Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Synthesis of original polymeric hydroperoxides as innovative oxidizing agents self-cure dental materials†

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Synthetic procedures

Determination of the $[T]_0$ for oligomers synthesis by telomerisation

The amount of 2-mercaptoethanol (2-ME) used as telogen agent (T) was calculated following the equation:

$$[T]_0 = [M]_0 / (C_T \times DP)$$

where $[T]_0$ and $[M]_0$ are the telogen and the monomers concentration at t = 0, respectively, DP is the degree of polymerization calculated depending on the targeted molecular weight and C_T the chain transfer constant who depends on the monomer and the telogen.[1, 2]

In our case, C_T had the same value for methyl methacrylate (MMA) and (4-isopropylbenzoate) 2-ethyl methacrylate (IBEMA), *i.e.* 0.67, considering that C_T has more or less the same value for the polymerization of methacrylate monomers when aliphatic thiols are used as telogen.[2-4]

Chain transfer constant:
$C_T = 0.67$

Synthesis of poly(methyl methacrylate-st-(4-(2-hydroxyperoxipropyl)benzoate) 2-ethyl methacrylate) (P(MMA-st-HPPBEMA)) oligomers in three steps

Amounts of reagents needed for the synthesis of P(MMA-st-IBEMA) oligomers by telomerization.

$P(MMA_x\text{-}st\text{-}IBEMA_y)_z$
x: molar proportion (in %) of MMA monomer in the statistical oligomer
y: molar proportion (in %) of IBEMA monomer in the statistical oligomer
z: targeted molecular weight of the statistical copolymer

Oligomer	MMA (mL)	IBEMA (g)	2-ME (µL)	AIBN (mg)	Toluene (mL)
$P(MMA_{50}\text{-}st\text{-}IBEMA_{50})_{5000}$	1.43	3.72	106	44	10
$P(MMA_{25}\text{-}st\text{-}IBEMA_{75})_{5000}$	0.58	4.52	106	36	10
$P(MMA_{50}\text{-}st\text{-}IBEMA_{50})_{2500}$	1.43	3.72	213	44	10
$P(MMA_{25}\text{-}st\text{-}IBEMA_{75})_{2500}$	0.58	4.52	213	36	10

MMA: methyl methacrylate; IBEMA: (4-isopropylbenzoate) 2-ethyl methacrylate; 2-ME: 2-mercaptoethanol; AIBN: 2,2'-azobis(2-methylpropionitrile)

Amounts of reagents needed for the synthesis of oxidized P(MMA-st-IBEMA) oligomers by oxidation reaction.

Oligomer	Corresponding P(MMA-*st*-IBEMA) (g)	MMPP (mg)	DCM/EtOH (mL)
oxidized $P(MMA_{50}\text{-}st\text{-}IBEMA_{50})_{5000}$	3	325	30
oxidized $P(MMA_{25}\text{-}st\text{-}IBEMA_{75})_{5000}$	3	325	30
oxidized $P(MMA_{50}\text{-}st\text{-}IBEMA_{50})_{2500}$	3	649	30
oxidized $P(MMA_{25}\text{-}st\text{-}IBEMA_{75})_{2500}$	3	649	30

MMPP: magnesium monoperoxyphthalate; DCM/EtOH: dichloromethane/ethanol mixture (2/1, v/v)

Amounts of reagents needed for the synthesis of P(MMA-st-HPPBEMA) oligomers by hydroperoxidation reaction.

Oligomer	Corresponding oxidized P(MMA-*st*-IBEMA) (g)	NHPI (mg)	AIBN (mg)	Acetonitrile (mL)
$P(MMA_{50}\text{-}st\text{-}HPPBEMA_{50})_{5000}$	2.35	50	60	25
$P(MMA_{25}\text{-}st\text{-}HPPBEMA_{75})_{5000}$	2.35	60	73	25
$P(MMA_{50}\text{-}st\text{-}HPPBEMA_{50})_{2500}$	2.35	49	60	25
$P(MMA_{25}\text{-}st\text{-}HPPBEMA_{75})_{2500}$	2.35	60	72	25

NHPI: N-hydroxyphthalimide; AIBN: 2,2′-azobis(2-methylpropionitrile)

General procedure for MMA and IBEMA reactivity ratios determination using Jaacks method

Reactivity ratios corresponding to the copolymerization of methyl methacrylate (MMA, M_1) and (4-isopropylbenzoate) 2-ethyl methacrylate (IBEMA, M_2) were determined following Jaacks method.[5] For such purpose, two free radical polymerization of MMA and IBEMA were carried out, each one with an excess of one monomer. The [Monomer]/[AIBN] molar ratio was equal to 100. The [MMA]/[IBEMA] molar ratio depended on the reactivity ratio determination. The [MMA]/[IBEMA] molar ratio was equal to 4 for r_{MMA} determination, and equal to 0.25 for r_{IBEMA} determination.

Determination of r_{MMA} (excess of MMA):
MMA (1.26 mL, 11.80 mmol), IBEMA (817 mg, 2.96×10^{-3} mmol), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (24 mg, 0.15×10^{-3} mmol) were dissolved in toluene (8 mL) in a Schlenk tube under nitrogen. The mixture was degassed by three freeze-pump-thaw cycles and then heated at 70 °C under nitrogen in a thermostated oil bath. In order to determine the evolution of the conversion of each monomer, samples were taken at specific different times: 5, 15, 30, 60, 90, 120, 180 and 240 minutes.

Determination of r_{IBEMA} (excess of IBEMA):
MMA (0.177 mL, 1.66×10^{-3} mmol), IBEMA (1.834 g, 6.64 mmol), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (14 mg, 0.085×10^{-3} mmol) were dissolved in toluene (8 mL) in a Schlenk tube under nitrogen. The mixture was degassed by three freeze-pump-thaw cycles and then heated at 70 °C under nitrogen in a thermostated oil bath. In order to determine the evolution of the conversion of each monomer, samples were taken at specific different times: 5, 15, 30, 60, 90, 120, 180 and 240 minutes.

Using the rate of conversion of each monomer, the curves $f\left(ln\frac{[M2]}{[M2]_0}\right) = ln\frac{[M1]}{[M1]_0}$ (for r_{MMA} determination) and $f\left(ln\frac{[M1]}{[M1]_0}\right) = ln\frac{[M2]}{[M2]_0}$ (for r_{IBEMA} determination) were plotted, and the fitting of these curves finally gave the reactivity ratio of each monomer (where M_1 is MMA and M_2 is IBEMA). Indeed, by using an excess of one monomer over the other, the Lewis & Mayo equation ($\frac{d[M1]}{d[M2]} = \frac{[M1](r1[M1]+[M2])}{[M2](r2[M2]+[M1])}$) can be simplified by neglecting the [M_1] or [M_2] concentration. The equation then becomes $\frac{d[M1]}{[M1]} = r1\frac{d[M2]}{[M2]}$ and $\frac{d[M2]}{[M2]} = r2\frac{d[M1]}{[M1]}$ by neglecting [M_2] and [M_1], respectively. Finally, the integrations $\int_{[M1]0}^{[M1]}\frac{d[M1]}{[M1]} = r1\int_{[M2]0}^{[M2]}\frac{d[M2]}{[M2]}$ and $\int_{[M2]0}^{[M2]}\frac{d[M2]}{[M2]} = r2\int_{[M1]0}^{[M1]}\frac{d[M1]}{[M1]}$ allowed us determining the reactivity ratios, as the equations can be simplified by $r1\left(ln\frac{[M2]}{[M2]_0}\right) = ln\frac{[M1]}{[M1]_0}$ (Fig. S1) and $r2\left(ln\frac{[M1]}{[M1]_0}\right) = ln\frac{[M2]}{[M2]_0}$ (Fig. S2).

