \frac{(I_{a''} * 100)}{I_{a''} + I_{a'_2}} \times \frac{1}{2} \]

The Index 2 in e.g. \( I_{a_2} \) indicates the hydrolysis product of the ester/amid product, while no index e.g. \( I_{a''} \) determines the unchanged molecule without hydrolysis.
$I_{a'}(M-1, \text{ range in ppm}) = 6.3$-$6.1$
$I_{a'}(M-1, \text{ range in ppm}) = 5.7$-$5.6$
$I_{a''}(M-1, \text{ range in ppm}) = 5.9$-$5.7$
$I_{a''}(M-1, \text{ range in ppm}) = 5.4$-$5.3$
$I_{a'}(M-2, \text{ range in ppm}) = 6.3$-$6.1$
$I_{a'}(M-2, \text{ range in ppm}) = 5.7$-$5.6$
$I_{a''}(M-2, \text{ range in ppm}) = 5.9$-$5.7$
$I_{a''}(M-2, \text{ range in ppm}) = 5.4$-$5.3$
$I_{a'}(M-3, \text{ range in ppm}) = 5.9$-$5.6$
$I_{a'}(M-3, \text{ range in ppm}) = \text{no signal}$
$I_{a''}(M-3, \text{ range in ppm}) = 5.6$-$5.4$
$I_{a''}(M-3, \text{ range in ppm}) = \text{no signal}$
$I_{a'}(M-4, \text{ range in ppm}) = 5.8$-$5.6$
$I_{a'}(M-4, \text{ range in ppm}) = \text{no signal}$
$I_{a''}(M-4, \text{ range in ppm}) = 5.6$-$5.4$
$I_{a''}(M-4, \text{ range in ppm}) = \text{no signal}$
$I_{a'}(\text{OEGMA, range in ppm}) = 6.3$-$6.1$
$I_{a'}(\text{OEGMA, range in ppm}) = 5.7$-$5.6$
$I_{a''}(\text{OEGMA, range in ppm}) = 5.8$-$5.7$
$I_{a''}(\text{OEGMA, range in ppm}) = 5.4$-$5.3$
$I_{a'}(\text{SPE, range in ppm}) = 6.3$-$6.1$
$I_{a'}(\text{SPE, range in ppm}) = 5.7$-$5.6$
$I_{a''}(\text{SPE, range in ppm}) = 5.9$-$5.7$
$I_{a''}(\text{SPE, range in ppm}) = 5.5$-$5.3$
$I_{a'}(\text{SPP, range in ppm}) = 5.9$-$5.6$
$I_{a'}(\text{SPP, range in ppm}) = \text{no signal}$
$I_{a''}(\text{SPP, range in ppm}) = 5.6$-$5.4$
$I_{a''}(\text{SPP, range in ppm}) = \text{no signal}$
Figure S 50  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of OEGMA in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 51  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of SPE in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 52  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of SPP in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S53  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-1 in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 54  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-2 in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 55  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-3 in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 56  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-4 in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 57  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-5 in carbonate buffer in D$_2$O (pH = 10) at room temperature over time.
Figure S 58  \(^1\)H-NMR spectrum showing the degradation of 0.1 M solution of M-6 in carbonate buffer in D\(_2\)O (pH = 10) at room temperature over time.
4.4. Monomer hydrolysis in 1 M sodium hydroxide solution (pH=14)

![Graph showing hydrolysis of monomers in sodium hydroxide solution](image)

**Figure S 59** Evolution of ester and amid hydrolysis of monomers in sodium hydroxide in D$_2$O (pH=14): (☐) = OEGMA, (□) = SPE, (⋆) = SPP, (△) = M-1, (◆) = M-2, (●) = M-3, (★) = M-4.

