Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic supplementary information for:

Understanding the emulsion copolymerization kinetics of vinyl acetate and vinyl silanes

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S.1. Bulk reactivity ratios

The estimation of the reactivity ratios requires the measurement of the individual conversion of each monomer during copolymerization reactions. For this reason, the reactions were carried out directly in the NMR tube. 500 µl of monomer mixture were heated at 50 ºC, to avoid the boiling of the monomer, and when the reaction temperature was achieved an initiator solution (5 µg di(4-tert-butylcyclohexyl) peroxydicarbonate in 50 µl $CDCl_3$) was added. The tube was inserted in the NMR equipment at 50 ºC and the ^{1}H-NMR spectra were obtained every 6 minutes in a Bruker AVANCE 500 MHz spectrometer with $CDCl_3$ as solvent. Table S.1 summarizes the compositions of the monomer mixtures used in the experiments.

The NMR data was used to calculate the individual conversion of each monomer. Then, plotting this over the overall conversion the reactivity ratios were estimated according to the method developed by De la Cal *et al*[1].

Table S.1. Monomer compositions used in the *in situ* NMR polymerization experiments.

	Composition [wt/wt]		**Composition [mol/mol]**	
Run	**VAc**	**VTMS**	**VAc**	**VTMS**
5 %	95	5	97	3
10 %	90	10	94	6
15 %	85	15	91	9

As an example, Figure S.1 shows the ^{1}H-NMR spectra of the experiment with VAc/VTMS 85/15 wt ratio at time 0 with the assignation of the signals of the monomers. As can be observed, the vinyl peaks of vinyl acetate and vinyl trimethoxysilane are well separated.

The vinyl peaks of both monomers decreased as the polymerization advanced, without the appearance of new peaks, indicating that the copolymerization was carried out without any relevant side reaction.

Figure S.2 shows the evolution of the conversion of each individual monomer *vs* the reaction time for the 3 monomer compositions obtained from the ^{1}H-NMR results. Figure S.3 shows the overall conversion over the reaction time for the three reactions.

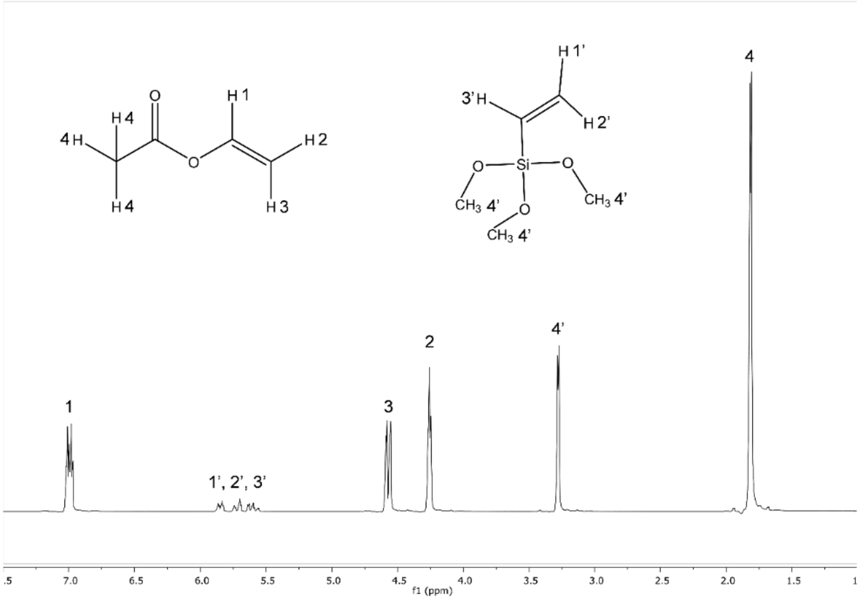
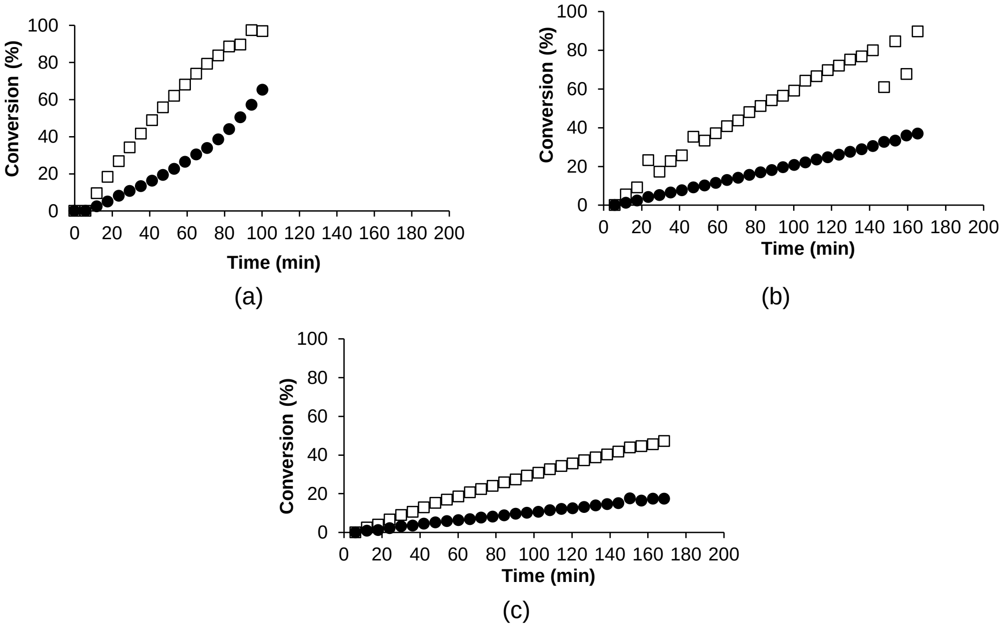


Figure S.1. ^{1}H-NMR spectrum with the assignation of the signals for the VAc/VTMS:85/15 run at time 0.