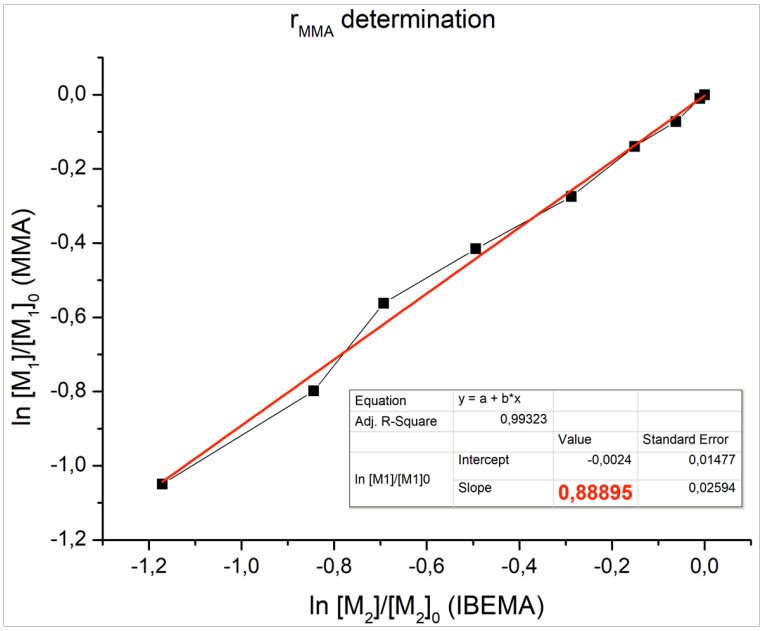

Fig. S1 MMA reactivity ratio determination using Jaacks method: r_{MMA} x $\ln([M_2]/[M_2]_0)=\ln([M_1]/[M_1]_0)$ (M_1 and M_2 are MMA and IBEMA, respectively).

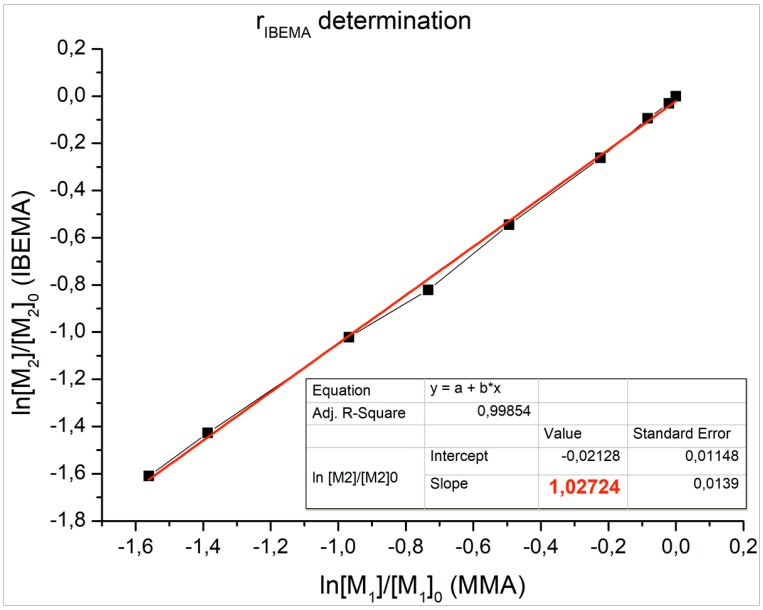

Fig. S2 IBEMA reactivity ratio determination using Jaacks method: r_{IBEMA} x $\ln([M_1]/[M_1]_0)=\ln([M_2]/[M_2]_0)$ (M_1 and M_2 are MMA and IBEMA, respectively).

Characterizations of synthesized monomer, model molecules and oligomers

Characterization of the (4-isopropylbenzoate) 2-ethyl methacrylate (IBEMA) monomer

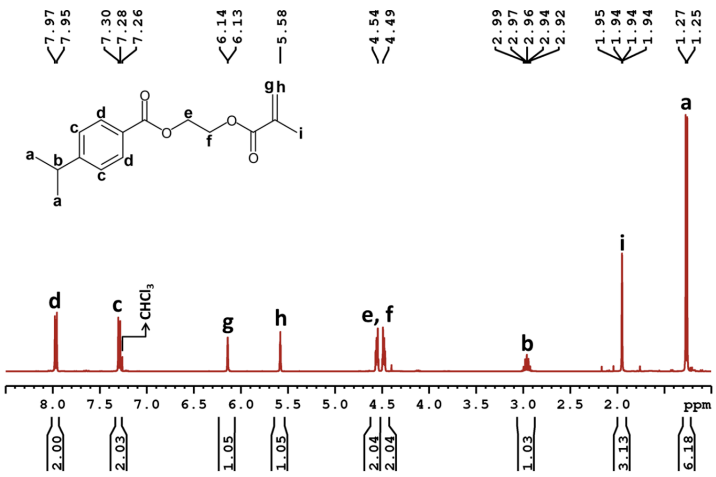

Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for the IBEMA monomer.

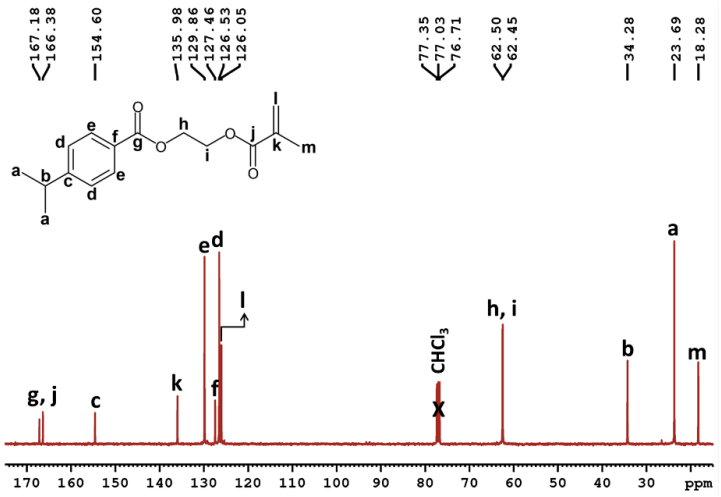

Fig. S4 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for the IBEMA monomer.

Characterization of the poly((4-isopropylbenzoate) 2-ethyl methacrylate) ($PIBEMA_{2500}$) oligomer ($M_{n\ targ}$ = 2500 g.mol^{-1})

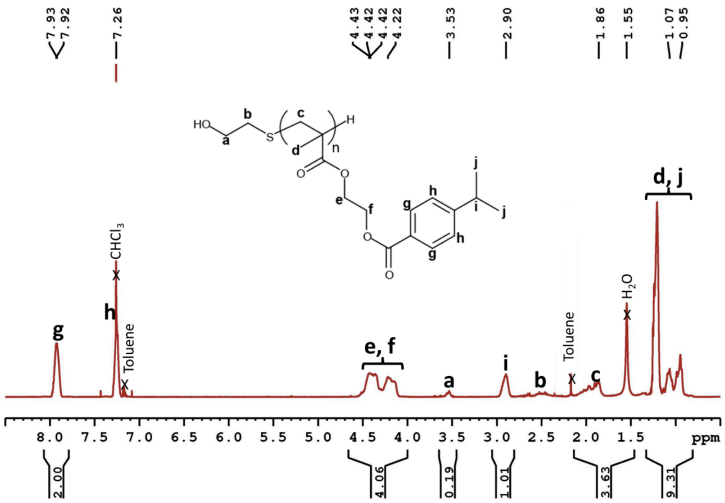

Fig. S5 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum, and proton assignments for $PIBEMA_{2500}$ oligomer.

