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Electronic Supplementary Information (ESI)

CeO_2/PVDC hybrid latex mediated by a phosphonated macro-RAFT agent

Jérôme Warnant,[a] Jérôme Garnier,[a,b] Alex van Herk,[b,c] Pierre-Emmanuel Dufils,[d] Jérôme Vinas,[e] and Patrick Lacroix-Desmazes*[a]

[a] *Institut Charles Gerhardt (ICG), Ingénierie et Architectures Macromoléculaires (IAM), Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France. Tel: 33-4-67-14-72-05; Fax: 33-4-67-14-72-20;*
E-mail: patrick.lacroix-desmazes@enscm.fr

[b] *Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.*

[c] *Present address: Institute of Chemical and Engineering Sciences, 1 Pesek Road, 627833 Singapore.*

[d] *High Barrier Polymers, Solvay Specialty Polymers, Avenue de la République, 39500 Tavaux, France.*

[e] *High Barrier Polymers, Solvay Specialty Polymers, Solvay Campus, Rue de Ransbeek 310, B-1120 Brussels, Belgium.*

1. Synthesis of dibenzyl trithiocarbonate (DBTTC) RAFT transfer agent

The synthesis of the DBTTC RAFT agent involved a phase-transfer catalysis mechanism and followed a protocol published in earlier literature.[1] Sodium trithiocarbonate was first obtained by reacting sodium sulfide (hydrate form, 30 wt%, 70.08 g, 269 mmol) with carbon disulfide (22.1 g, 291 mmol) at room temperature for 1h in water (89.75 g) in the presence of tetrabutylammonium bromide (2.05 g). In a second step benzyl chloride (63.91 g, 505 mmol) was added dropwise to the solution for 30 min. The reaction was performed at room temperature for 3h, followed by a period of 1h at 70°C. Once the reaction medium was back to room temperature, an additional charge of tetrabutylammonium bromide (2.36 g) dissolved in water (4.73 g) was added. The solution was then stirred overnight to complete the reaction. After separation of the organic and aqueous phases, DBTTC was obtained by precipitating the organic phase in 150 mL cold ethanol. The resulting yellow crystals were then filtered and rinsed with cold ethanol on a sintered glass filter, and dried in a vacuum oven at 30°C. Mass of DBTTC obtained: 59.91 g. ^1H NMR (Fig.SI.1) ($CDCl_3$), δ : 4.68 (CH_2), 7.38 ($H_{aromatic}$). Yield: 82 %.

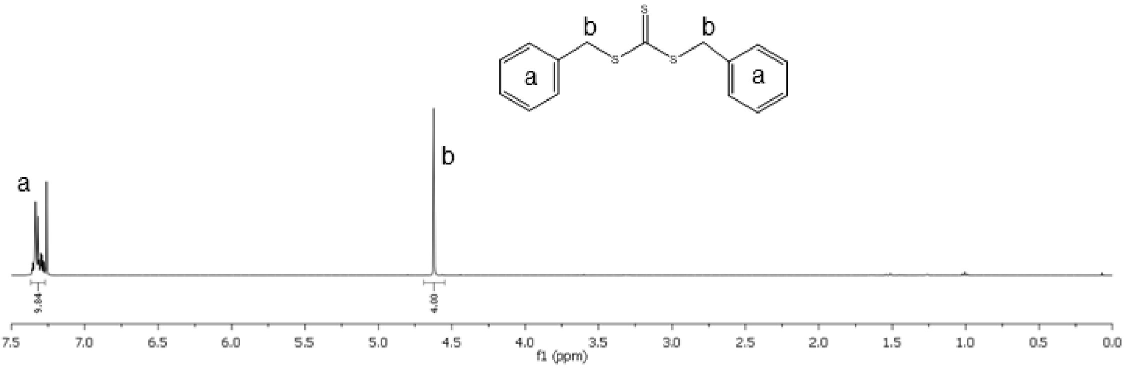


Fig.SI.1 ^1H NMR (400MHz) spectrum of dibenzyl trithiocarbonate in $CDCl_3$.

