Supporting Information for

Poly(ethylene glycol-*co*-allyl glycidyl ether)s: A PEG-based modular synthetic platform for multiple bioconjugation

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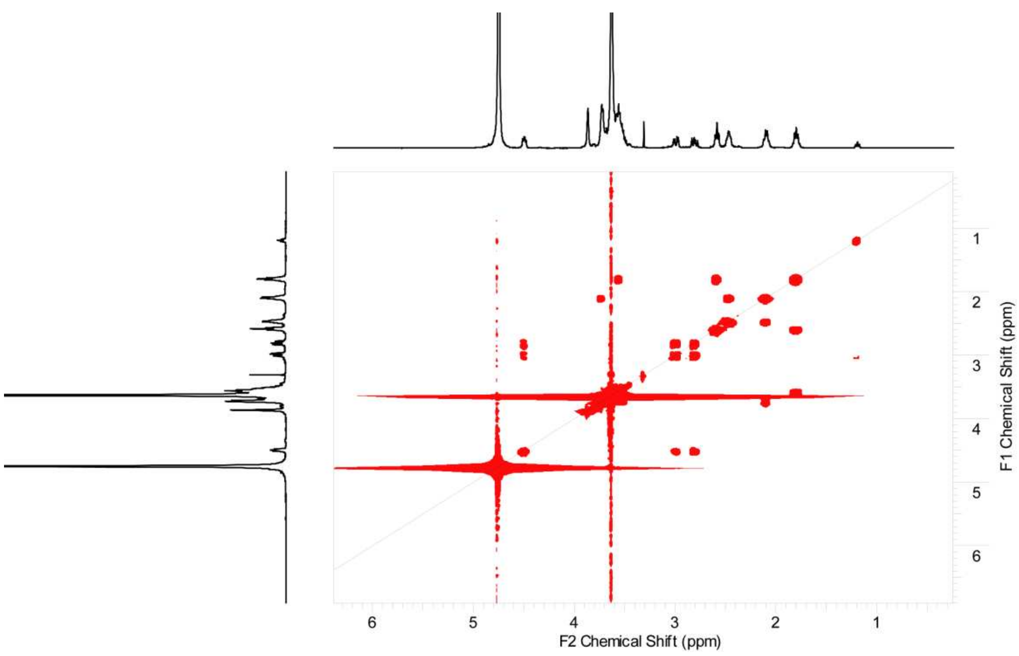
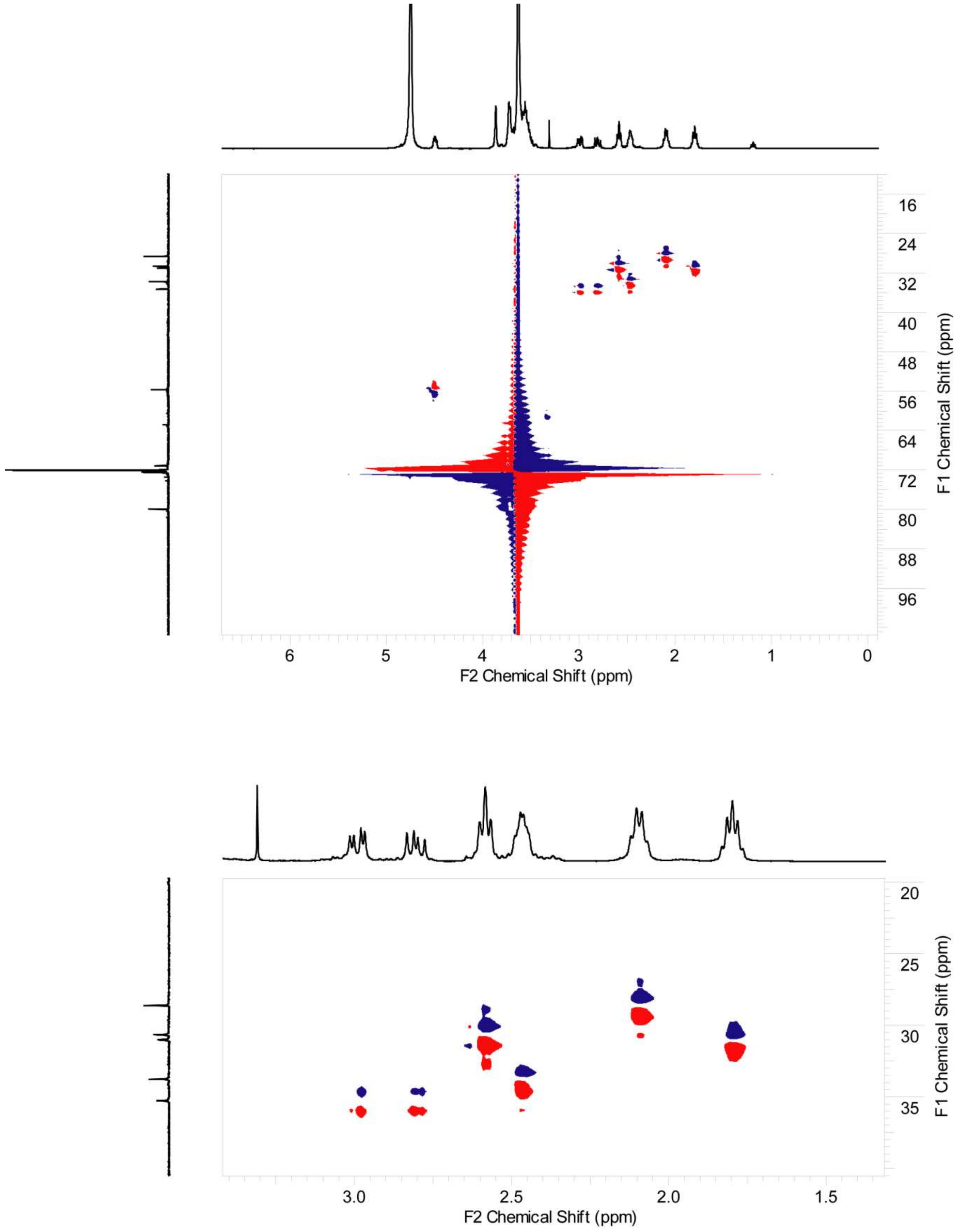
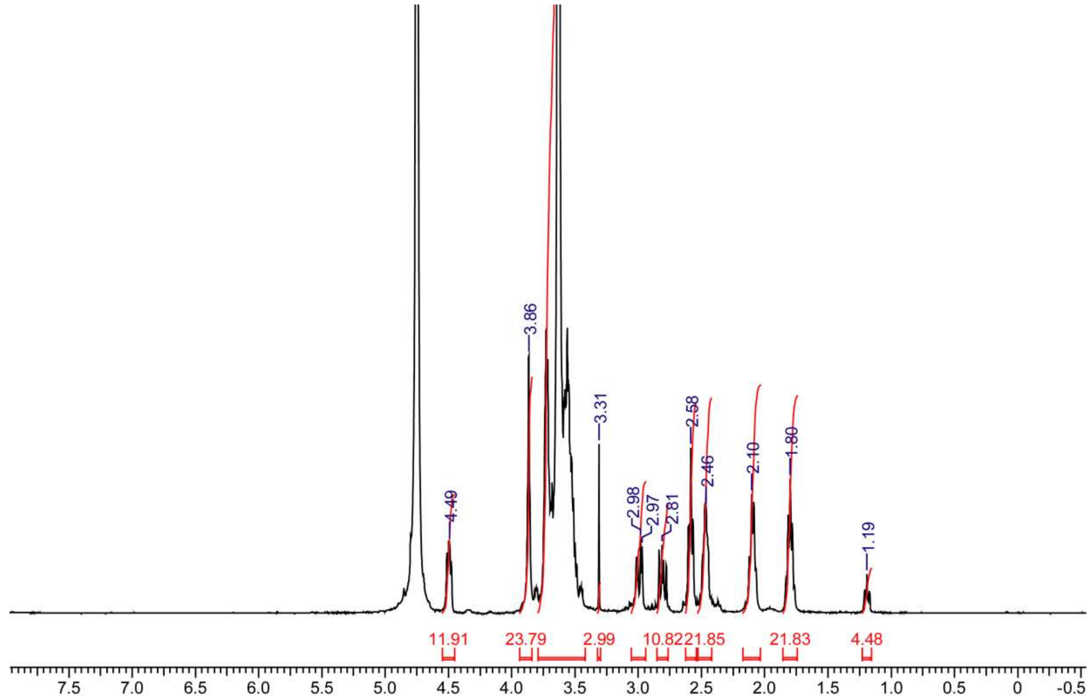