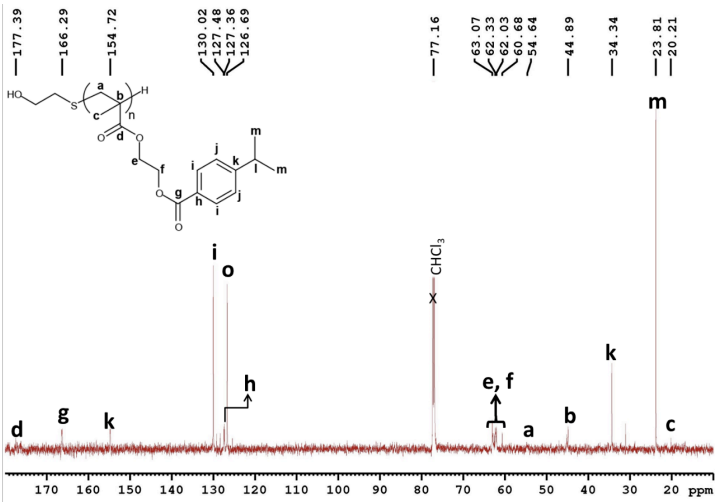

Fig. S6 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for $PIBEMA_{2500}$ oligomers

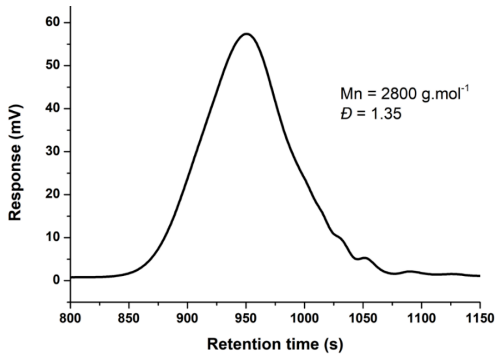

Fig. S7 Size exclusion chromatogram of $PIBEMA_{2500}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{5000}$ oligomer*

[MMA]/[IBEMA] = 50/50 (mol %/ mol %), $M_{n\ targ}$ = 5000 g.mol^{-1}

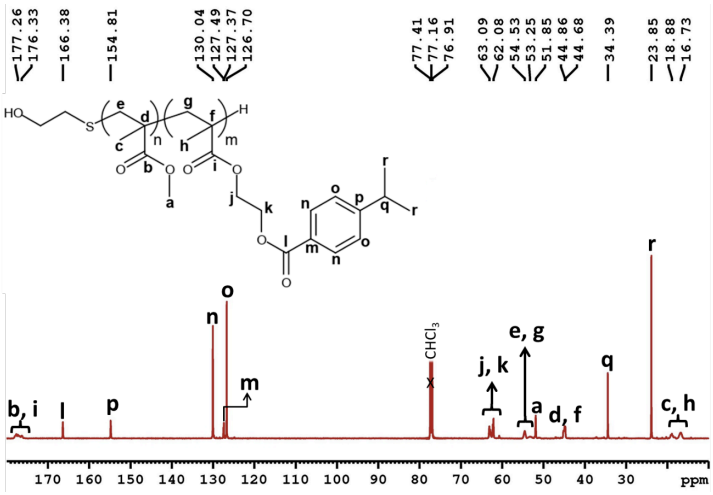

Fig. S8 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{5000}$ oligomer.

*Characterization of the poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{5000}$ oligomer*

[MMA]/[IBEMA] = 25/75 (mol %/ mol %), $M_{n\ targ}$ = 5000 g.mol^{-1}

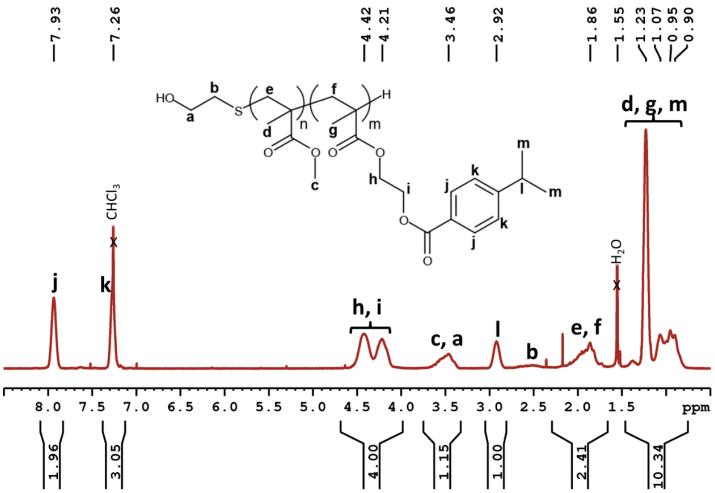

Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{5000}$ oligomer.

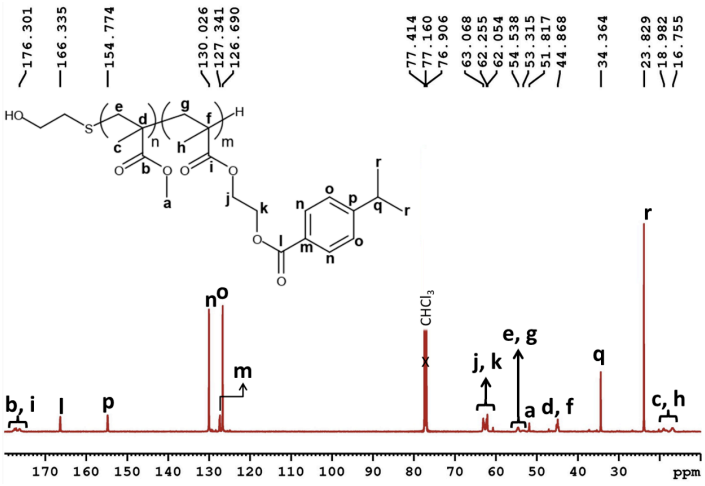

Fig. S10 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{5000}$ oligomer.

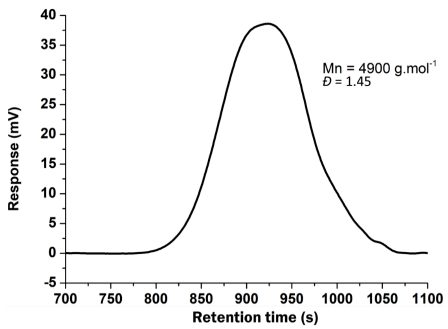

Fig. S11 Size exclusion chromatogram of P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{5000}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{2500}$ oligomer*

[MMA]/[IBEMA] = 50/50 (mol %/ mol %), $M_{n\ targ}$ = 2500 g.mol^{-1}

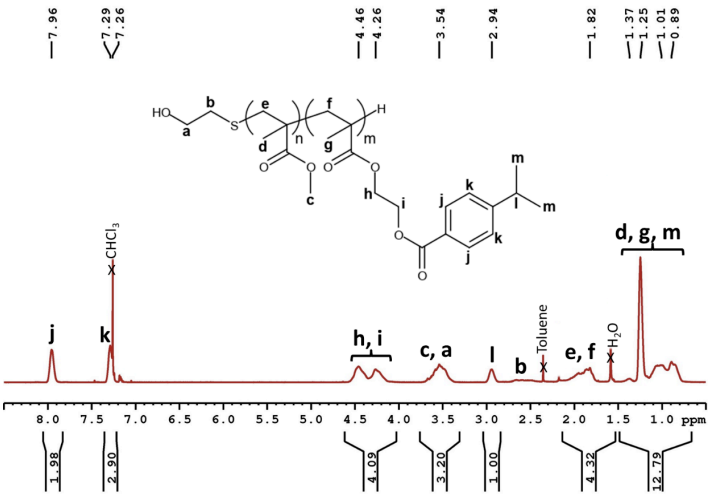

Fig. S12 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum, and proton assignments for P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{2500}$ oligomer.