(a)

(b)

(c)

Figure S.2. Time evolution of the individual conversion of vinyl acetate (●) and VTMS (□) for the *in situ* bulk copolymerization with 5 % (a), 10 % (b) and 15 % (c) VTMS.

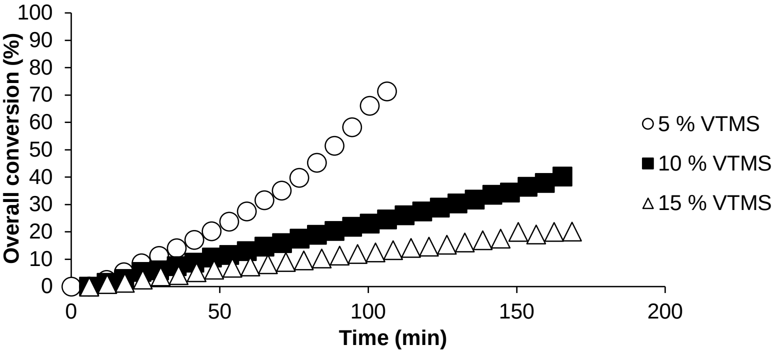
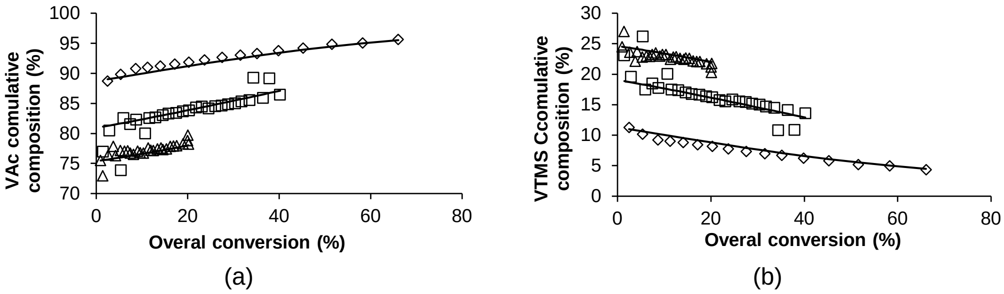


Figure S.3. Time evolution of the overall conversion for the 3 copolymer compositions during the reactions performed *in situ* in the NMR tube.

The evolution of individual comonomer conversions over overall conversion were used in order to get an estimation of the reactivity ratios, following the method developed by De la Cal *et al*[1]. The resulting values for the reactivity ratios are: r_{VAc}= 0.211 and r_{VTMS}= 0.

To show that there is a good agreement between the experimental values and the model predictions using the estimated values, Figure S.4 shows the cumulative composition of each monomer *vs* the overall conversion, comparing both of them.



(a) (b)

Figure S.4. Comparison of the experimental values of the VAc (a) and VTMS (b) cumulative composition over the overall conversion for the 5 % VTMS (O), 10 %VTMS (□) and 15 % VTMS (Δ) reactions. The continuous line shows the theoretical values.

r_{VAc} < 1 means that the chains bearing the radical in a VAc unit has a higher probability to react with VTMS monomers. On the other hand, r_{VTMS} is 0 due to the inability of VTMS to homopropagate, and does not give additional information about propagation of the VTMS radical with VAc. However, as the overall polymerization rate decreases with an increasing concentration of silane, the propagation of a VTMS terminated radical with a VAc monomer unit must be significantly slower than the propagation of a vinyl acetate radical with a VAc monomer; otherwise the overall polymerization rate would not be decreased.

To have more insight on the cross-propagating ability of the silane terminated radical, the reactions were repeated in a stirred tank batch reactor, and the molar mass distribution and the copolymer composition were measured at low conversion (~15 %) by size exclusion chromatography (SEC) and ^{13}C-NMR, respectively, to determine the number of silane units per chain.

Figure S.5 shows the ^{13}C-NMR of the copolymer with 85-15 (VAc-VTMS) composition.

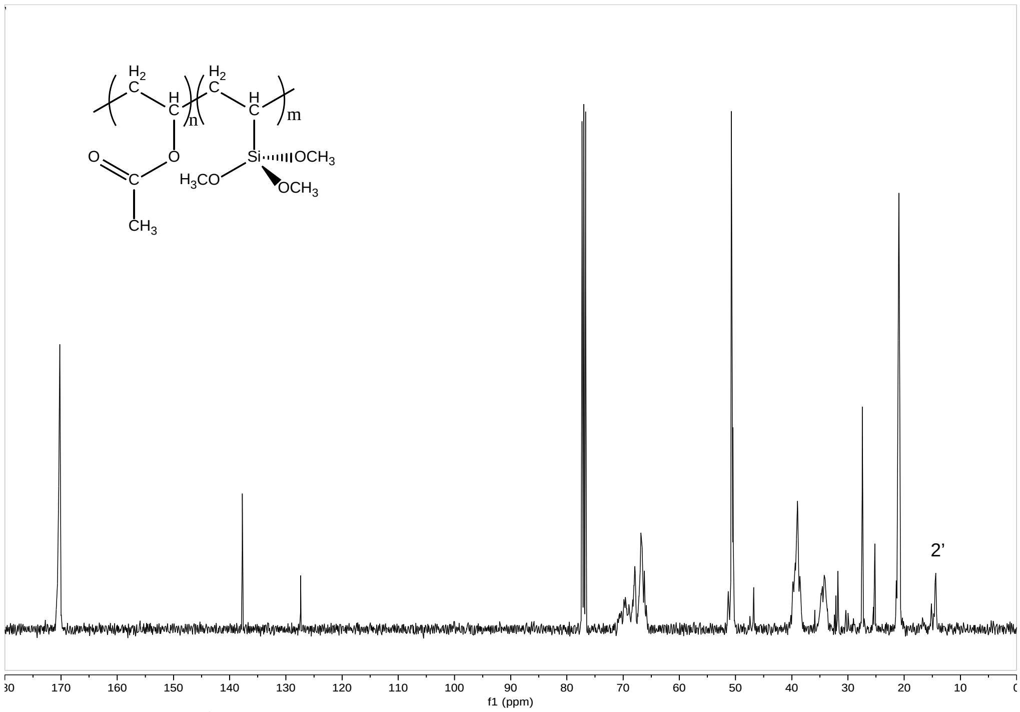


Figure S.5. ^{13}C-NMR of the bulk copolymer with 85-15 VAc-VTMS composition at 15 % conversion.