2. Synthesis of vinylbenzyl phosphonyl diethyl ester (VBPDE) monomer

NaH (60% in grease, M=24.00 g mol^{-1}, 6.88 g, 0.287 mol) was suspended in anhydrous THF (dried on molecular sieve, 140 mL) at 0°C. Diethylphosphite (M=138.10 g mol^{-1}, 41.7 g, 0.302 mol) was added drop wise. The mixture was allowed to come to RT, then a solution of 1-chloromethyl-vinylbenzene (mixture of meta and para isomers 53/47, 96%) M=152.62 g mol^{-1}, 41.5 g, 0.288 mol) and NaI (M=149.89 g mol^{-1}, 4.08 g, 27 mmol) in anhydrous THF (70 mL) was transferred to the first solution by cannula at 0°C. The solution turned from pale yellow to orange. The mixture was stirred overnight. Salts were precipitated by the addition of AcOEt, and the mixture was filtered through celite. Volatiles were removed and the residue was purified by column chromatography (eluent: AcOEt, Rf (ethyl acetate) = 0.4). The product VBPDE was isolated as a pale yellow oil (45 g, 66%). ^{1}H NMR and ^{31}P NMR are shown in Fig.SI.2 and Fig.SI.3 respectively. 4 % of diethylphosphite remained in the monomer.

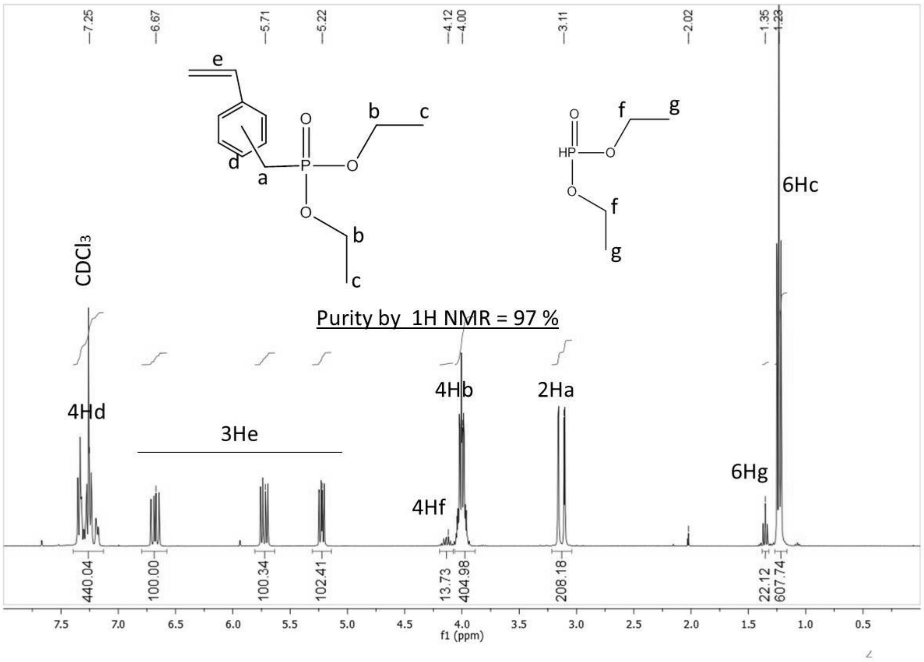


Fig.SI.2 ^{1}H NMR (400MHz in $CDCl_3$) **of vinylbenzyl phosphonyl diethyl ester monomer after purification.**

