Electronic supporting information

Enhanced hydrolytic degradation of heterografted polyglycidols: Phosphonoethylated monoester – and polycaprolactone grafts

Jens Köhler,[a] Fabian Marquardt,[a] Michael Teske,[b] Helmut Keul,[a,] Katrin Sternberg [b,*] and Martin Möller [a,*]*

[a] Institute of Technical and Macromolecular Chemistry, RWTH Aachen University and Interactive Materials Research - DWI at RWTH Aachen e.V., Forckenbeckstr. 50, D-52056 Aachen, Germany.

[b] Institute for Biomedical Engineering, University of Rostock, Friedrich-Barnewitz-Straße 4, D-18119 Rostock, Germany

* Correspondence to:

H. Keul, Email: keul@dwi.rwth-aachen.de

K. Sternberg, Email: katrin.sternberg@uni-rostock.de

M. Möller, Email: moeller@dwi.rwth-aachen.de

Synthesis of polyglycidol, PG_{26} (2)

Table S1. Ratio of monomer to initiator adjusted in the feed, degree of polymerization (P_n) and molecular weight (M_n) determined by end group analysis (^{1}H NMR) and SEC data of linear $P(EEGE)_{26}$ **(1)** and PG_{26} **(2)**.

Polymer	[EEGE]/[3-PP][a]	$P_{n,\,NMR}$ [b]	$M_{n,\,NMR}$ [b] (g/mol)	$M_{n,\,SEC}$ [c] (g/mol)	M_w/M_n [c]	Yield / %
$P(EEGE)_{26}$ (1)	24	26	3801	2900	1.2	100
PG_{26} (2)	---	26	1926	2500	1.2	78

[a] Ratio of ethoxy ethyl glycidyl ether (EEGE) to 3-phenyl-1-propanol (3-PP), which was used as initiator. [b] Degree of polymerization (P_n) and molecular weight ($M_{n,NMR}$) calculated from ^{1}H NMR. The accuracy of integration in ^{1}H NMR spectra is ± 5 %. [c] Number average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) determined by size exclusion chromatography (SEC) in THF as eluent for P(EEGE) **(1)** and DMF as eluent for PG **(2)**. Narrow distributed poly(methyl methacrylate) standards were used for calibration.

Synthesis of $P(G^{DEPE}_x$-*co*-$G_y)$

Table S2. Synthesis of $P(G^{DEPE}_x$-*co*-$G_y)$ **(3a-c)** (t = 66 h, T = rt): Reagent ratios and yields.

Polymer	PG_{26} (2) / g, (mmol OH)	KO^tBu / [a] mL, (mmol)	DEVP / g, (mmol)	[DEVP]/[OH] x, (%) [b]	Yield / [c] %
$P(G^{DEPE}_4$-*co*-$G_{22})$ (3a)	4.812, (64.957)	0.81, (0.81)	2.050, (12.490)	5, (19)	86
$P(G^{DEPE}_{10}$-*co*-$G_{16})$ (3b)	4.866, (65.686)	1.64, (1.64)	4.147, (25.265)	10, (38)	81
$P(G^{DEPE}_9$-*co*-$G_{17})$ (3c)	4.233, (57.143)	1.43, (1.43)	3.607, (21.975)	10, (38)	91

[a] 1 M solution in THF. 6.5 mol% relative to the amount of DEVP. [b] Molar ratio of DEVP to hydroxyl groups of PG, which was adjusted in the feed. [c] Yield after purification by precipitation in cold pentane.

SEC analysis of the macroinitiators (2), (3a), (3b) and (3c)

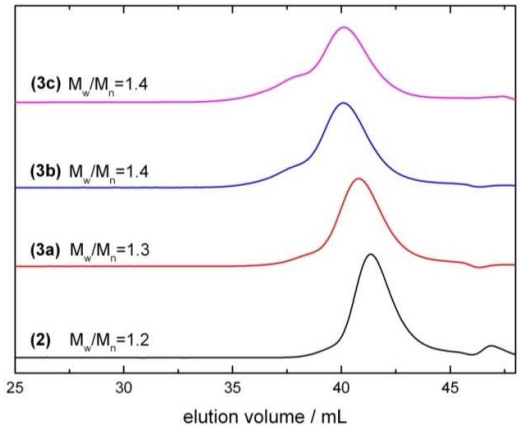

Figure S1. SEC analysis of the macroinitiators: DMF-SEC traces of PG_{26} **(2)**, $P(G^{DEPE}{}_4\text{-}co\text{-}G_{22})$ **(3a)**, $P(G^{DEPE}{}_{10}\text{-}co\text{-}G_{16})$ **(3b)** and $P(G^{DEPE}{}_9\text{-}co\text{-}G_{17})$ **(3c)**.