**Calculation of hydrolysis in mol %:**

\[
Hydrolyse_{M-1} \text{ [mol %]} = \left( \frac{I_{a_2}^*100 + I_{a_2''}^*100}{I_{a_2}^* + I_{a_2''}^*} \right) / 2
\]

\[
Hydrolyse_{M-2} \text{ [mol %]} = \left( \frac{I_{a_2}^*100 + I_{a_2''}^*100}{I_{a_2}^* + I_{a_2''}^*} \right) / 2
\]

\[
Hydrolyse_{M-3} \text{ [mol %]} = \left( \frac{I_{a_2}^*100}{I_{a''} + I_{a_2''}} \right)
\]

\[
Hydrolyse_{M-4} \text{ [mol %]} = \left( \frac{I_{a_2}^*100}{I_{a''} + I_{a_2''}} \right)
\]

\[
Hydrolyse_{OEGMA} \text{ [mol %]} = \left( \frac{I_{a_2}^*100 + I_{a_2''}^*100}{I_{a_2}^* + I_{a_2''}^*} \right) / 2
\]

\[
Hydrolyse_{SPE} \text{ [mol %]} = \left( \frac{I_{a_2}^*100 + I_{a_2''}^*100}{I_{a_2}^* + I_{a_2''}^*} \right) / 2
\]

\[
Hydrolyse_{SPP} \text{ [mol %]} = \left( \frac{I_{a_2}^*100 + I_{a_2''}^*100}{I_{a_2}^* + I_{a_2''}^*} \right) / 2
\]

The Index 2 in e.g. \(I_{e_2}\) indicates the hydrolysis product of the ester/amid product, while no index e.g. \(I_{a''}\) determines the unchanged molecule without hydrolysis.
$I_{a'}(M-1, \text{ range in ppm}) = \text{no signal}$

$I_{a_2'}(M-1, \text{ range in ppm}) = 5.8-5.6$

$I_{a''}(M-1, \text{ range in ppm}) = \text{no signal}$

$I_{a_2''}(M-1, \text{ range in ppm}) = 5.5-5.3$

$I_{a'}(M-2, \text{ range in ppm}) = \text{no signal}$

$I_{a_2'}(M-2, \text{ range in ppm}) = 5.7-5.6$

$I_{a''}(M-2, \text{ range in ppm}) = \text{no signal}$

$I_{a_2''}(M-2, \text{ range in ppm}) = 5.4-5.3$

$I_{a'}(M-3, \text{ range in ppm}) = \text{no signal}$

$I_{a_2'}(M-3, \text{ range in ppm}) = 5.6-5.4$

$I_{a''}(M-3, \text{ range in ppm}) = 5.4-5.3$

$I_{a''}(M-4, \text{ range in ppm}) = 5.4-5.3$

$I_{a_2''}(M-4, \text{ range in ppm}) = 5.3-5.2$

$I_{a'}(OEGMA, \text{ range in ppm}) = \text{no signal}$

$I_{a_2'}(OEGMA, \text{ range in ppm}) = 5.8-5.6$

$I_{a''}(OEGMA, \text{ range in ppm}) = \text{no signal}$

$I_{a_2''}(OEGMA, \text{ range in ppm}) = 5.4-5.3$

$I_{a'}(SPE, \text{ range in ppm}) = \text{no signal}$

$I_{a_2'}(SPE, \text{ range in ppm}) = 5.8-5.6$

$I_{a''}(SPE, \text{ range in ppm}) = \text{no signal}$

$I_{a_2''}(SPE, \text{ range in ppm}) = 5.4-5.3$

$I_{a'}(SPP, \text{ range in ppm}) = 5.8-5.7$

$I_{a_2'}(SPP, \text{ range in ppm}) = 5.7-5.6$

$I_{a''}(SPP, \text{ range in ppm}) = 5.5-5.4$

$I_{a_2''}(SPP, \text{ range in ppm}) = 5.4-5.3$
Figure S 60  Evolution of sulfate and sulfonate hydrolysis of monomers in sodium hydroxide in D\textsubscript{2}O (pH=14): (□) = SPE, (*) = SPP, (□) = M-1, (□) = M-2, (+) = M-3, (X) = M-4, (□) = M-5, (□) = M-6.