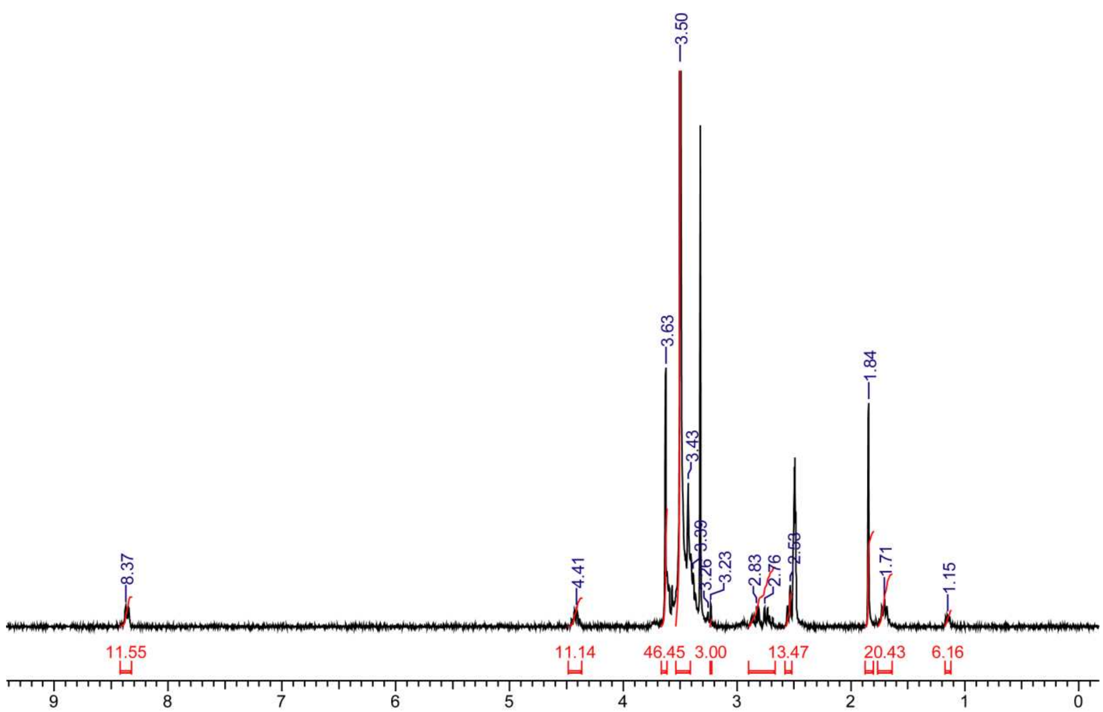
SF 01. COSY spectrum (400 MHz, D_2O) of coupling product of L-glutathione and P(EO_{90}-*co*-AGE_{11}).