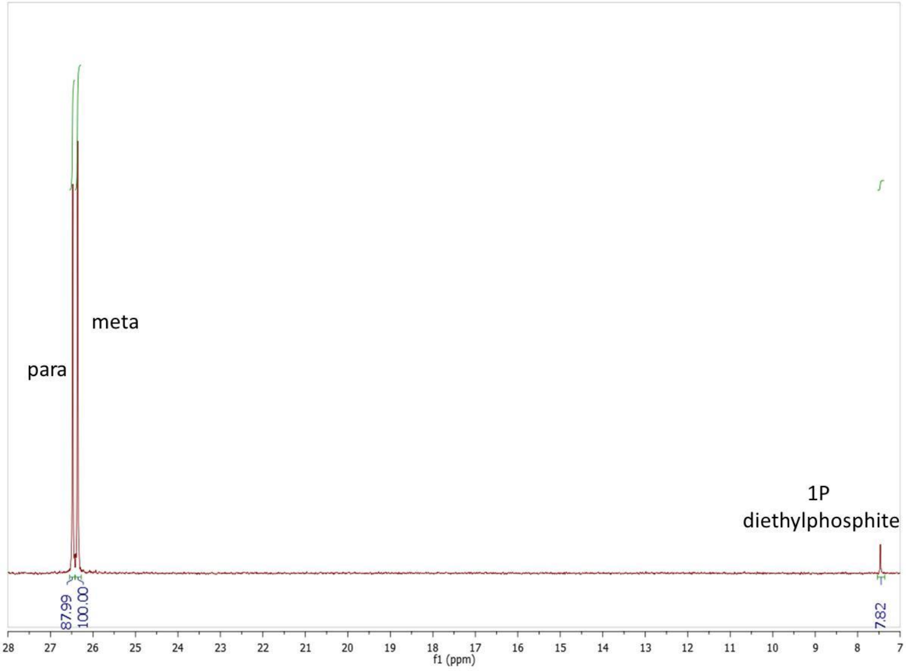


Fig.SI.3 ^{31}P NMR (101MHz in $CDCl_3$) **of vinylbenzyl phosphonyl diethyl ester monomer after purification.**

3. Characterization of poly(vinylbenzylphosphonic acid-*co*-styrene) RAFT oligomer

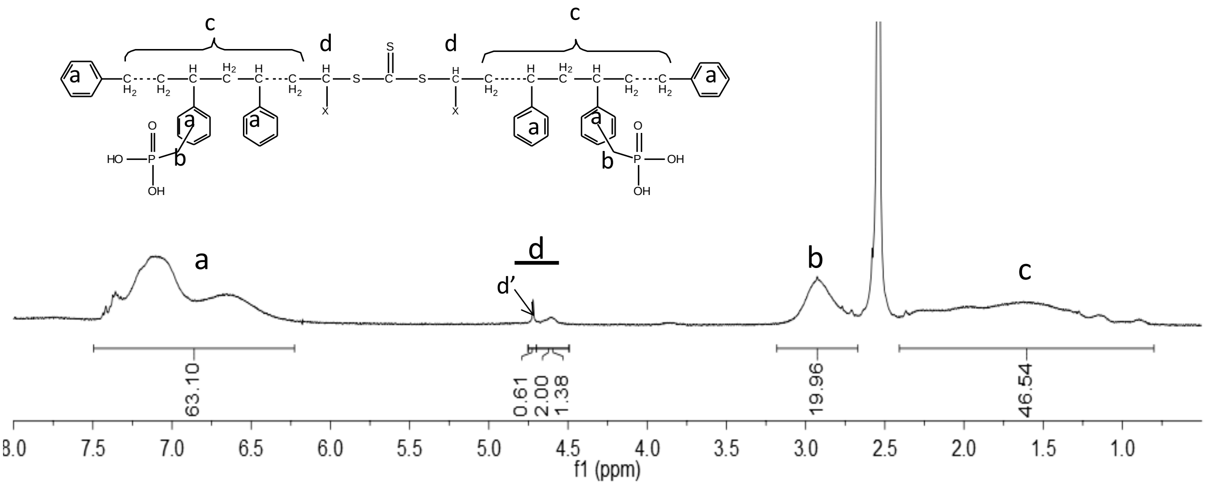
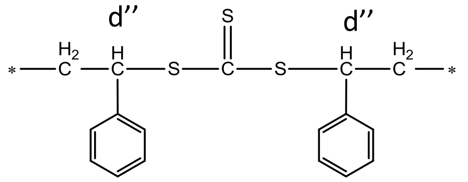
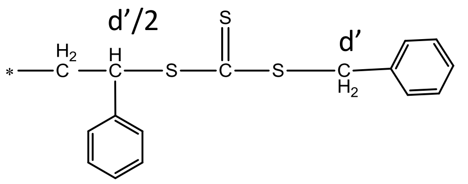


Fig.SI.4 ^{1}H NMR spectrum and corresponding integration peaks of poly(VBPDA$_{12}$-*co*-St$_5$) RAFT copolymers in DMSO-d$_6$.

GC-MS analyses of the soluble fraction of the product in ethyl acetate (bad solvent of the polymer but good solvent of DBTTC) indicated that the amount of residual DBTTC was negligible. Our analysis is that the singlet **d'** corresponds to the unreacted benzyl moiety of the oligomers $PhCH_2$-$(CH_2CHX)_p$SC(S)S-**$\underline{CH_2}$**Ph. So, the product is composed of two types of chains: $PhCH_2$-$(CH_2CHX)_m$-SC(S)S-$(CHXCH_2)_n$$CH_2Ph$ and $PhCH_2$-$(CH_2CHX)_p$-SC(S)S-CH_2Ph (with X being either Ph or $PhCH_2P(O)(OH)_2$).