As observed, each comonomer has at least one peak that is well separated and identified. Carbons 1 (for VAc) and 1' (for VTMS) were used to calculate the comonomer composition in the copolymer. Figure S.6 shows that the copolymer composition in moles measured with the ^{13}C-NMR (X axis) is in good agreement with the theoretical values calculated using the Mayo-Lewis equation and the reactivity ratios estimated in this work (Y axis), validating the reactivity ratios.

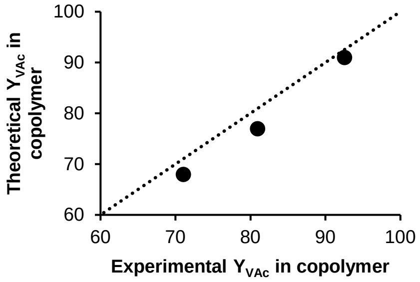


Figure S.6. Comparison between the theoretical and experimental vinyl acetate mol content in the copolymers.

In addition to the copolymer composition, the molar mass distribution was measured too. Figure S.7 shows the molar mass distribution of the copolymers measured by Size Exclusion Chromatography with a Multi Angle Light Scattering and Refractive Index detectors (SEC/MALS/RI).

The equipment was composed of a LC20 pump (Shimadzu) coupled to a DAWN Heleos II multiangle (18 angles) light scattering laser photometer equipped with an He–Ne laser (λ = 658 nm), and an Optilab

Rex differential refractometer (λ = 658 nm). Separation was carried out using three columns in series (Styragel HR2, HR4, and HR6; with pore sizes from 10^2 to 10^6 Å). The analyses were performed at 35 °C and THF was used as mobile phase at a flow rate of 1 ml/min. The SEC/MALS data were analyzed by using the ASTRA software version 6.1. (Wyatt Technology, USA). The absolute molar masses and radius of gyration were calculated at each elution time from the RI and MALS detectors using the Debye plot (with first order Zimm formalism). A dn/dc value for poly(vinyl acetate) of 0.0471 ml/g was used[2].

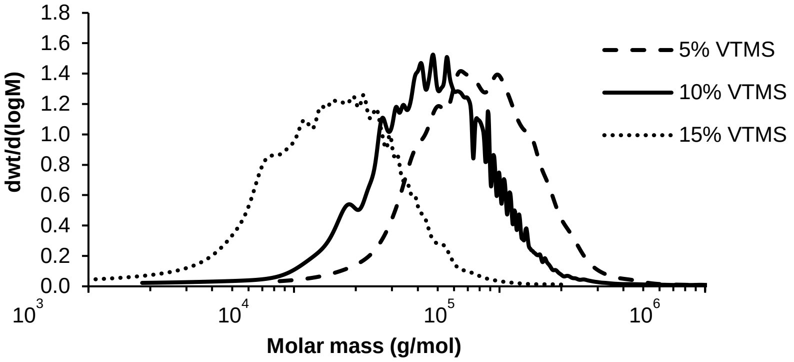


Figure S.7. Molar mass distribution of the bulk copolymers by SEC/MALS.

As observed, there is a clear shift towards lower molar masses as the VTMS concentration increases, because of the decrease in the overall propagation rate.

Combining the data from the copolymer composition and average molar mass, it is possible to calculate the average number of units of each comonomer in the chains, as presented in Table S.2. According to these results, many silane units are incorporated into each chain, which is an indication that the VTMS terminated radical is able to propagate with the vinyl acetate monomer.

Table S.2. Calculation of the monomer units per chain of the bulk copolymers.

Sample	DPn	VAc units	VTMS units
95-5	698	667	31
90-10	449	395	54
85-15	125	101	24

Finally, a simple mathematical model was built in the commercial software Predici for the bulk copolymerization of vinyl acetate and VTMS. More details about the simulation are given in the following section (S.2). Using the parameter estimation tool and the experimental data gathered from the three experiments (the individual conversion of each monomer and the weight and number-average molar masses) a propagation rate constant of a VTMS terminated radical with vinyl acetate monomer was estimated with the resulting value of $k_{p,\text{VTMS-VAc}}$ = 411 ± 168 l/mol·s.

Note that the amount of experimental data is not sufficient to have an accurate estimation of the cross propagation rate coefficient, but for the purpose of this work, it is enough to infer that the order of magnitude of the propagation of VTMS radical with vinyl acetate is about 20 times lower than the homopropagation of vinyl acetate.