Chemical catalyzed grafting of εCL

^{31}P NMR analysis of the graft copolymers – Inertness of phosphonate groups

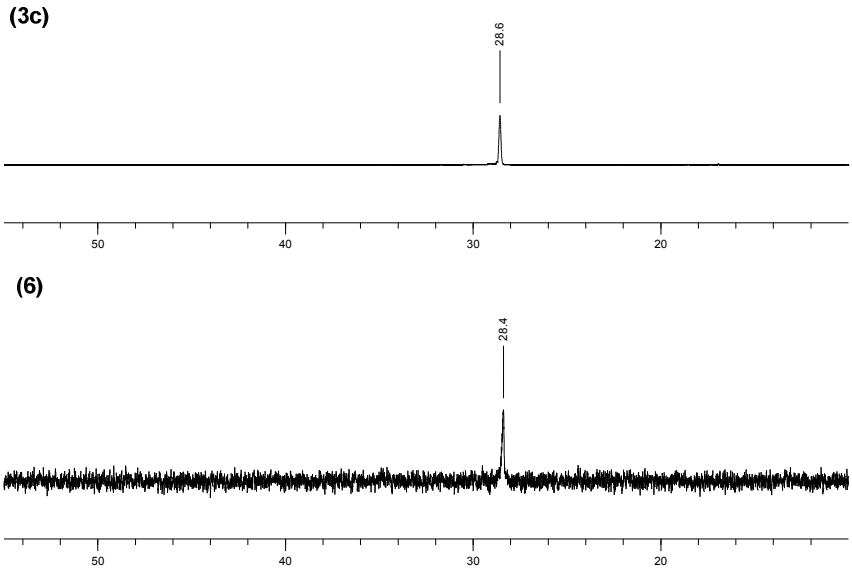

Figure S2. ^{31}P NMR spectra of $P(G^{DEPE}{}_9\text{-}co\text{-}G_{17})$ **(3c)** in DMSO-d_6 and $P(G^{DEPE}{}_9\text{-}co\text{-}(G\text{-}g\text{-}\varepsilon CL_{33})_{17})$ **(6)** in $CDCl_3$.

SEC traces of 4a and 5a prepared by chemical catalysis

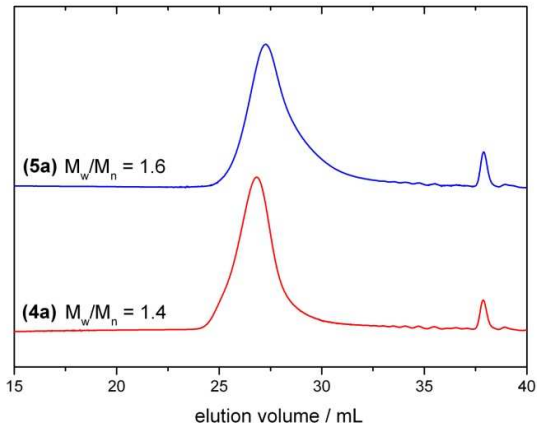

Figure S3. THF-SEC of P(G^{DEPE}_4-*co*-(G-g-εCL_8)$_{14}$-*co*-G_8) **(4a)** and P(G^{DEPE}_{10}-*co*-(G-*g*-εCL_6)$_{10}$-*co*-G_6) **(5a)**.