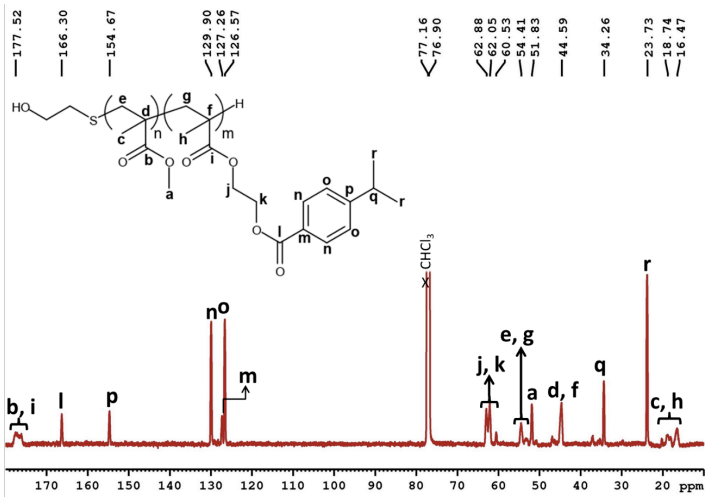

Fig. S13 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{2500}$ oligomer.

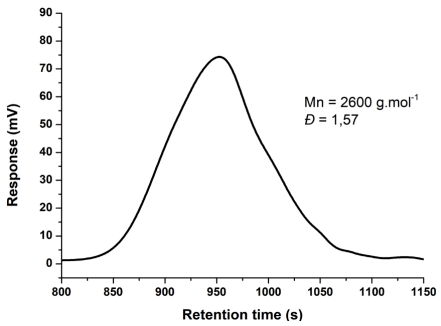

Fig. S14 Size exclusion chromatogram of P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{2500}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{2500}$ oligomer*

[MMA]/[IBEMA] = 25/75 (mol %/ mol %), $M_{n\ targ}$ = 2500 g.mol^{-1}

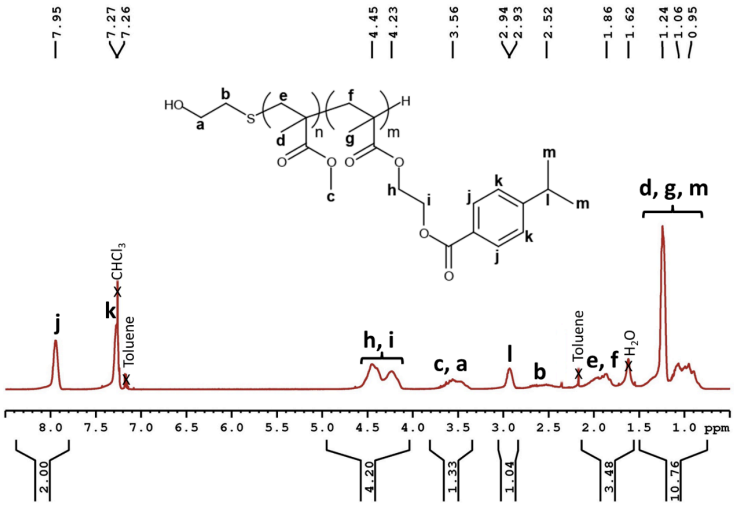

Fig. S15 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum, and proton assignments for P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{2500}$ oligomer.

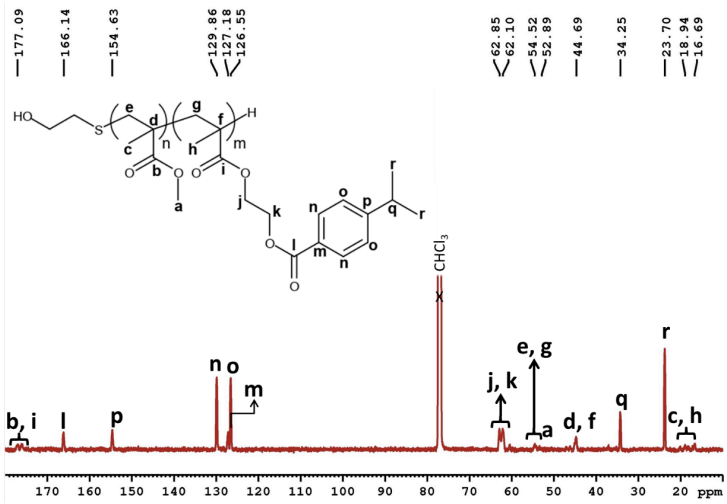

Fig. S16 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{2500}$ oligomer.

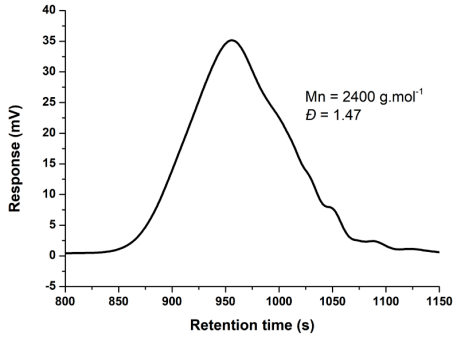

Fig. S17 Size exclusion chromatogram of P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{2500}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

Characterization of oxidized poly((4-isopropylbenzoate) 2-ethyl methacrylate) (oxidized PIBEMA$_{2500}$) oligomer ($M_{n\ targ}$ = 2500 g.mol^{-1})

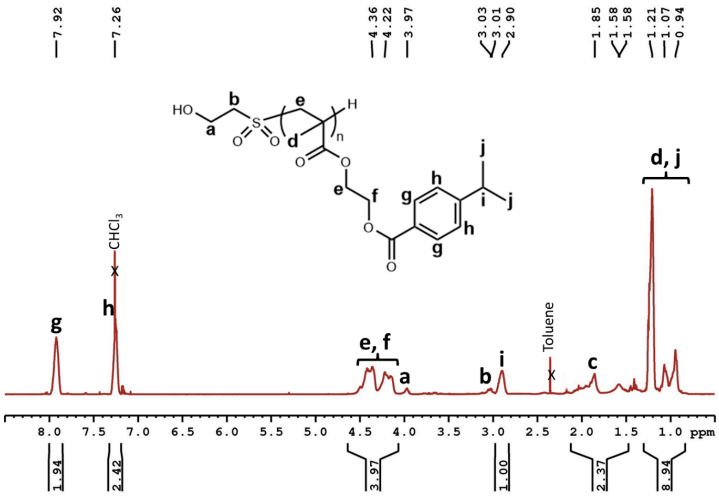

Fig. S18 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for oxidized PIBEMA$_{2500}$ oligomer.