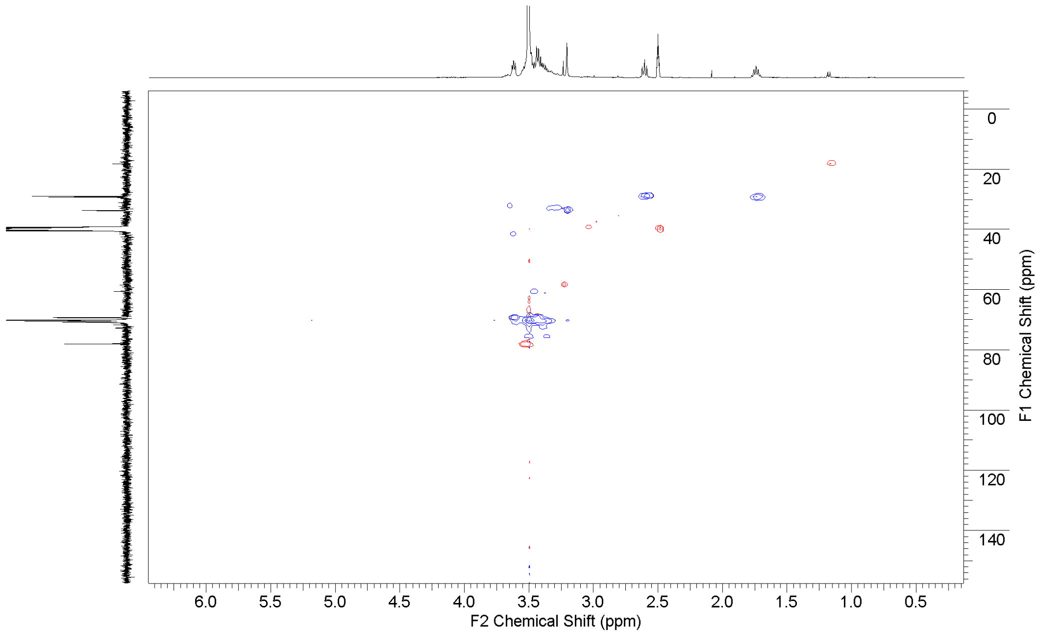
SF 02. HSQC spectrum (D_2O) of coupling product of L-glutathione and P(EO_{90}-*co*-AGE_{11}) and enhanced region below.



SF 03. ^{1}H NMR (400 MHz, D_2O) for conjugate of random P(EO_{90}-*co*-AGE_{11}) and L-glutathione.



SF 04. ^{1}H NMR (300 MHz, DMSO-*d6*) for conjugate of random P(EO_{132}-*co*-AGE_{13}) and *N*-acetyl-L-cysteine methyl ester.



SF 05. HSQC (DMSO-*d6*) of coupling product of thioglycolic acid and P P(EO_{132}-*co*-AGE_{13}).

Experimental data for functional PEG derivates.

General procedure is described in experimental part.

Glutathione conjugated random P(EO-co-AGE). L-Glutathione reduced was used as thiol reactant to obtain the PEG derivative with attached glutathione moieties. ^{1}H NMR (300 MHz, D_2O) δ = 4.51 (1H, $C\mathit{H}CH_2S$), 3.91 (2H, Gly-$C\mathit{H}_2$), 3.80-3.44 (backbone, Glu-$C\mathit{H}$, $C\mathit{H}_2OC\mathit{H}_2CH_2CH_2S$), 3.32 (s, 3H, H_3CO), 3.05-2.76 (2H, $CHC\mathit{H}_2S$), 2.59 (2H, $CHCH_2SC\mathit{H}_2$), 2.49 (2H, Glu-$C\mathit{H}_2CO$), 2.12 (2H, Glu-$CHC\mathit{H}_2$), 1.81 (2H, $OCH_2C\mathit{H}_2CH_2S$), 1.20 (3H, H_3CCHS). ^{13}C NMR (75.5 MHz, D_2O) δ = 175.52 (Glu-*C*ON, Gly-*C*OO), 173.59 (Glu-*C*OO), 172.35 (Cys-*C*ON), 77.32 ($OCH_2\mathit{C}HO$), 71.62-68.32 ($O\mathit{C}H_2\mathit{C}H_2O\mathit{C}H_2CHO$ + $OCH_2CH(\mathit{C}H_2O\mathit{C}H_2)O$), 60.17 ($OCH_2\mathit{C}H_2OH$), 57.88 ($H_3\mathit{C}OCH_2$), 53.42 (Glu-*C*H), 52.96 (Cys-*C*H), 41.87 (Gly-$\mathit{C}H_2$), 32.57 (Cys-$\mathit{C}H_2$), 31.07 (Glu-$\mathit{C}H_2CO$), 28.32 ($OCH_2\mathit{C}H_2CH_2S$), 27.97 ($OCH_2CH_2\mathit{C}H_2S$), 25.93 (Glu-$CH\mathit{C}H_2$).