$I_d = 2$

$I_{d'} = 0.61$, $H_{d'} = I_{d'}/2 = 0.61/2 = 0.305$

$H_{d''} = (I_d - I_{d'} - I_{d'}/2)/2 = (2 - 0.61 - 0.305)/2 = 0.54$

Percentage of chains that have propagated on only one side $PhCH_2$-$(CH_2CHX)_p$-SC(S)S-**CH_2**Ph: $H_{d'}/(H_{d'}+H_{d''})\times100 = 0.305/(0.305+0.54) = 36\%$

VBPDA: $H_b = I_b/2 = 19.96/2 = 9.98$

Aromatics: $I_a = 63.10$

Styrene: $H_{a'} = (I_a - 4 \times H_b)/5 = (63.10 - 4 \times 9.98)/5 = 4.64$

%mol styrene: St/(Sty + VBPDA) = $H_{a'}/(H_{a'}+H_b) = 4.64/(4.64+9.98)\times100= 31.7\%$

Molar ratio St/VBPDA: $H_{a'}/H_b = 31.7/68.3=0.46$

Number of chains: $N_{chains} = H_{d'} + H_{d''} = 0.305+0.54 = 0.845$

Remark: both type of chains have similar DP_n according to the SEC chromatogram of the parent copolymer poly(VBPDE-*co*-St) (monomodal chromatogram with low value of M_w/M_n = 1.19).

$DP_{VBPDA}= H_b/N_{chains} = 9.98/0.845 = 11.8$ (1)

$DP_{St} = DP_{VBPDA} \times$ (Molar ratio St/VBPDA) $= 11.8 \times 0.46= 5.4$ (2)

This copolymer will be designed as poly($VBPDA_{12}$-*co*-St_5).

In order to confirm that styrene and vinylbenzyl phosphonyl diethyl ester copolymerized randomly, the synthesis of a poly(St_5-*co*-$VBPDE_{10}$) macro-RAFT agent was also carried out to follow the conversions of both monomers versus time. Samples were taken regularly and analyzed by ^{1}H NMR. The integration peak **g** corresponding to ethyl protons of VBPDE - C_6H_4-CH_2-P(O)$(OC\underline{H}_2CH_3)_2$ was taken as an internal standard and the integrations of the different signals of trans protons methylene for styrene (5.75 ppm) and VBPDE (para 5.71 ppm and meta 5.73 ppm) were used to calculate the conversions of the two monomers as a function of time (Fig.SI.5 and Fig.SI.6) :

$$\text{Conversion VBPDE(meta) (\%)}=1-I_{5.73}(t)/I_{5.73}(t=0)\times100 \qquad (3)$$

$$\text{Conversion VBPDE(para) (\%)}=1-I_{5.71}(t)/I_{5.71}(t=0)\times100 \qquad (4)$$