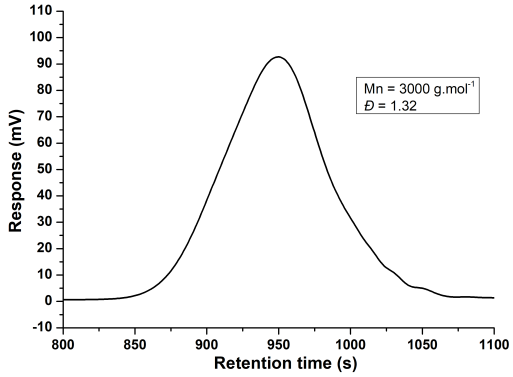

Fig. S19 Size exclusion chromatogram of oxidized PIBEMA$_{2500}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the oxidized poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (oxidized P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{5000}$ oligomer*

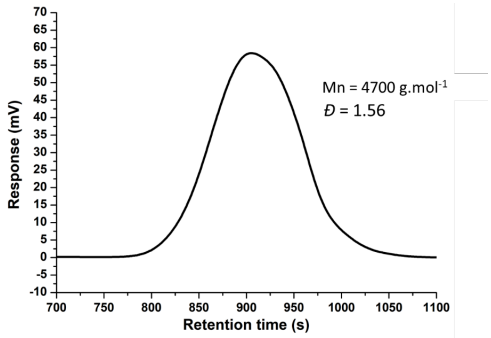

Fig. S20 Size exclusion chromatogram of oxidized P(MMA$_{50}$- *st*-IBEMA$_{50}$)$_{5000}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the oxidized poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (oxidized P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{5000}$ oligomer*

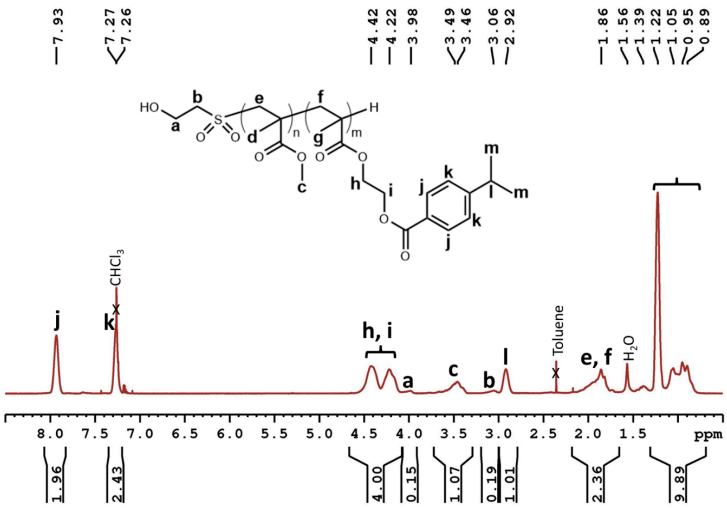

Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for oxidized P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{5000}$ oligomer.

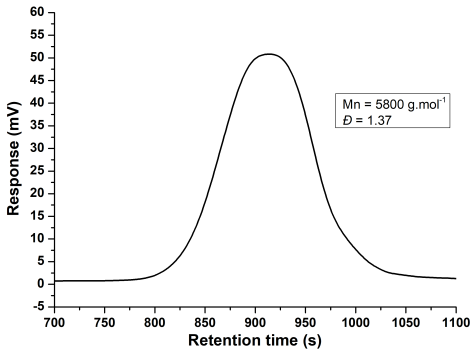

Fig. S22 Size exclusion chromatogram of oxidized P(MMA$_{25}$- *st*-IBEMA$_{75}$)$_{5000}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the oxidized poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (oxidized P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{2500}$ oligomer*

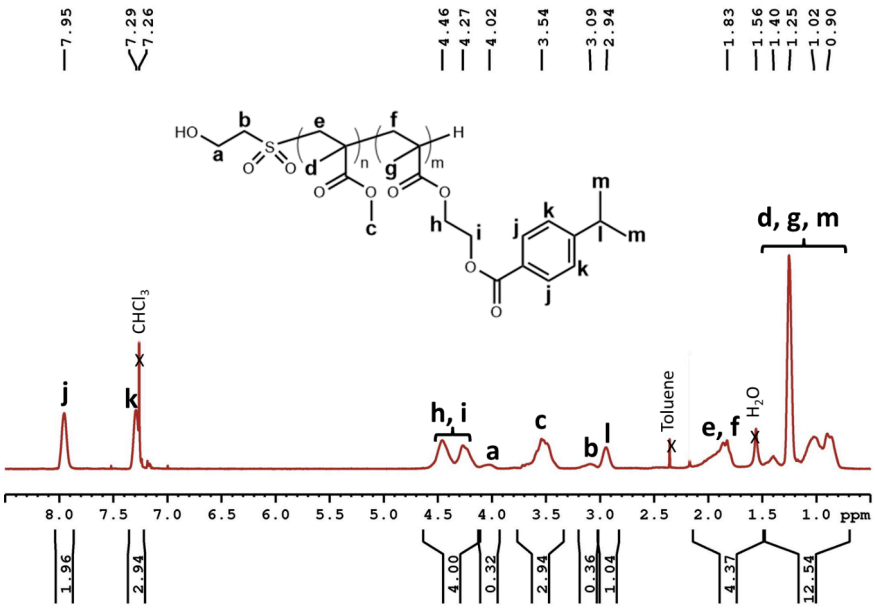

Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for oxidized P(MMA$_{50}$-*st*-IBEMA$_{50}$)$_{2500}$ oligomer.

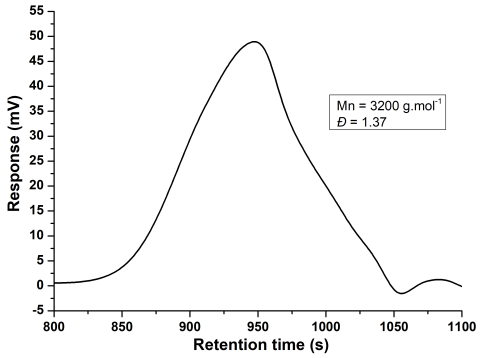

Fig. S24. Size exclusion chromatogram of oxidized P(MMA$_{50}$- *st*-IBEMA$_{50}$)$_{2500}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

*Characterization of the oxidized poly(methyl methacrylate-*st*-(4-isopropylbenzoate) 2-ethyl methacrylate) (oxidized P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{2500}$ oligomer*

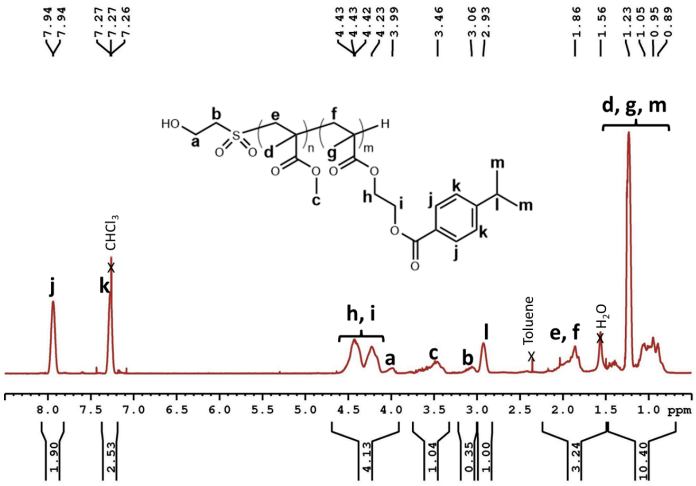

Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for oxidized P(MMA$_{25}$-*st*-IBEMA$_{75}$)$_{2500}$ oligomer.

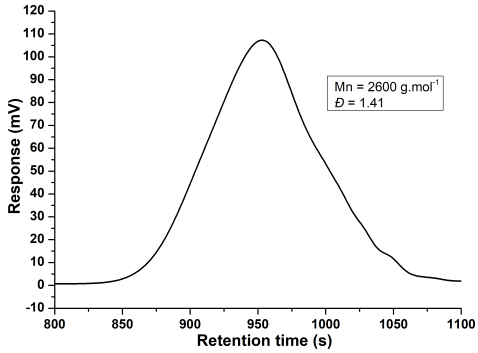

Fig. S26 Size exclusion chromatogram of oxidized P(MMA$_{25}$- *st*-IBEMA$_{75}$)$_{2500}$ oligomer (eluent: THF + 0.05 wt % toluene, PMMA standards).