Monodealkylation of phosphonate functionalized graft copolymers

^{31}P spectra of DEPE and EPE containing polyglycidols (3a) and (7a)

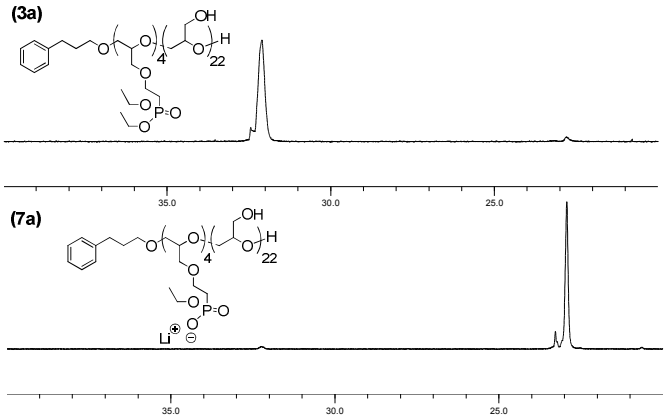

Figure S4. ^{31}P NMR spectra of P(G^{DEPE}_4-*co*-G_{22}) **(3a)** (*top*) and P(G^{EPE}_4-*co*-G_{22}) **(7a)** (*bottom*) recorded in D_2O.

^{31}P NMR spectra of DEPE and EPE containing graft copolymers (5b) and (8b)

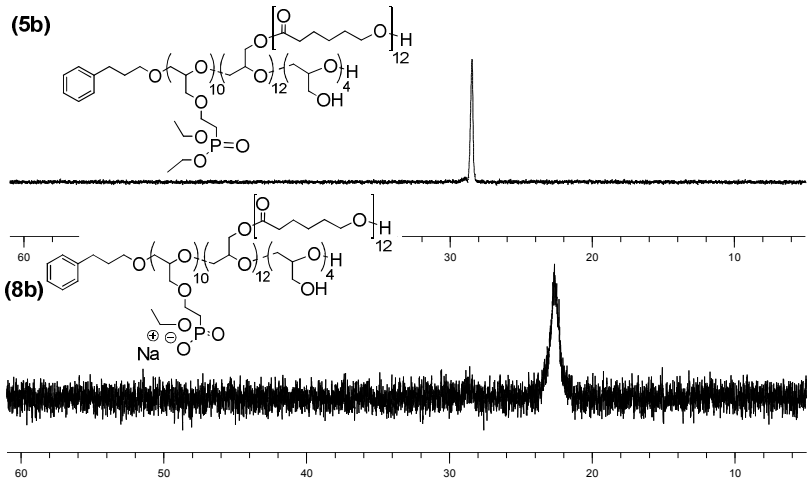

Figure S5. ^{31}P NMR spectra of P(G$^{DEPE}_{10}$-*co*-(G-*g*-εCL$_{12}$)$_{12}$-*co*-G$_4$) **(5b)** (*top*) and P(G$^{EPE}_{10}$-*co*-(G-*g*-εCL$_{12}$)$_{12}$-*co*-G$_4$) **(8b)** (*bottom*) recorded in $CDCl_3$.

SEC analysis of P(G$^{DEPE}_{10}$-*co*-(G-*g*-εCL$_{11}$)$_{12}$-*co*-G$_4$) (5b), P(G$^{DEPE}_{2}$-*co*-G$^{EPE}_{8}$-*co*-(G-*g*-εCL$_{11}$)$_{12}$-*co*-G$_4$) (8a) and P(G$^{EPE}_{10}$-*co*-(G-*g*-εCL$_{11}$)$_{12}$-*co*-G$_4$) (8b)

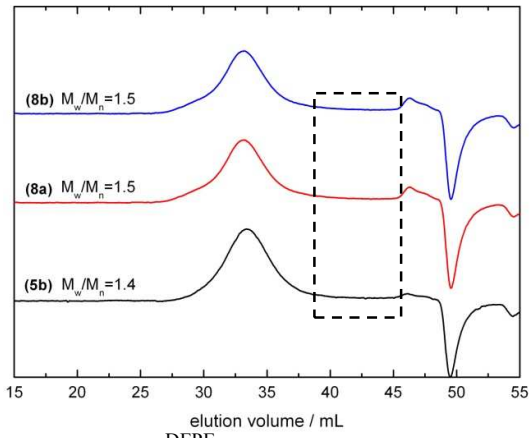

Figure S6. DMF-SEC traces of P(G$^{DEPE}_{10}$-*co*-(G-*g*-εCL$_{12}$)$_{12}$-*co*-G$_4$) **(5b)** and P(G$^{DEPE}_{2}$-*co*-G$^{EPE}_{8}$-*co*-(G-*g*-εCL$_{12}$)$_{12}$-*co*-G$_4$) **(8a)** and P(G$^{EPE}_{10}$-*co*-(G-*g*-εCL$_{12}$)$_{12}$-*co*-G$_4$) **(8b)** measured with DMF as eluent and narrow distributed poly(methyl methacrylate) standards.