S.2. Kinetic model

The simulation was performed considering two monomers: vinyl acetate (A) and vinyl silane (B). The kinetic model used for the simulations included the following reactions:

Initiation

$$\mathrm{I} \xrightarrow{\mathrm{k_I}} 2\mathrm{fI^*} \qquad \text{(S.1)}$$

$$\mathrm{I^*} + \mathrm{M_A} \xrightarrow{\mathrm{k_i^A}} \mathrm{P_1^A} \qquad \text{(S.2)}$$

$$\mathrm{I^*} + \mathrm{M_B} \xrightarrow{\mathrm{k_i^B}} \mathrm{P_1^B} \qquad \text{(S.3)}$$

Propagation

$$\mathrm{P_n^A} + \mathrm{M_A} \xrightarrow{\mathrm{k_{p,AA}}} \mathrm{P_{n+1}^A} \qquad \text{(S.4)}$$

$$\mathrm{P_n^A} + \mathrm{M_B} \xrightarrow{\mathrm{k_{p,AB}}} \mathrm{P_{n+1}^B} \qquad \text{(S.5)}$$

$$\mathrm{P_n^B} + \mathrm{M_A} \xrightarrow{\mathrm{k_{p,BA}}} \mathrm{P_{n+1}^A} \qquad \text{(S.6)}$$

$$\mathrm{P_n^B} + \mathrm{M_B} \xrightarrow{\mathrm{k_{p,BB}}} \mathrm{P_{n+1}^B} \qquad \text{(S.7)}$$

Chain transfer to VAc monomer

$$\mathrm{P_n^A} + \mathrm{M_A} \xrightarrow{\mathrm{k_{tr}^{mon,AA}}} \mathrm{D_n} + \mathrm{P_1^A} \qquad \text{(S.8)}$$

$$\mathrm{P_n^B} + \mathrm{M_A} \xrightarrow{\mathrm{k_{tr}^{mon,BA}}} \mathrm{D_n} + \mathrm{P_1^A} \qquad \text{(S.9)}$$

Chain transfer to Polymer

$$\mathrm{P_n^A} + \mathrm{D_m} \xrightarrow{\mathrm{k_{tr}^{pol,AA}}} \mathrm{D_n} + \mathrm{P_m^A} \qquad \text{(S.10)}$$

$$\mathrm{P_n^B} + \mathrm{D_m} \xrightarrow{\mathrm{k_{tr}^{pol,BA}}} \mathrm{D_n} + \mathrm{P_m^A} \qquad \text{(S.11)}$$

Termination*

$$P_n^A + P_m^A \xrightarrow{k_{td}} D_n + D_m \qquad (S.12)$$

$$P_n^A + P_m^B \xrightarrow{k_{td}} D_n + D_m \qquad (S.13)$$

$$P_n^B + P_m^B \xrightarrow{k_{td}} D_n + D_m \qquad (S.14)$$

*Only bimolecular termination by a disproportionation mechanism was considered.

A. Mass balances

The mass balance of the different components present in a batch reaction is given by the general equation S.15:

$$\frac{di}{dt} = \pm R_i \qquad [\mathrm{mol \cdot s^{-1}}] \qquad (S.15)$$

Where i is the total amount of moles of component i in the reactor, and R_i is the generation or disappearance rate by reaction.

Initiator decomposition

The rate of thermal decomposition of the initiator to generate radicals is given by the following equation:

$$R_I = 2fk_I[I_2]V \qquad [\mathrm{mol \cdot s^{-1}}] \qquad (S.16)$$

Where R_I [mol·s^{-1}] is the rate of generation of primary radicals (I^*) by the decomposition of the thermal initiator (of concentration $[I_2]$, [mol·l^{-1}]), k_I is the decomposition rate coefficient [s^{-1}] and V [l] is the volume of the reactor.

Chain initiation

The rate of chain initiation from the primary initiator radicals with the first monomer unit is given by equation S.17.

$$R_i = k_i^i[M_i][I^*]V \qquad [\mathrm{mol \cdot s^{-1}}] \qquad (S.17)$$

Where R_i is the chain initiation rate [mol·s^{-1}], k_i^i the chain initiation rate coefficient for monomer i [l·mol^{-1}·s^{-1}], $[M_i]$ is the concentration of monomer i [mol·l^{-1}] and $[I^*]$ the concentration of primary initiator radicals [mol·l^{-1}].

Propagation

The average propagation rate (R_p) is given by equation S.18.

$$\mathrm{R_p} = \Big[k_{p,AA}[M_A][P^A] + k_{p,AB}[M_{AB}][P^A] + k_{p,BA}[M_A][P^B] + + k_{p,BB}[M_B][P^B]\Big]\mathrm{V} \qquad [\mathrm{mol\cdot s^{-1}}] \qquad (\mathrm{S.18})$$

Where R_p is the average propagation rate [$\mathrm{mol\cdot s^{-1}}$], $k_{p,AA}$ and $k_{p,BB}$ [$\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$] are the homopropagation rate coefficients of monomers A and B, respectively, $k_{p,BA}$ is the propagation rate coefficient of a B monomer terminated radical with monomer A [$\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$], $k_{p,AB}$ is the propagation rate coefficient of a A monomer terminated radical with monomer B [$\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$], [$M_A$] and [$M_B$] [$\mathrm{mol\cdot l^{-1}}$] are the monomer concentrations of monomers A and B, and [P^A] and [P^B] are the concentration or radicals terminated in monomer units A and B.

Chain transfer to monomer

Only chain transfer to monomer A (vinyl acetate) was considered in the model.

$$\mathrm{R_{tr}^{mon,iA}} = \mathrm{k_{tr}^{mon,iA}}[\mathrm{M_A}][\mathrm{P^i}]\mathrm{V} \qquad [\mathrm{mol\cdot s^{-1}}] \qquad (\mathrm{S.22})$$

Where $\mathrm{R_{tr}^{mon,iA}}$ is the chain transfer rate from monomer i terminated radical with monomer A [$\mathrm{mol\cdot s^{-1}}$], $\mathrm{k_{tr}^{mon,iA}}$ is the chain transfer rate coefficient of a i terminated radical with monomer A [$\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$], [$M_A$] is the concentration of monomer A [$\mathrm{mol\cdot l^{-1}}$] and [P^i] is the concentration of active chains terminated in monomer i [$\mathrm{mol\cdot l^{-1}}$].

$$[\mathrm{P^i}] = [\mathrm{P_{tot}}]\cdot \mathrm{p_i} \qquad [\mathrm{mol\cdot l^{-1}}] \qquad (\mathrm{S.23})$$