Calculation of hydrolysis in mol %:

General (without use of product integral):

\[ \text{Hyd}_{M,X} [\text{mol\%}] = \left( \frac{I_{a_2''}}{k_3 + k_2} \right) \times 100 = \frac{2 \times I_{a_2''} - k_2}{2 \times I_{a_2''} - k_2} \times 100 = \frac{2 \times I_{a_2''} - k_2}{2 \times I_{a_2''}} \times 100 \]

\[ \text{Hydrolyse}_{M-1} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} - k_2}{2 \times I_{a_2''}} \right) \times 100 \]

\[ \text{Hydrolyse}_{M-2} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} - I_{k_2}}{2 \times I_{a_2''}} \right) \times 100 \]

\[ \text{Hydrolyse}_{M-3} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} + a'' - I_{k_2}}{2 \times I_{a_2''} + a''} \right) \times 100 \]

\[ \text{Hydrolyse}_{M-4} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} + a'' - I_{k_2}}{2 \times I_{a_2''} + a''} \right) \times 100 \]

\[ \text{Hydrolyse}_{M-5} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} - I_{k_2}}{2 \times I_{a_2''}} \right) \times 100 \]

\[ \text{Hydrolyse}_{M-6} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} - I_{k_2}}{2 \times I_{a_2''}} \right) \times 100 \]

\[ \text{Hydrolyse}_{SPE} [\text{mol\%}] = \left( \frac{2 \times I_{a_2''} - k_2}{2 \times I_{a_2''}} \right) \times 100 \]
\[ \text{Hydrolyse}_{SPP} \text{ [mol %]} = \left( \frac{2 \cdot I_{a_2''} - I_{k_2}}{2 \cdot I_{a_2''}} \right) \times 100 \]

The Index 2 in e.g. \( I_{e_2} \) indicates the hydrolysis product of the ester/amid product, while no index e.g. \( I_{a_2''} \) determines the unchanged molecule without hydrolysis. Index 3 in e.g. \( I_{e_3} \) indicates the sulfate hydrolysis product.

\[
\begin{align*}
I_{k_2}(M-1, \text{ range in ppm}) &= 4.5-4.35 \\
I_{I_{a_2''}}(M-1, \text{ range in ppm}) &= 5.4-5.1 \\
I_{k_2}(M-2, \text{ range in ppm}) &= 4.3-4.1 \\
I_{I_{a_2''}}(M-2, \text{ range in ppm}) &= 5.4-5.3 \\
I_{k_2}(M-3, \text{ range in ppm}) &= 4.6-4.4 \\
I_{I_{a_2''}}(M-3, \text{ range in ppm}) &= 5.6-5.4 \\
I_{k_2}(M-4, \text{ range in ppm}) &= 4.3-4.0 \\
I_{I_{a_2''}}(M-4, \text{ range in ppm}) &= 5.6-5.3 \\
I_{k_2}(M-5, \text{ range in ppm}) &= 3.9-3.6 \\
I_{I_{a_2''}}(M-5, \text{ range in ppm}) &= 6.1-5.8 \\
I_{I_{a_2''}}(M-6, \text{ range in ppm}) &= 6.1-5.8 \\
I_{k_2}(M-6, \text{ range in ppm}) &= \text{no decomposition} \\
I_{I_{a_2''}}(SPE, \text{ range in ppm}) &= 5.4-5.3 \\
I_{k_2}(SPE, \text{ range in ppm}) &= \text{no decomposition} \\
I_{I_{a_2''}}(SPP, \text{ range in ppm}) &= 5.5-5.3 \\
I_{k_2}(SPP, \text{ range in ppm}) &= \text{no decomposition}
\end{align*}
\]
Figure S 61  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of OEGMA in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 62  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of SPE in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S63  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of SPP in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 64  
$^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-1 in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 65  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-2 in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 66  
$^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-3 in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 67  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-4 in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 68  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-5 in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
Figure S 69  $^1$H-NMR spectrum showing the degradation of 0.1 M solution of M-6 in sodium hydroxid in D$_2$O (pH = 14) at room temperature over time.
3.1. 2D-Spektra (¹H-¹H-COSY) - Monomer hydrolysis pH=14

Figure S 70 ¹H-¹H-COSY NMR spectra of 0.1 M solution of SPE sodium hydroxide in D₂O (pH = 14), after 124 days.

Figure S 71 ¹H-¹H-COSY NMR spectra of 0.1 M solution of SPP sodium hydroxide in D₂O (pH = 14), after 124 days.
Figure S 72  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of M-1 sodium hydroxide in D$_2$O (pH = 14), after 124 days.

Figure S 73  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of M-2 sodium hydroxide in D$_2$O (pH = 14), after 124 days.
Figure S74  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of $\text{M-3}$ sodium hydroxide in $\text{D}_2\text{O}$ (pH = 14), after 124 days.