^{31}P NMR spectra of prototype copolymers (6) and (9)

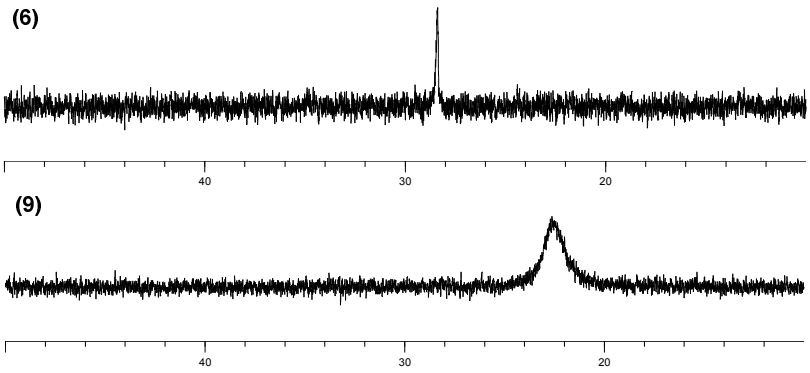

Figure S7. ^{31}P NMR spectra of P(G$^{DEPE}_{9}$-*co*-(G-*g*-εCL$_{33}$)$_{17}$) **(6)** (*top*) and P(G$^{EPE}_{10}$-*co*-(G-*g*-εCL$_{33}$)$_{17}$) **(9)** (*bottom*) recorded in $CDCl_3$.

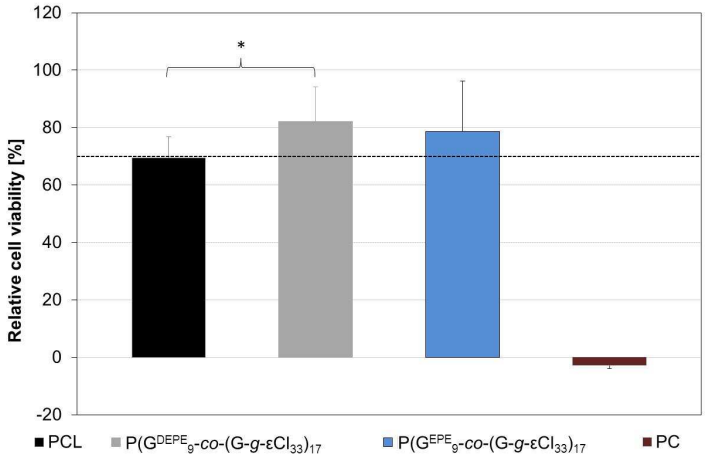

Figure S8. Relative viability of L929 fibroblasts grown on PCL, copolymer **6** and **9**. Data are presented as mean±SD, n = 8.

SEC traces of PCL reference after 0, 63 and 147 days

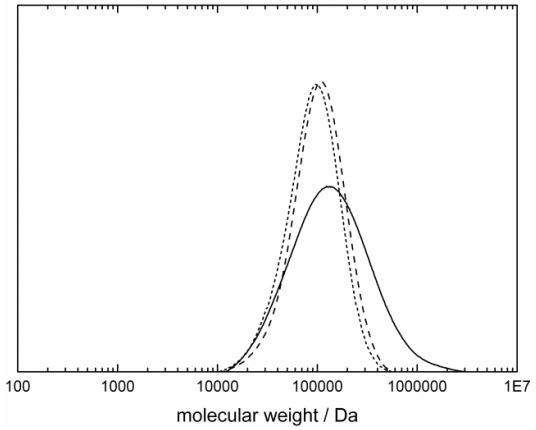

Figure S9. Molecular weight distribution of PCL in Sørensen buffer (0.1 M, pH 7.4) at 55 °C after 0 (—), 63 (···) and 147 (---) days.