$$\text{Conversion St (\%)}=1-I_{5.75}(t)/I_{5.75}(t=0)\times100 \qquad (5)$$

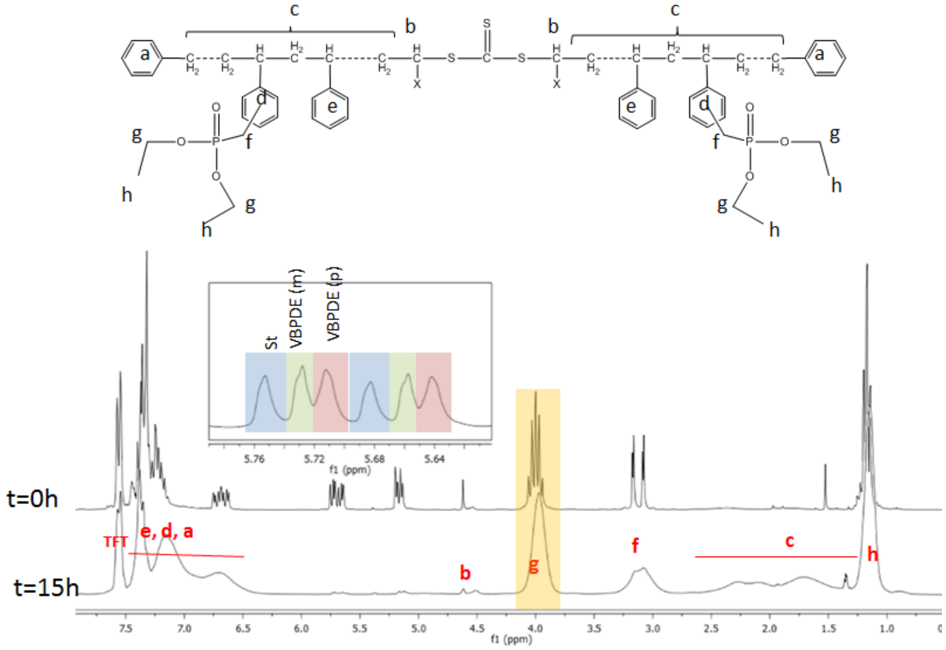


Fig.SI.5 ^1H NMR (250 MHz) spectra used for kinetic measurements in the case of poly(St_5-*co*-$VBPDE_{10}$) in TFT with capillaries of C_6D_6.

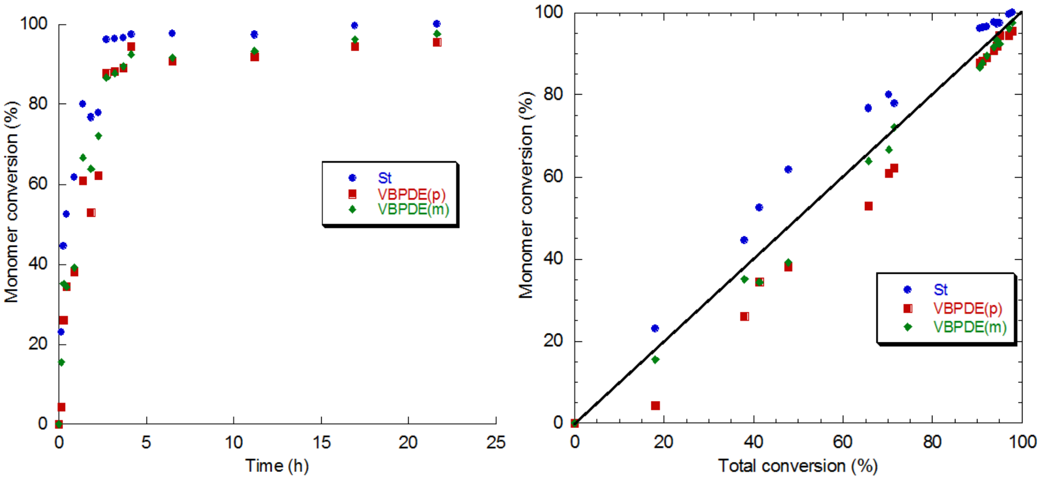


Fig.SI.6 Vinylbenzyl phosphonyl diethyl ester (para and meta) and styrene conversions as a function of time (left) and as a function of the total monomer conversion (right).

4. Characterization of the adsorption of amphiphatic macro-RAFT agents by UV-visible spectrometry

For the poly(VBPDA-*co*-St), a calibration curve (Fig.SI.7), giving the maximum absorbance (at 317 nm, specific of the trithiocarbonate function) as a function of the oligomer concentration in water (from 0.2 to 8 g/L) was plotted. The calibration curves followed a linear trend for values of absorbance below 3.

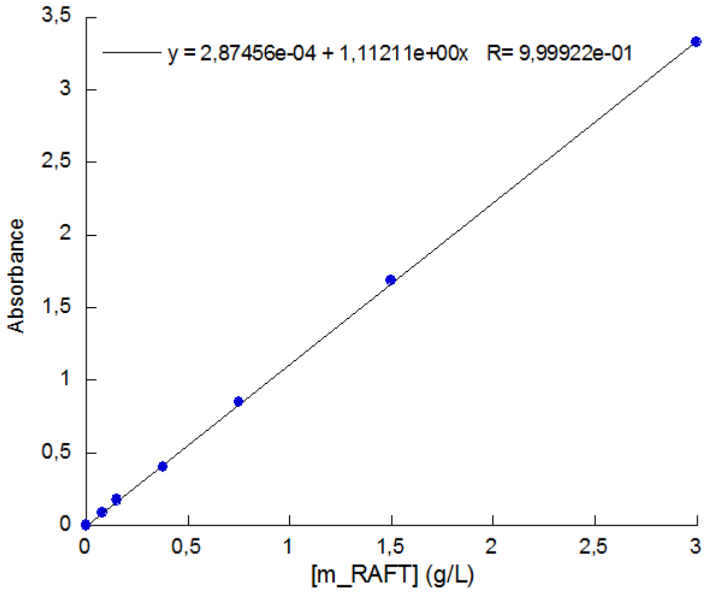


Fig.SI.7 Calibration curve obtained in UV-visible spectrometry with poly(VBPDA$_{12}$-*co*-St$_5$).