Figure S75  $^1$H-$^1$H-COSY NMR spectra of 0.1 M solution of $\text{M-4}$ sodium hydroxide in $\text{D}_2\text{O}$ (pH = 14), after 124 days.
Figure S 76  $^1$$^1$H-$$^1$H-COSY NMR spectra of 0.1 M solution of M-5 sodium hydroxide in D$_2$O (pH = 14), after 124 days.

Figure S 77  $^1$$^1$H-$$^1$H-COSY NMR spectra of 0.1 M solution of M-6 sodium hydroxide in D$_2$O (pH = 14), after 124 days.
4.5. Polymer hydrolysis in phosphate buffered saline (pH = 7.4)

Figure S 78  $^1$H-NMR spectrum showing the degradation of P-OEGMA in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 79  $^1$H-NMR spectrum showing the degradation of P-SPE and P-SPP in phosphate buffered saline (PBS) in D$_2$O (pH = 7.4) at room temperature over time.
Figure S 80  $^1$H-NMR spectrum showing the degradation of P-1 and P-2 in phosphate buffered saline (PBS) in D$_2$O saturated with sodium chloride (pH = 7.4) at room temperature over time.
Figure S 81  $^1$H-NMR spectrum showing the degradation of P-3 and P-4 in phosphate buffered saline (PBS) in D$_2$O saturated with sodium chloride (pH = 7.4) at room temperature over time.
4.6. Polymer hydrolysis in 1 M hydrochloric acid pH=0

![Graph showing the evolution of sulfate and sulfonate hydrolysis of polymers in 1 M hydrochloric acid in D$_2$O (pH=0).](Image)

Figure S 82  Evolution of sulfate and sulfonate hydrolysis of polymers in 1 M hydrochloric acid in D$_2$O (pH=0): ($\square$) = SPE, (*) = SPP, (□) = M1, (□) = M2, (+) = M3, (X) = M4, (□) = M5, (□) = M6.

Calculation of hydrolysis in mol %:

- $Hydrolyse_{M-1}$ [mol %] = \[
\frac{[I_{k_3} + e_3] - 2 \cdot I_{a_2}'}{2 + [I_{k_3} + e_3] - 2 \cdot I_{a_2}'} \times 100
\]

- $Hydrolyse_{M-2}$ [mol %] = \[
\frac{I_{j_3} \times 100}{I_{j_2} + I_{j_3}}
\]

- $Hydrolyse_{M-3}$ [mol %] = \[
\frac{I_{k_3} \times 100}{I_{k} + I_{k_3}}
\]

- $Hydrolyse_{M-4}$ [mol %] = \[
\frac{I_{i_3} \times 100}{I_{i} + I_{i_3}}
\]

- $Hydrolyse_{M-5}$ [mol %] = \[
\frac{I_{k_3} \times 100}{I_{k} + I_{k_3}}
\]

- $Hydrolyse_{M-6}$ [mol %] = \[
\frac{I_{j_3} \times 100}{I_{j_2} + I_{j_3}}
\]

- $Hydrolyse_{SPE}$ [mol %] = \[
\frac{I_{k_3} \times 100}{I_{k} + I_{k_3}}
\]

- $Hydrolyse_{SPP}$ [mol %] = \[
\frac{I_{k_3} \times 100}{I_{k} + I_{k_3}}
\]

The Index 2 in e.g. $I_{e_2}$ indicates the hydrolysis product of the ester/amid product, while no index e.g. $I_{a''}$ determines the unchanged molecule without hydrolysis.
$I_{k_3+e_3}(M-1, \text{ range in ppm}) = 4.6-4.4$