Cysteine conjugated random P(EO-co-AGE). *N*-acetyl-L-cysteine methyl ester was used as thiol reactant to obtain the PEG derivative with attached cysteine moieties. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.37 (1H, CON*H*CH), 4.47-4.37 (1H, NC*H*COCH$_3$), 3.63 (3H, COOC*H*$_3$), 3.62-3.26 (backbone + C*H*$_2$OC*H*$_2$CH$_2$CH$_2$S), 3.23 (s, 3H, *H*$_3$COCH$_2$), 2.90-2.67 (m, 2H, SC*H*$_2$CH), 2.53 (2H, OCH$_2$CH$_2$C*H*$_2$S), 1.84 (3H, *H*$_3$CCON), 1.71 (2H, OCH$_2$C*H*$_2$CH$_2$S). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 171.33 (H$_3$C*C*ON), 169.35 (*C*OOCH$_3$), 77.61 (OCH$_2$*C*HO), 72.36 (O*C*H$_2$CH$_2$OH), 70.61-69.00 (O*C*H$_2$*C*H$_2$O*C*H$_2$CHO + OCH$_2$CH(*C*H$_2$O*C*H$_2$)O), 60.22 (OCH$_2$*C*H$_2$OH), 58.05 (H$_3$*C*OCH$_2$), 52.00 (COO*C*H$_3$), 32.64 (S*C*H$_2$CH), 29.19 (OCH$_2$CH$_2$*C*H$_2$S), 28.25 (OCH$_2$*C*H$_2$CH$_2$S), 22.24 (H$_3$*C*CON), 18.08 (OCH$_2$CSH*C*H$_3$).

Amino functional random P(EO-co-AGE). Cysteamin hydrochlorid was employed as thiol reactant to give the amino functional product as hydrochloride salt. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.20 ppm (3H, N*H*$_3$), 3.80-3.25 (backbone + C*H*$_2$OC*H*$_2$CH$_2$CH$_2$S), 3.23 (3H, *H*$_3$CO), 2.93 (2H, C*H*$_2$N), 2.74 (2H, OCH$_2$CH$_2$C*H*$_2$S), 2.56 (2H, SC*H*$_2$CH$_2$NH$_2$), 1.74 (2H, OCH$_2$C*H*$_2$CH$_2$S), 1.18 (OCH$_2$CSHC*H*$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 78.09-77.59 (OCH$_2$*C*HO), 72.46 (*C*H$_2$CH$_2$OH), 70.69-69.00 (O*C*H$_2$*C*H$_2$O*C*H$_2$CHO + OCH$_2$CH(*C*H$_2$O*C*H$_2$)O), 60.29 (CH$_2$*C*H$_2$OH), 58.18 (H$_3$*C*OCH$_2$CH$_2$), 38.52 (H$_2$N*C*H$_2$), 29.23 (OCH$_2$*C*H$_2$CH$_2$S), 27.94 (O*C*H$_2$CH$_2$N), 27.48 (OCH$_2$CH$_2$*C*H$_2$S).