DSC analysis of 6 and 9 after 0, 63 and 147 days of degradation

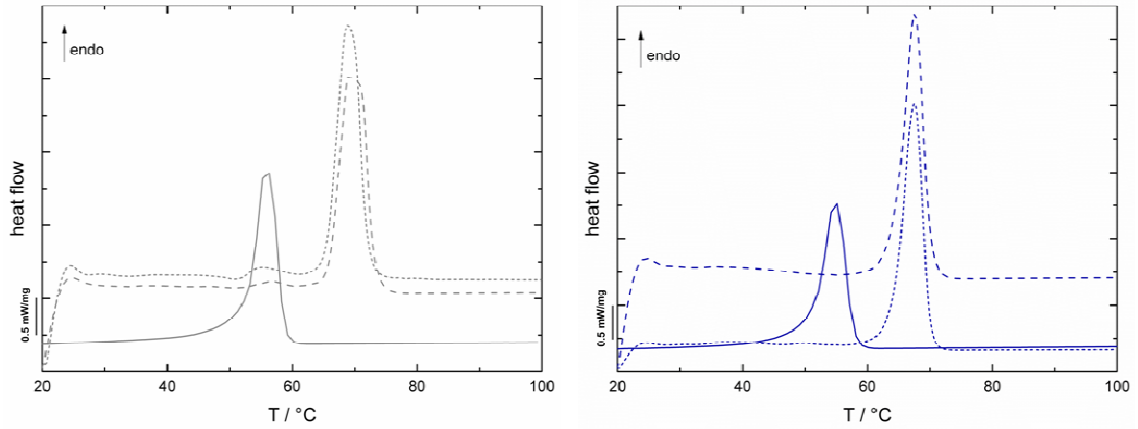

Figure S10. DSC first heating curves of P(G^{DEPE}_{9}-*co*-(G-*g*-εCL_{33})$_{17}$ **(6)** (*left*), P(G^{EPE}_{9}-*co*-(G-*g*-εCL_{33})$_{17}$ **(9)** (*right*) after 63 (···) and 147 (---) days in comparison to the second heating curve after 0 days (—) measured at a heating rate of 10 K/min.

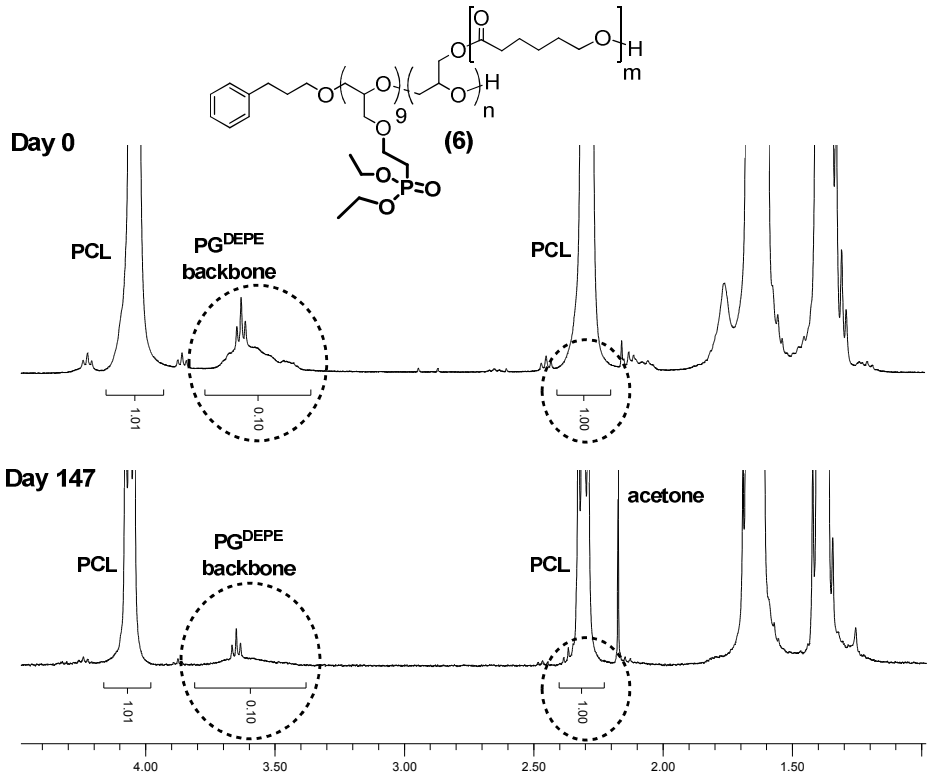

Figure S11. ^{1}H NMR spectrum of **6** after 0 days and 147 days of degradation (measured in $CDCl_3$).