$I_{a'_3}(M-1, \text{ range in ppm}) = 6.1-6.2$

$I_{g+i}(M-1, \text{ range in ppm}) = 4.2-4.0$

$I_{j_2}(M-2, \text{ range in ppm}) = 2.2-2.0$

$I_{j_2}(M-2, \text{ range in ppm}) = 2.4-2.2$

$I_{k_3}(M-3, \text{ range in ppm}) = 4.2-3.9$

$I_{k}(M-3, \text{ range in ppm}) = 4.6-4.3$

$I_{k_3}(M-4, \text{ range in ppm}) = 3.8-3.6$

$I_{k}(M-4, \text{ range in ppm}) = 4.3-4.0$

$I_{e_3}(M-5, \text{ range in ppm}) = 3.6-3.4$

$I_{i}(M-5, \text{ range in ppm}) = 3.9-3.6$

$I_{j_3}(M-6, \text{ range in ppm}) = 2.2-2.0$

$I_{j}(M-6, \text{ range in ppm}) = 2.4-2.2$

$I_{k_3}(SPE, \text{ range in ppm}) = \text{no signal}$

$I_{k+k_2}(SPE, \text{ range in ppm}) = 3.1-2.9$

$I_{k_3}(SPP, \text{ range in ppm}) = \text{no signal}$

$I_{k}(SPP, \text{ range in ppm}) = 3.1-2.9$
Figure S 83  $^1$H-NMR spectrum showing the degradation of P-OEGMA in 1 M hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 84 $^1$H-NMR spectrum showing the degradation of **P-SPE** in 1 M hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 85  $^1$H-NMR spectrum showing the degradation of P-SPP in 1 M hydrochloric acid in D$_2$O (pH = 0) at room temperature over time.
Figure S 86  $^1$H-NMR spectrum showing the degradation of P-1 in 1 M hydrochloric acid in D$_2$O (pH = 0) saturated with sodium chloride at room temperature over time.
Figure S 87  $^1$H-NMR spectrum showing the degradation of P-2 in 1 M hydrochloric acid in D$_2$O (pH = 0) saturated with sodium chloride at room temperature over time.
Figure S88  $^1$H-NMR spectrum showing the degradation of P-3 in 1 M hydrochloric acid in D$_2$O (pH = 0) saturated with sodium chloride at room temperature over time.
Figure S 89  $^1$H-NMR spectrum showing the degradation of P-4 in 1 M hydrochloric acid in D$_2$O (pH = 0) saturated with sodium chloride at room temperature over time.
Figure S 90  \(^1\)H-NMR spectrum showing the degradation of P-6 in 1 M hydrochloric acid in D\(_2\)O (pH = 0) saturated with sodium chloride at room temperature over time.
Figure S 91 \(^1\)H-NMR spectrum showing the degradation of **P-OEGMA** and **P-SPP** in carbonate buffer in (pH = 10) at room temperature over time.
Figure S 92  $^1$H-NMR spectrum showing the degradation of P-1 and P-2 in carbonate buffer in D$_2$O saturated with sodium chloride (pH = 10) at room temperature over time.
Figure S 93  $^1$H-NMR spectrum showing the degradation of P-3 and P-4 in carbonate buffer in D$_2$O saturated with sodium chloride (pH = 10) at room temperature over time.
Figure S 94  \(^1\)H-NMR spectrum showing the degradation of **P-1** and **P-2** in carbonate buffer in D\(_2\)O (pH = 10) (in case of P-6 saturated with sodium chloride) at room temperature over time.
4.8. Polymer hydrolysis in 1 M sodium hydroxide solution (pH=14)

Figure S 95 $^1$H-NMR spectrum showing the degradation of P-OEGMA in sodium hydroxide in D$_2$O (pH = 14) at room temperature over time.
Figure S 96  $^1$H-NMR spectrum showing the degradation of P-SPE in sodium hydroxide in D$_2$O (pH = 14) at room temperature over time.
Figure S 97 $^1$H-NMR spectrum showing the degradation of P-SPP in sodium hydroxide in D$_2$O (pH = 14) at room temperature over time.
Figure S 98 $^{1}$H-NMR spectrum showing the degradation of P-1 in sodium hydroxide in D$_2$O saturated with sodium chloride (pH = 14) at room temperature over time.
Figure S99  \(^1\)H-NMR spectrum showing the degradation of P-2 in sodium hydroxide in D\(_2\)O saturated with sodium chloride (pH = 14) at room temperature over time.
Figure S 100  $^1$H-NMR spectrum showing the degradation of P-3 in sodium hydroxide in D$_2$O saturated with sodium chloride (pH = 14) at room temperature over time.
Figure S101 ¹H-NMR spectrum showing the degradation of P-4 in sodium hydroxide in D₂O saturated with sodium chloride (pH = 14) at room temperature over time.
Figure S 102 ¹H-NMR spectrum showing the degradation of P-6 in sodium hydroxide in D₂O saturated with sodium chloride (pH = 14) at room temperature over time.