Chain transfer to polymer

The chain transfer to polymer reaction was only considered to happen to a vinyl acetate unit in the terminated polymer chains.

$$\mathrm{R_{tr}^{pol,iA}} = \mathrm{k_{tr}^{pol,iA}}[\mathrm{D}]\mathrm{y_A}[\mathrm{P^i}]\mathrm{V} \qquad [\mathrm{mol\cdot s^{-1}}] \qquad (\mathrm{S.24})$$

Where $\mathrm{R_{tr}^{pol,iA}}$ is the chain transfer to polymer rate of i terminated active chain to a A unit in the dead chain [$\mathrm{mol\cdot s^{-1}}$], $\mathrm{k_{tr}^{pol,iA}}$ is the chain transfer to polymer rate coefficient of i terminated active chain to a A unit in the dead chain [$\mathrm{l\cdot mol^{-1}\cdot s^{-1}}$], [D] is the concentration of dead chains [$\mathrm{mol\cdot l^{-1}}$], y_A is the cumulative copolymer composition of monomer A [-] and [P^i] is the concentration of monomer i terminated active chains [$\mathrm{mol\cdot l^{-1}}$].

Termination

In the model, only termination by disproportionation was considered, with the same rate coefficient for all the radicals. It was calculated with the following equation:

$$\mathrm{R_{td}} = \mathrm{k_{td}}[\mathrm{P_{tot}}]^2\mathrm{V} \qquad [\mathrm{mol\cdot s^{-1}}] \qquad \text{(S.25)}$$

Where R_{td} is the termination rate [mol·s^{-1}] and k_{td} is the termination (by disproportionation) rate coefficient [l·mol^{-1}·s^{-1}] and [P_{tot}] is the overall radical concentration, as calculated in equation S.26.

Radical concentration

The overall radical concentration is the sum of all active chains, given by equation S.26.

$$[\mathrm{P_{tot}}] = \sum_{\mathrm{n=1}}^{\infty}[\mathrm{P_n}] \qquad [\mathrm{mol\cdot l^{-1}}] \qquad \text{(S.26)}$$

The mass balances of the active chains terminated in monomer i of length 1 ($\mathrm{P_1^i}$) or length n ($\mathrm{P_n^i}$, when n > 1) is calculated by the following differential equations.

$$\frac{\mathrm{d}[\mathrm{P_1^i}]}{\mathrm{dt}} = \left[\mathrm{k_i^i}[\mathrm{M_i}][\mathrm{I^*}] + \mathrm{k_{tr}^{mon,iA}}[\mathrm{M_A}]\sum_{\mathrm{n=1}}^{\infty}[\mathrm{P_n^i}] - \mathrm{k_p^{ij}}[\mathrm{M_j}][\mathrm{P_1^i}] - \mathrm{k_{td}}[\mathrm{P_1^i}]\sum_{\mathrm{n=1}}^{\infty}[\mathrm{P_n^j}] - \mathrm{k_{tr}^{mon,iA}}[\mathrm{M_A}][\mathrm{P_1^i}]\right]\mathrm{V} \qquad [\mathrm{mol\cdot l^{-1}\cdot s^{-1}}] \quad \text{(S.27)}$$

$$\frac{\mathrm{d}[\mathrm{P_n^i}]}{\mathrm{dt}} = \left[\mathrm{k_p^{ji}}[\mathrm{M_i}][\mathrm{P_{n-1}^j}] - \mathrm{k_p^{ij}}[\mathrm{M_j}][\mathrm{P_n^i}] - \mathrm{k_{tr}^{mon,ij}}[\mathrm{M_j}][\mathrm{P_n^i}] + \mathrm{k_{tr}^{pol,iA}}\mathrm{n}[\mathrm{D_n}]\mathrm{y_A}\sum_{\mathrm{m=1}}^{\infty}[\mathrm{P_m^i}] - \right.$$
$$\left. -\mathrm{k_{tr}^{pol,iA}}[\mathrm{P_n^i}]\sum_{\mathrm{m=1}}^{\infty}\mathrm{m}[\mathrm{D_m}] - \mathrm{k_{td}}[\mathrm{P_n^i}]\sum_{\mathrm{m=1}}^{\infty}[\mathrm{P_m^j}]\right]\mathrm{V} \qquad [\mathrm{mol\cdot l^{-1}\cdot s^{-1}}] \quad \text{(S.28)}$$

Monomer conversion

The monomer conversion (x) was calculated by the following equation:

$$\mathrm{x} = \frac{[\mathrm{M}]_0 - [\mathrm{M}]_\mathrm{t}}{[\mathrm{M}]_0} \qquad [\text{-}] \qquad \text{(S.29)}$$

Where $[M]_0$ is the (total) initial monomer concentration and $[M]_t$ is the total monomer concentration at time t calculated by equation S.30.

$$\frac{d[M_i]}{dt} = -R_{p,i} - R_{i,i} - R_{tr}^{mon,iA} \qquad [mol \cdot l^{-1} \cdot s^{-1}] \qquad (S.30)$$

Dead chains

The mass balances of the dead chains of length n (D_n) are calculated by the following differential equation.

$$\frac{d[D_n]}{dt} = \left[k_{tr}^{mon,iA}[M_j][P_n^i] + k_{td}[P_n^i]\sum_{m=1}^{\infty}[P_m^j] + k_{tr}^{pol,iA}[P_n^i]\sum_{m=1}^{\infty} m[D_m] - k_{tr}^{pol,iA} n[D_n]y_A \sum_{m=1}^{\infty}[P_m^i]\right]V$$

$$[mol \cdot l^{-1} \cdot s^{-1}] \quad (S.31)$$

The resulting set of differential equations was solved using the commercial software Predici version 7.45[3].

B. Reaction rate coefficients

a) Bulk and solution copolymerizations

The reaction rate coefficients that were used in the model to simulate the bulk and solution copolymerization are listed in Table S.3.