UV-visible measurements were carried out on the serum solutions, diluted or not in order to fit the range of absorbance of the calibration curve (Fig.SI.8). From this curve, the concentration of the free macro-RAFT agent present in the serum could then be calculated (Table.SI.1).

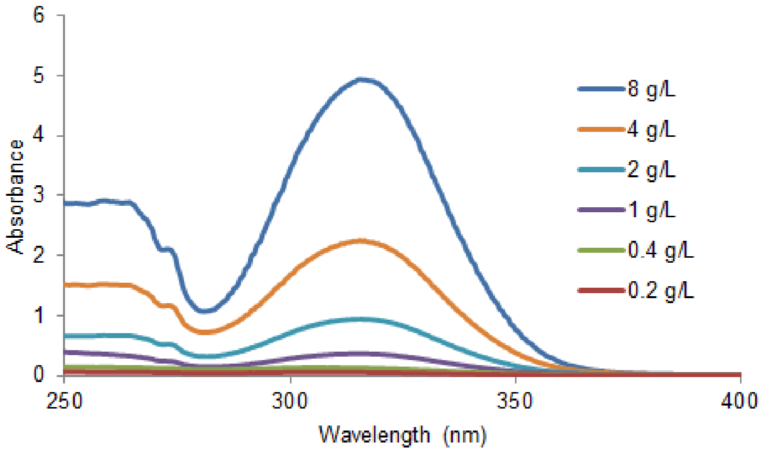


Fig.SI.8 UV-visible absorption curves of serum of poly(VBPDA$_{12}$-*co*-St$_5$), with initial concentration of macro-RAFT agents of 8*, 4, 2, 1, 0.4 and 0.2 g/L, obtained after ultracentrifugation. (*: absorbance corrected by the factor of dilution)

Table.SI.1 Characterization of the adsorption of the macro-RAFT agent poly($VBPDA_{12}$-*co*-St_5) at the surface of CeO_2 nanoparticles via UV-visible spectroscopy. (*: absorbance corrected by the factor of dilution)

	Initial CeO_2 dispersion		Characterization of serum solutions			
Entry	[CeO_2] (g/L)	[m_RA]$_0$ (g/L)	Dilution	Absorbance	[m_RA]$_{serum}$ (g/L)	m_RA serum (wt %)
0	4	0	none	0	0.000	0%
1	4	0.2	none	0.05	0.048	76%
2	4	0.4	none	0.12	0.116	71%
3	4	1	none	0.36	0.346	65%
4	4	2	none	0.94	0.898	55%
5	4	4	None	2.22	2.135	47%
6	4	8	3	4.91*	4.717	41%

5. Characterization of the adsorption of amphiphatic macro-RAFT agents by ^{31}P NMR

For the poly($VBDPA_{12}$-*co*-St_5), a calibration curve giving the relative integrals of phosphorus of VBPDA, defined as the ratio between the signal at 20.9 ppm ($I_{20.9}$) and the signal of the reference at 0 ppm (I_0), as function of the oligomer concentration in water at pH=7 was plotted (Fig.SI.9).