The ratio of PCL-grafts to PG^{DEPE} backbone remains constant during the degradation study: [PCL]/[PG^{DEPE} backbone] = 1.00/0.10 after 0 days and 147 days, respectively.

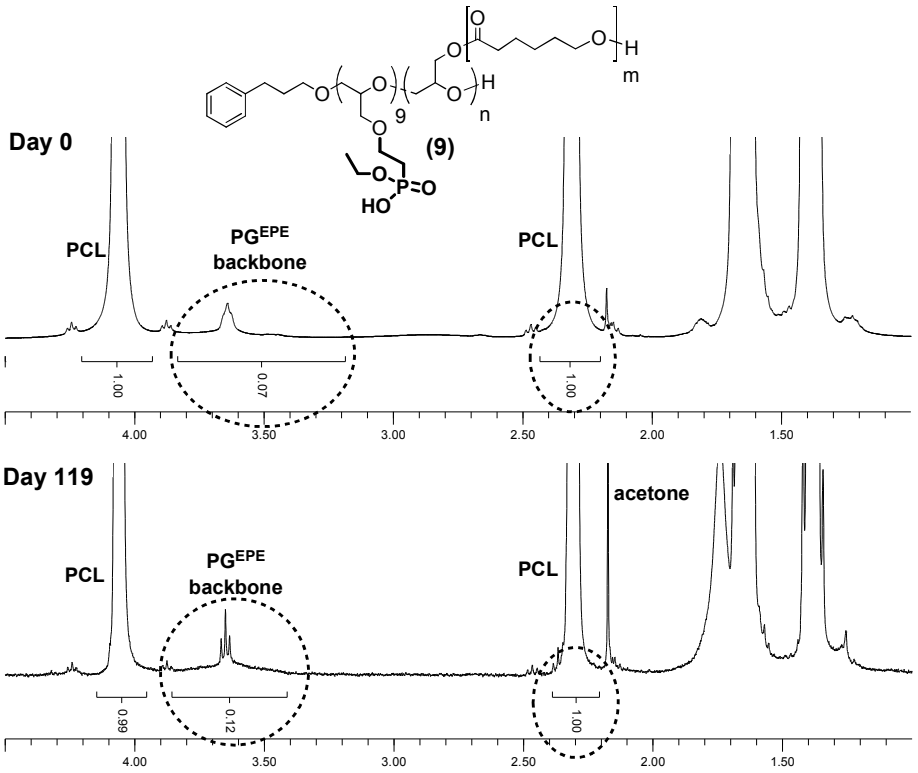

Figure S12. ^{1}H NMR spectrum of **9** after 0 days and 119 days of degradation (measured in $CDCl_3$). The ratio of PCL-grafts to PG^{DEPE} backbone decreases.

The ratio of PCL-grafts to PG^{EPE} backbone changes during the degradation study: [PCL]/[PG^{EPE} backbone] = 1.00/0.07 (0 days) and 1.00/0.12 (119 days).

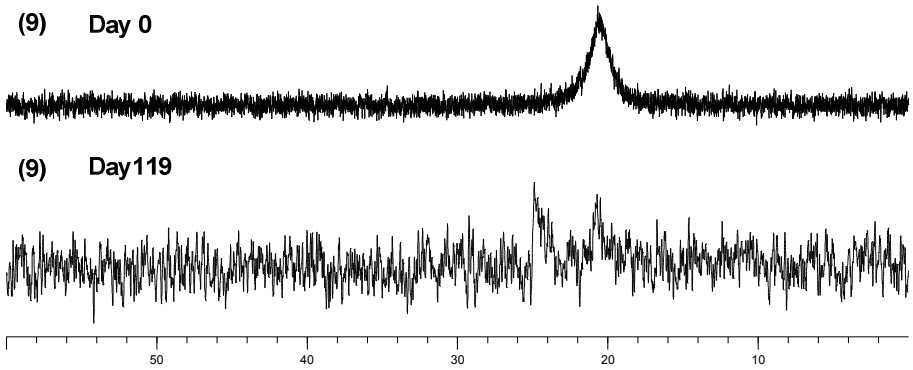

Figure S13. ^{31}P NMR spectrum of copolymer **9** after 0 days and 119 days of degradation (measured in DMSO-d_6).