Table S.3. Reaction rate coefficients used for the bulk and solution polymerization models.

Coefficient	Unit	Reference
$k_I = 3.2 \cdot 10^{15} \cdot \exp^{-131100/8.31 \cdot T}$ (AIBN)	$L \cdot mol^{-1} \cdot s^{-1}$	[4]
$f = 0.65$	-	Assumed
$k_i^A = k_{p,AA}$	$L \cdot mol^{-1} \cdot s^{-1}$	Assumed
$k_i^B = k_{p,BB}$	$L \cdot mol^{-1} \cdot s^{-1}$	Assumed
$k_{p,AA} = 2.72 \cdot 10^7 \cdot \exp^{-21800/8.31 \cdot T}$	$L \cdot mol^{-1} \cdot s^{-1}$	[5]
$k_{p,AB} = k_{p,AA}/r_A$	$L \cdot mol^{-1} \cdot s^{-1}$	Defined
$k_{p,BA} = 411$	$L \cdot mol^{-1} \cdot s^{-1}$	Estimated in this work
$k_{p,BB} = 0$	$L \cdot mol^{-1} \cdot s^{-1}$	Estimated in this work
$r_A = 0.211$	-	Estimated in this work
$k_{tr}^{mon,AA} = k_{tr}^{mon,BA} = 4.55 \cdot 10^{-4} \cdot k_{pAA}$	$L \cdot mol^{-1} \cdot s^{-1}$	[4]
$k_{tr}^{pol,AA} = k_{tr}^{pol,BA} = 2 \cdot 10^{-4} \cdot k_{pAA}$	$L \cdot mol^{-1} \cdot s^{-1}$	[4]
$k_{td} = 1 \cdot 10^7$	$L \cdot mol^{-1} \cdot s^{-1}$	[4]

b) Aqueous phase of the emulsion polymerization

The reaction rate coefficients that were used in the model to simulate the aqueous phase of the emulsion copolymerization are listed in Table S.4.

Table S.4. Reaction rate coefficients used for the simulation of the water phase of the emulsion polymerization.

Coefficient	Unit	Reference
$k_I = 8.0\cdot10^{15}\cdot\exp^{-135000/8.31\cdot T}$ (KPS)	$L\cdot mol^{-1}\cdot s^{-1}$	[6]
$f = 0.9$	-	Assumed
$k_i^A = k_{p,AA}$	$L\cdot mol^{-1}\cdot s^{-1}$	Assumed
$k_i^B = k_{p,BB}$	$L\cdot mol^{-1}\cdot s^{-1}$	Assumed
$k_{p,ij}$	$L\cdot mol^{-1}\cdot s^{-1}$	Calculated in this work
$k_{td} = 1\cdot10^7$	$L\cdot mol^{-1}\cdot s^{-1}$	[4]

S.3. Simulation of the solution copolymerization of VAc and VTMS

The solution copolymerization of vinyl acetate and VTMS was simulated using the data from the reactivity ratios in section S.1 and the model presented in section S.2. In Figure S.8 the time evolution of the conversion, during the batch solution copolymerization of VAc and VTMS is presented.

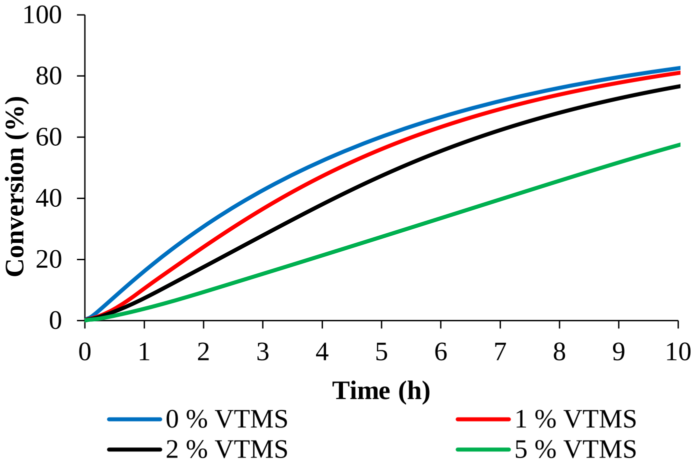


Figure S.8. Simulated evolution of conversion during the solution copolymerization of VAc with different concentrations of VTMS.

As it was observed experimentally, as the VTMS concentration increases the overall polymerization rate decreases. Moreover, when 5 wt% of VTMS is used the polymerization is not stopped. These results are very close to the experimental solution copolymerization results, particularly considering that no fitting of the unknown rate coefficients (that were taken from literature) was done.

S.4. Characterization of the water-soluble species in the copolymerization of vinyl acetate and vinyl trimethoxysilane

The aqueous phase and the polymer particles of the latex were separated by centrifugation, in a Sorvall Legend XTR (Thermofisher) centrifuge at 12,000, rpm and 4ºC for 3h.

A. Molar mass distribution

The molar mass distribution of the supernatant was measured by SEC directly injecting the supernatant without further purification. The equipment was composed by a LC20 pump (Shimadzu) coupled to an Optilab Rex differential refractometer (658 nm) (all from Wyatt Technology Corp., USA). Separation was carried out using three columns in series (Ultrahydrogel 120, 250, and 2000 with pore sizes of 120, 250, and 2000 Å, respectively, Waters, Barcelona, Spain). The analyses were carried out at 35°C and ultrapure water was used as mobile phase at a flow rate of 0.6 ml min-1. Universal calibration of 3rd order with PEG/PEO standards between 1,970g/mol and 44,000g/mol was used.

Figure S.9 shows the molar mass distributionof the copolymers with 0, 1 and 2 wt% of VTMS.