Characterization of poly(4-(2-hydroxyperoxipropyl)benzoate) 2-ethyl methacrylate) (PHPPBEMA$_{2500}$) oligomer

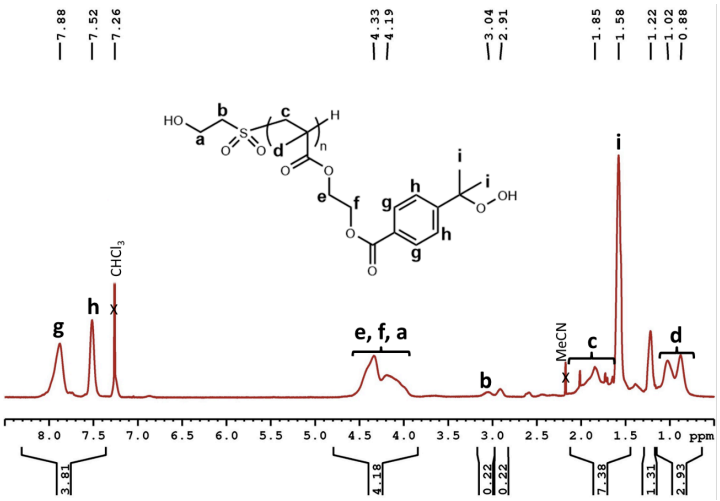

Fig. S27 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum, and proton assignments for PHPPBEMA$_{2500}$ oligomer.

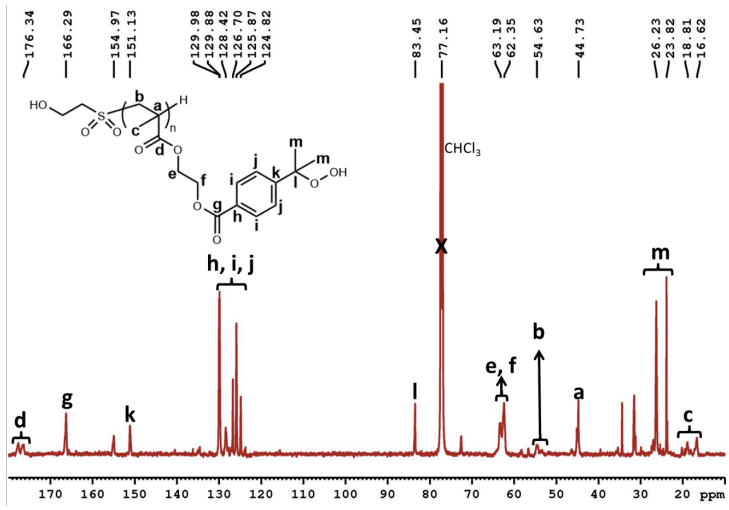

Fig. S28 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for PHPPBEMA$_{2500}$ oligomer.

*Characterization of poly(methyl methacrylate-*st*-(4-(2-hydroxyperoxipropyl)benzoate) 2-ethyl methacrylate) (P(MMA$_{50}$-*st*-HPPBEMA$_{50}$)$_{5000}$) oligomer*

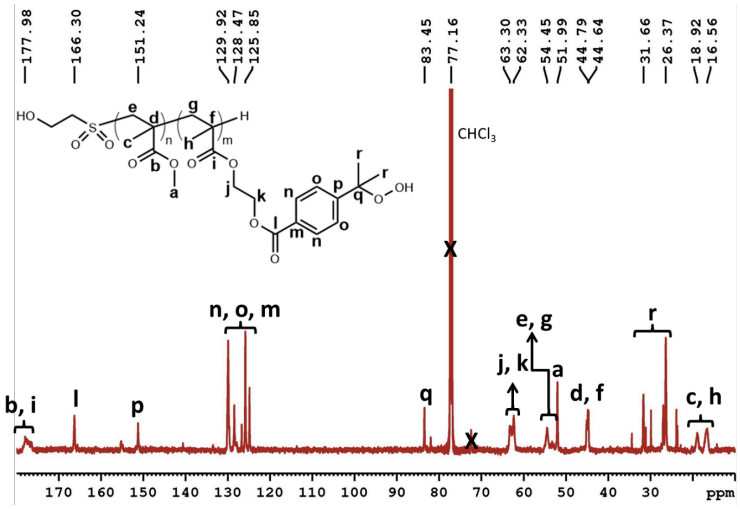

Fig. S29 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{50}$-*st*-HPPBEMA$_{50}$)$_{5000}$ oligomer.

*Characterization of poly(methyl methacrylate-*st*-(4-(2-hydroxyperoxipropyl)benzoate) 2-ethyl methacrylate) (P(MMA$_{25}$-*st*-HPPBEMA$_{75}$)$_{5000}$) oligomer*

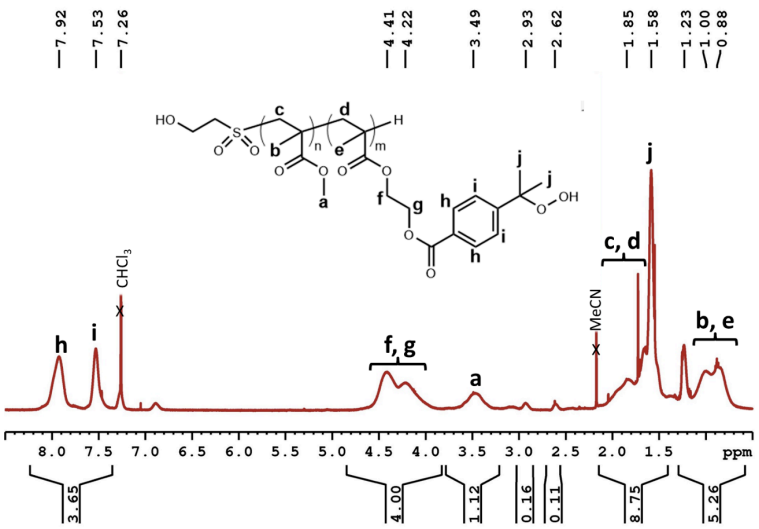

Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for P(MMA$_{25}$-*st*-HPPBEMA$_{75}$)$_{5000}$ oligomer.

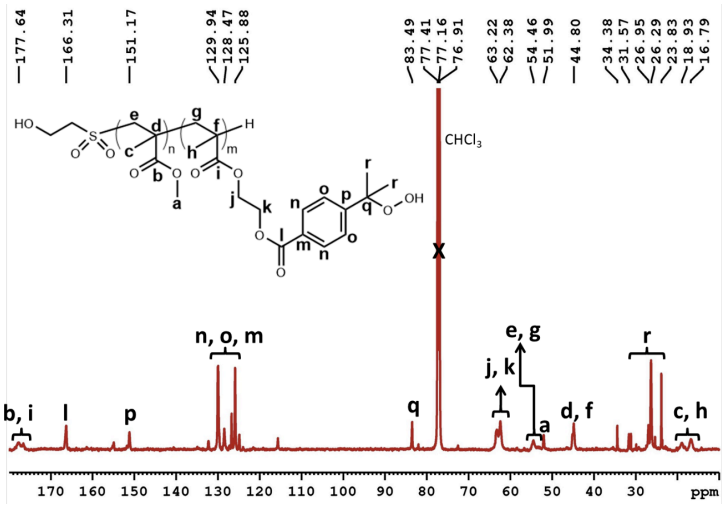

Fig. S31 ^{13}C NMR (600 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{25}$-*st*-HPPBEMA$_{75}$)$_{5000}$ oligomer.