Carboxy functional random P(EO-co-AGE). Thioglycolic acid was employed as thiol reactant to obtain the carboxy functional PEG derivative. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 3.77-3-25 (backbone + C*H*$_2$OC*H*$_2$CH$_2$CH$_2$S), 3.23 (3H, *H*$_3$CO), 3.20 (2H, SC*H*$_2$COOH), 2.60 (2H, OCH$_2$CH$_2$C*H*$_2$S), 1.73 (2H, OCH$_2$C*H*$_2$CH$_2$S), 1.17 (OCH$_2$CSHC*H*$_3$). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 171.73 (*C*OOH), 78.73-77.50 (OCH$_2$*C*HO), 72.47 (*C*H$_2$CH$_2$OH), 70.61-69.01 (O*C*H$_2$*C*H$_2$O*C*H$_2$CHO + OCH$_2$CH(*C*H$_2$O*C*H$_2$)O), 33.38 (*C*H$_2$COOH), 28.90 (OCH$_2$*C*H$_2$CH$_2$S), 28.65 (OCH$_2$CH$_2$*C*H$_2$S), 18.08 (OCH$_2$CSH*C*H$_3$).

Hydroxy functional random P(EO-co-AGE). 2-Mercaptoethanol was employed as thiol reactant to obtain the hydroxy functional PEG derivative. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 4.74 (1H, SCH_2CH_2OH), 3.80-3.25 (backbone + $CH_2OCH_2CH_2CH_2S$), 2.53 ($CH_2SCH_2CH_2OH$), 1.71 (2H, $OCH_2CH_2CH_2S$), 1.18 (2H OCH_2CSHCH_3). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 77.74 (OCH_2CHO), 72.47 (CH_2CH_2OH), 71.41 (CH_3OCH_2), 70.62-69.06 ($OCH_2CH_2OCH_2CHO$ + $OCH_2CH(CH_2OCH_2)O$), 60.69 (SCH_2CH_2OH), 60.21 (OCH_2CH_2OH), 58.17 (H_3COCH_2), 33.99 (SCH_2CH_2OH), 29.66 ($OCH_2CH_2CH_2S$), 28.21 ($OCH_2CH_2CH_2S$).

Random P(EO-co-AGE) benzamide. 100 mg of the amino functional polymer (0.127 mmol-NH_2, 1 eq) and 82 mg *N*,*N*-diisopropylethylamin (0.635 mmol, 5 eq) were dissolved in 2 mL DMF, 72 mg pentafluorophenyl benzoate (2.54 mmol, 2 eq) were added and the reaction mixture stirred at 50 °C for 16 h. Dialysis (MWCO = 1000 g/mol) against DMF and ethanol afforded the benzamide in good yields (> 70 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.84 (1H, CONH), 7.80 (2H, arom), 7.48-7.34 (3H, arom), 3.63 (2H, SCH_2CH_2N), 3.58-3.27 (backbone + $CH_2OCH_2CH_2CH_2S$), 3.25 (3H, H_3COCH_2), 2.65 (2H, $CH_2CH_2CH_2S$), 2.57 (2H, SCH_2CH_2N), 1.76 (2H, $CH_2CH_2CH_2S$). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 166.73 (NHCO), 134.81, 131.31, 128.40, 127.50 (arom), 78.91-78.13 (OCH_2CHO), 72.89 (CH_2CH_2OH), 71.15-69.4 ($OCH_2CH_2OCH_2CHO$ + $OCH_2CH(CH_2OCH_2)O$), 60.79 (CH_2CH_2OH), 58.60 ($H_3COCH_2CH_2$), 30.95 ($OCH_2CH_2CH_2S$), 29.76 ($OCH_2CH_2CH_2S$), 28.25 (SCH_2CH_2N).