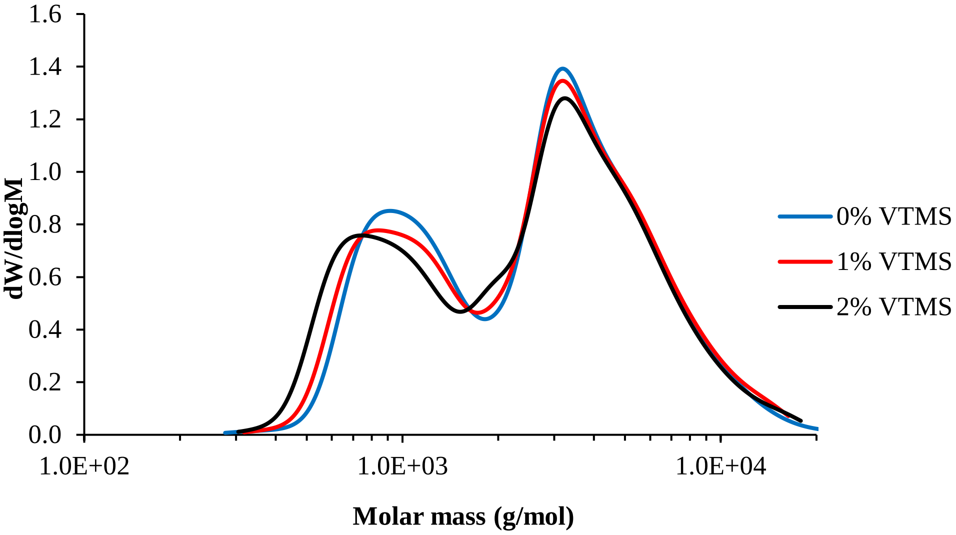


Figure S.9. Concentration chromatogram and molar mass distribution of the water-soluble species found in the supernatant after centrifugation.

The sample with 5 wt% of VTMS could not be analyzed, because of the negligible conversion of the polymer. The molar mass distribution of the other three samples is nearly identical. In all cases, a bimodal distribution is obtained, but similar concentrations of water-soluble species was found for experiments with and without VTMS. The only noticeable difference is that there is a shift towards lower molar mass in the low molar mass population as the VTMS content increases. This is in agreement with a lower propagation rate with an increasing concentration of VTMS.

B. Composition

^{1}H-NMR was used to study the composition of the supernatant. The analysis were performed in a Bruker AVANCE 400 MHz spectrometer with D_2O as solvent and using the WATERGATE pulse sequence for suppression of the signal from water. Figure S.10 shows the ^{1}H-NMR spectra of the supernatants. As a reference, the ^{1}H-NMR spectra of the monomers in water and the surfactant (Dowfax 2A1) are also included.

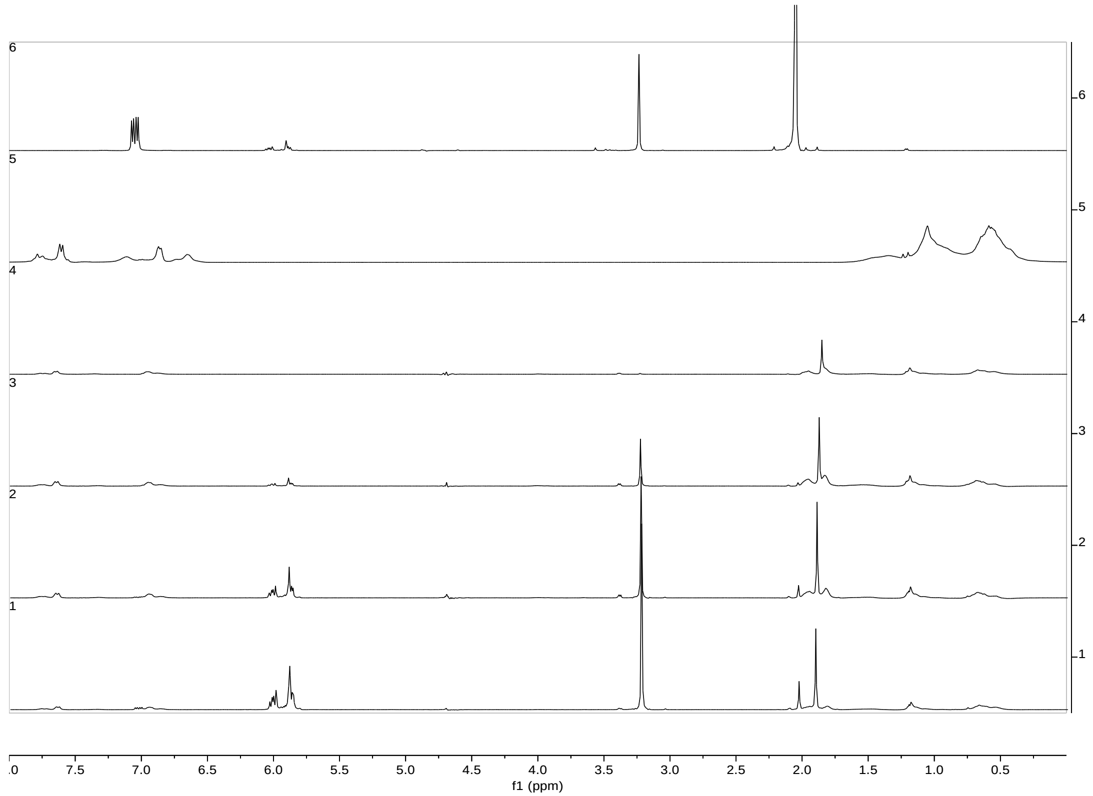


Figure S.10. ^{1}H-NMR of the VAc and VTMS in water (6), Dowfax 2A1 in water (5) and the supernatants of VAc-VTMS latexes containing 0 wt% of VTMS (4), 1 wt% of VTMS (3), 2 wt% of VTMS (2) and 5 wt% of VTMS (1).