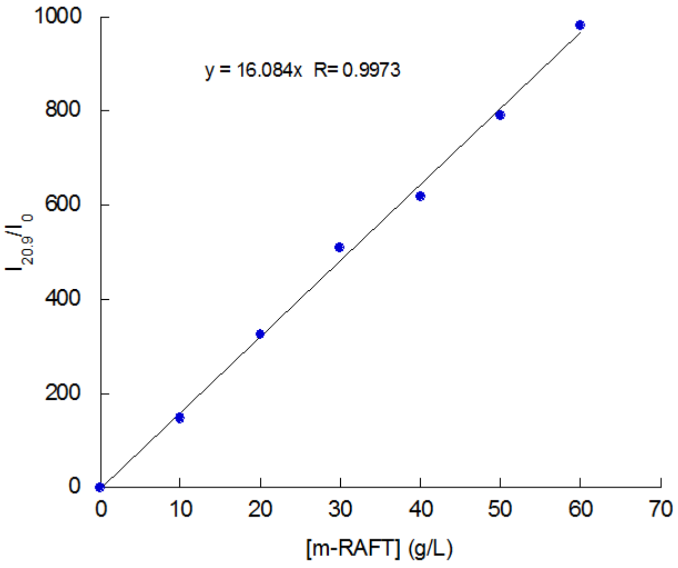


Fig.SI.9 Calibration curve obtained by ^{31}P NMR with the poly($VBPDA_{12}$-*co*-St_5).

Then, we measured the relative intensity of VBPDA in the presence of CeO_2 ($I(Ce)_{20.9}/I(Ce)_0$) and via the curve of calibration for each preparation a concentration of the phosphonated functions complexed on the cerium oxide could be calculated with the following equation (Fig.SI.10 and Table.SI.2):

$$\%VBPDA_{cplx} = 1 - \frac{I(CeO_2)_{20.9}}{I_{20.9}} \times 100 \qquad (6)$$

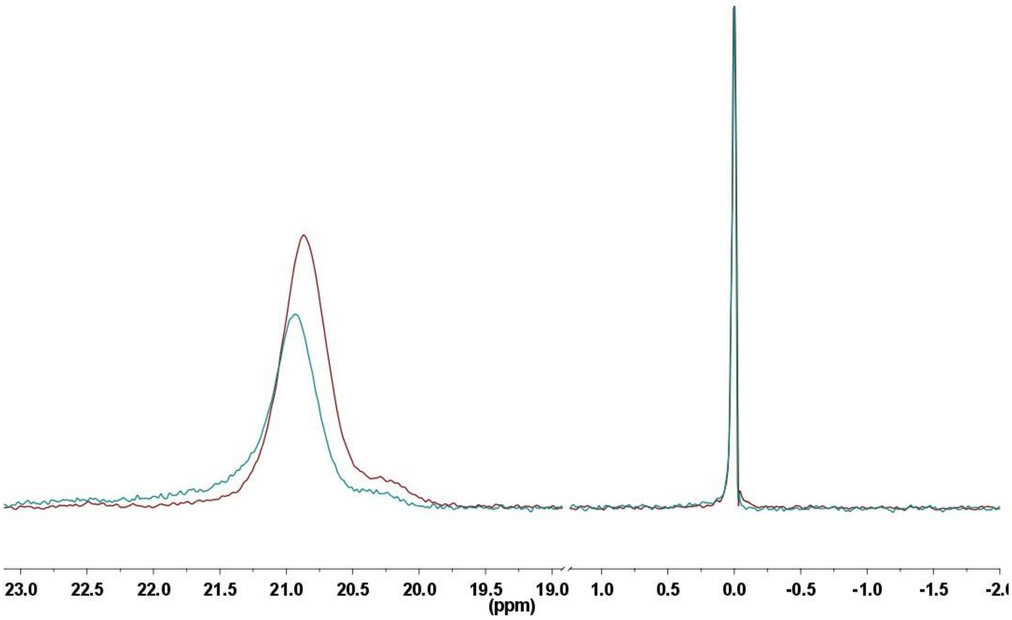


Fig.SI.10 ^{31}P **NMR (101 MHz) of solution of poly(VBPDA$_{12}$-*co*-St$_5$) at 40g L^{-1} without ceria (red line) and in the presence of nanoceria particles at 40 g L^{-1} (green line) (cf. Entry 3 in Table.SI.2).**

Table.SI.2 Characterization of the adsorption of the poly(VBPDA$_{12}$-*co*-St$_5$) at the surface of CeO_2 nanoparticles via ^{31}P NMR (101 MHz).

Entry	m-RAFT (g/L)	CeO_2 (g/L)	I rel (CeO_2) $I(Ce)_{20.9}/I(Ce)_0$	free VBPDA %	cplx VBPDA %
0	0	40	0	100%	0%
1	10	40	89	55%	45%
2	18	40	198	68%	32%
3	40	40	494	77%	23%
4	57	40	729	80%	20%
5	72	40	959	83%	17%