*Characterization of poly(methyl methacrylate-*st*-(4-(2-hydroxyperoxipropyl)benzoate) 2-ethyl methacrylate) (P(MMA$_{50}$-*st*-HPPBEMA$_{50}$)$_{2500}$) oligomer*

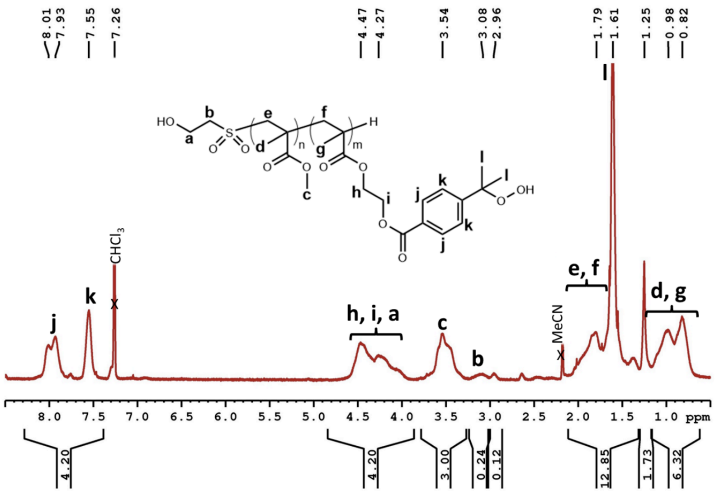

Fig. S32 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum, and proton assignments for P(MMA$_{50}$-*st*-HPPBEMA$_{50}$)$_{2500}$ oligomer.

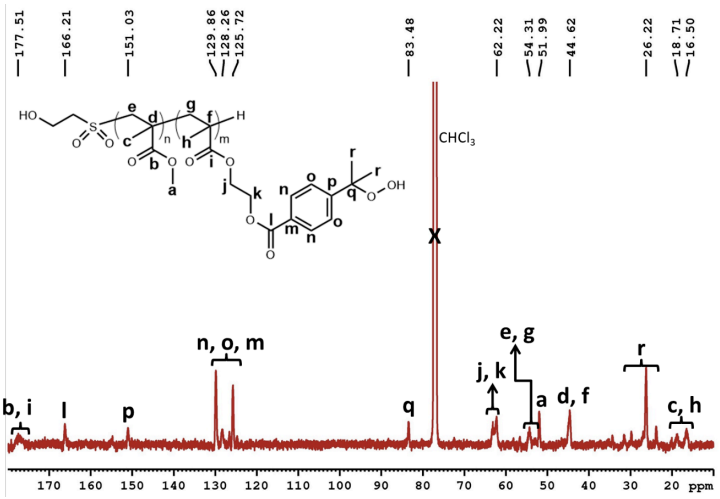

Fig. S33 ^{13}C NMR (500 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{50}$-*st*-HPPBEMA$_{50}$)$_{2500}$ oligomer.

*Characterization of poly(methyl methacrylate-*st*-(4-(2-hydroxyperoxipropyl)benzoate) 2-ethyl methacrylate) (P(MMA$_{25}$-*st*-HPPBEMA$_{75}$)$_{2500}$) oligomer*

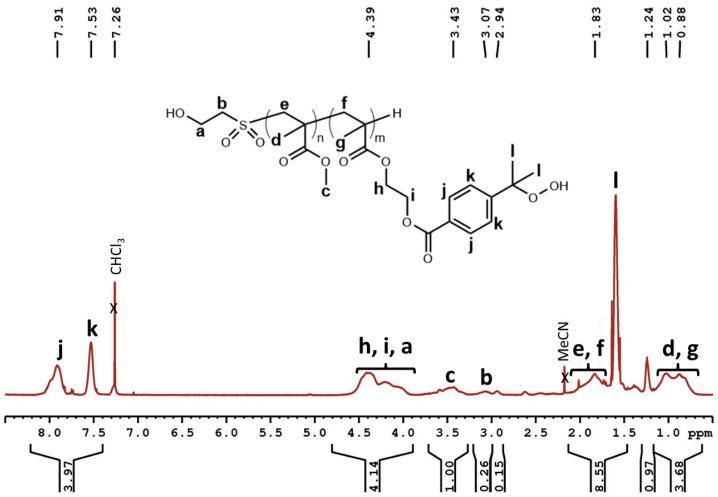

Fig. S34 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum, and proton assignment for P(MMA$_{25}$-*st*-HPPBEMA$_{75}$)$_{2500}$ oligomer.

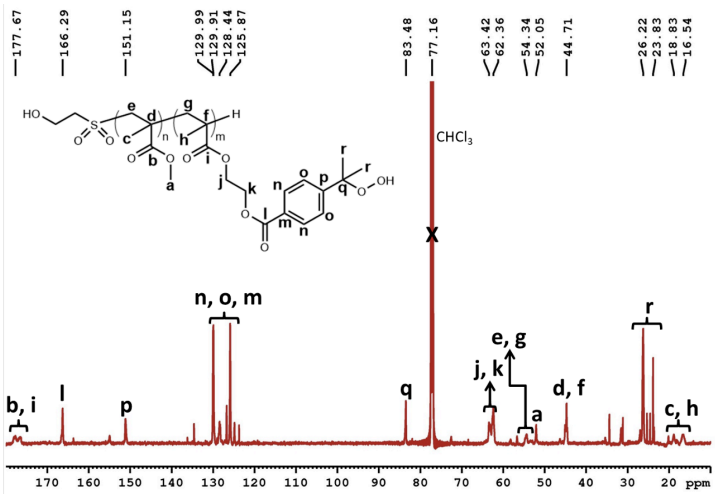

Fig. S35 ^{13}C NMR (500 MHz, $CDCl_3$) spectrum, and carbon assignments for P(MMA$_{25}$-*st*-HPPBEMA$_{75}$)$_{2500}$ oligomer.

Characterization of (2-methylthioethyl) 4-isopropylbenzoate (MTEPB)

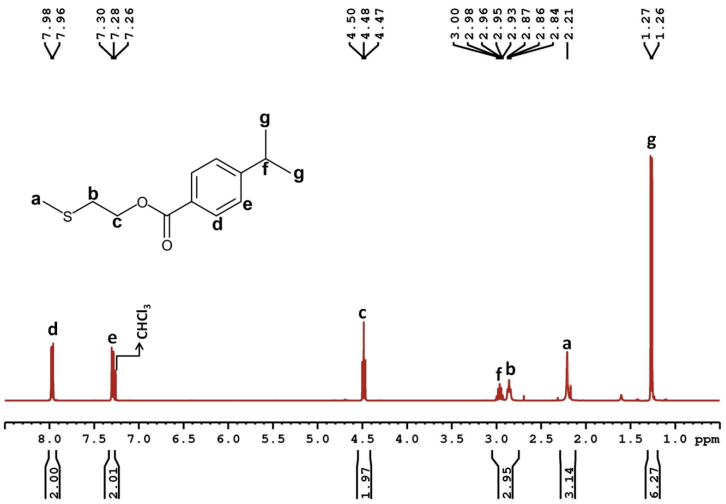

Fig. S36 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum and proton assignments for MTEPB.

Characterization of (2-methylsulfonylethyl) 4-isopropylbenzoate (MSEPB)

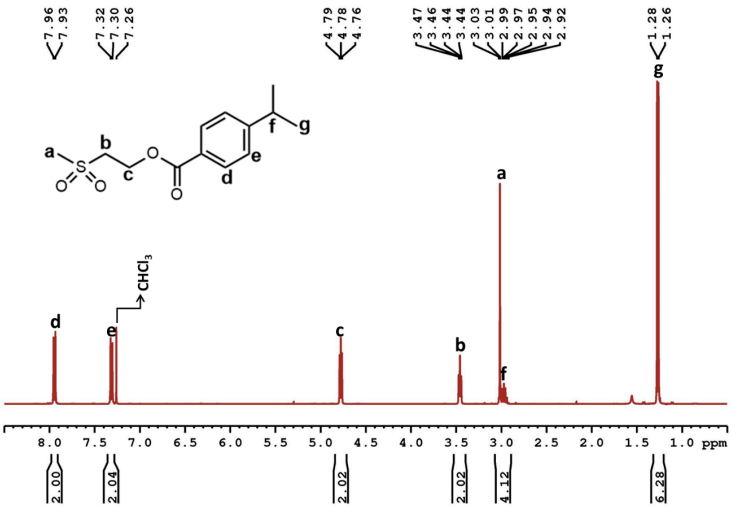

Fig. S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for MSEPB.

Characterization of (2-methylsulfonylethyl) 4-hydroxyperoxipropylbenzoate (MSEHPB)

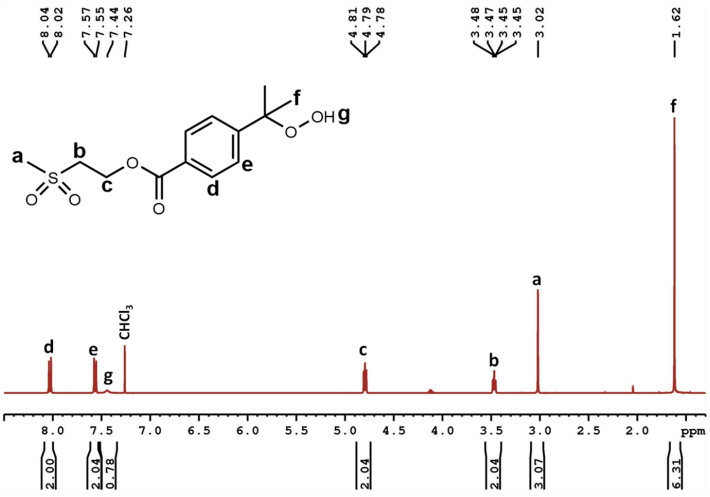

Fig. S38 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum, and proton assignments for MSEHPB.

Mechanical properties of the different cements

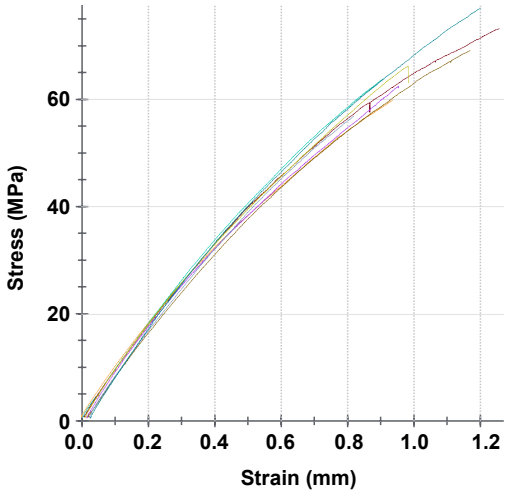

Fig. S39 Flexural curves for the SCC1 cement (flexural strength and flexural modulus correspond to the average value of eight measurements).

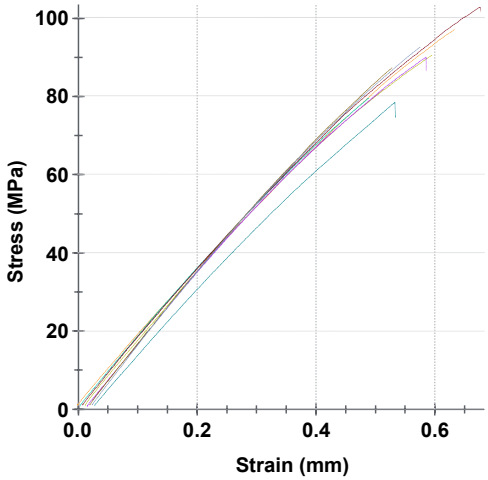

Fig. S40 Flexural curves for the SCC2 cement (flexural strength and flexural modulus correspond to the average value of eight measurements).

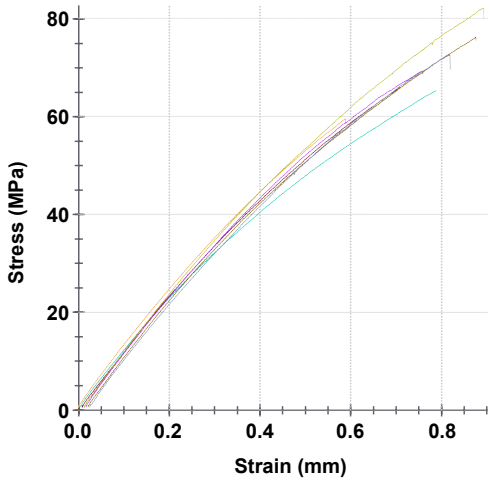

Fig. S41 Flexural curves for the SCC3 cement (flexural strength and flexural modulus correspond to the average value of eight measurements).

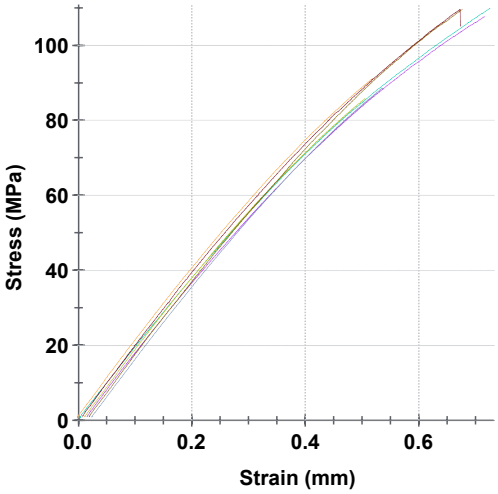

Fig. S42 Flexural curves for the SCC4 cement (flexural strength and flexural modulus correspond to the average value of eight measurements).

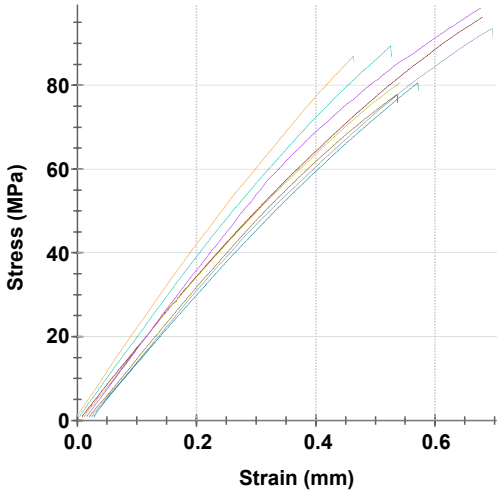

Fig. S43 Flexural curves for the SCC5 cement (flexural strength and flexural modulus correspond to the average value of eight measurements).

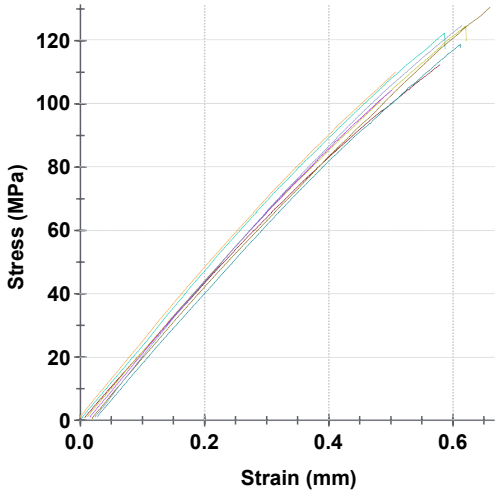

Fig. S44 Flexural curves for the SCC6 cement (flexural strength and flexural modulus correspond to the average value of eight measurements).

References

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