Very similar spectra are obtained for all compositions. The signals from the surfactant (Dowfax 2A1) between 7 and 8 ppm and between 0.5 and 1.25 ppm have similar intensities in all cases. The vinyl acetate monomer traces (at 2.04 ppm), on the other hand, have higher intensities as the VTMS concentration in the sample increases, indicating a lower overall monomer conversion. More significantly, the signals of the unreacted vinyl bonds of the vinyl silane (between 5.85 and 6.50 ppm) are much more intense with an increasing VTMS concentration. Figure 10 shows a zoom of the signals that change with the silane concentration.

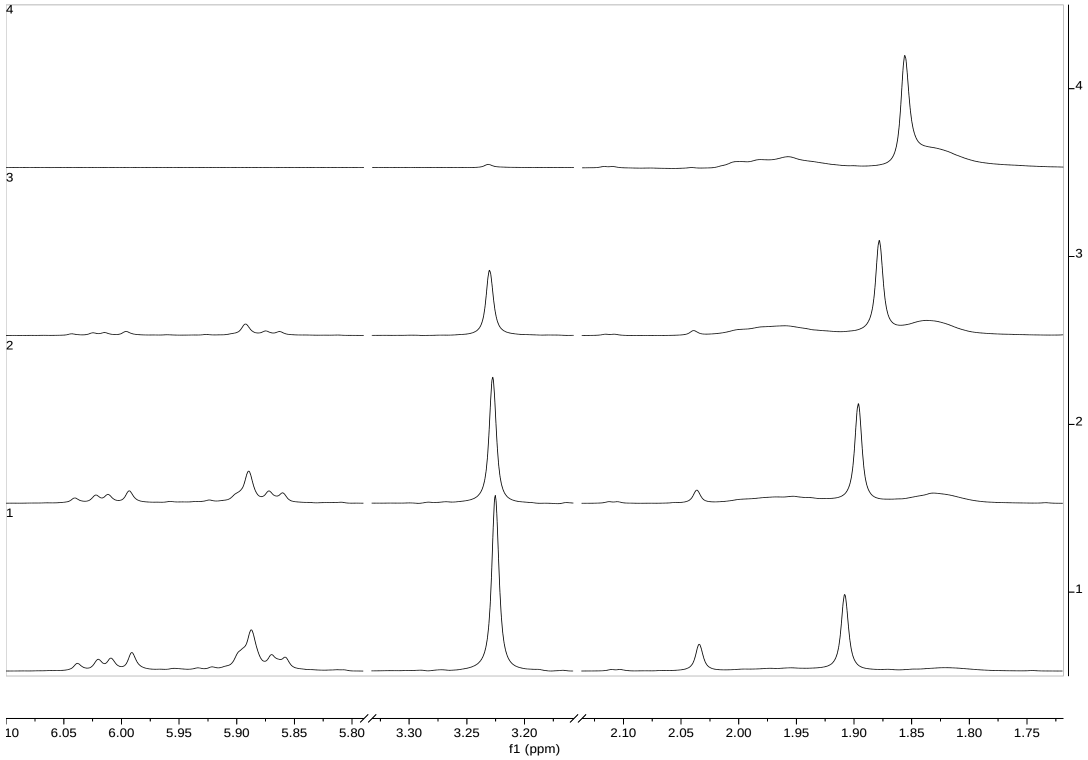


Figure S.11. Zoom of the relevant regions on the ^{1}H-NMR of the VAc-VTMS latexes containing 0 wt% of VTMS (4), 1 wt% of VTMS (3), 2 wt% of VTMS (2) and 5 wt% of VTMS (1).

There are some interesting features on the spectra. The signals that correspond to the unreacted vinyl group of the VTMS (between 5.85 and 6.50 ppm) are easier to see. An increasing intensity of the vinyl signals as the VTMS concentration increases shows that a higher concentration of unreacted monomer is present in the aqueous phase, as observed in the conversion plots (Figure 1). The intense peak at 3.23 ppm also corresponds to the VTMS (the methoxy groups), and increases with the VTMS concentration too. The signal at 2.04 ppm belongs to the unreacted VAc monomer, as discussed above.

On the other hand, the sharp signal around 1.80-1.90 ppm and the broad band between 1.75 and 1.85 belong to the poly(vinyl acetate). Interestingly, the sharp signal shifts towards lower fields as the VTMS concentration increases, which suggests that the copolymer composition is slightly different for the four cases.

S.5. Partitioning coefficients of the vinyl silane monomers between vinyl acetate and water

Silane partitioning was determined by mixing different amounts of silane with monomer/water mixtures and measuring the concentration of silane in one or both of the phases. The concentration of the non-hydrolyzed silanes (VTMS, VTES) was measured in the water phase by gas chromatography, whereas the concentration of the hydrolyzed vinyl silane (VSTO) was determined by gravimetric analysis in both phases.

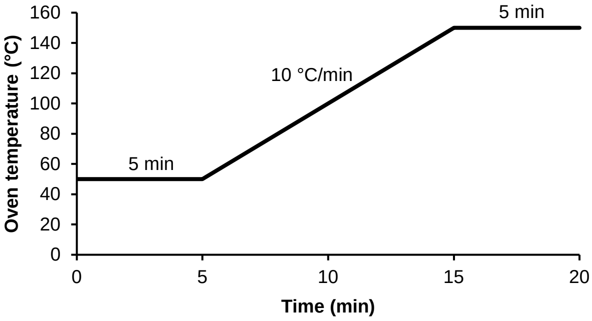
A. Experimental

a) Vinyl trimethoxysilane and vinyl triethoxysilane

In a 27 ml vial, the silane was weighted. Then the necessary amount of vinyl acetate and pH 6 buffered water were added in that order. The vial was hand-shaken for 1 minute, and then the phases were left to separate for 5 minutes. 4 ml from the water phase were taken with a syringe and after adding a known amount of internal standard (10 µl, butanol), 0.5 µl were injected in the gas chromatograph.

Gas chromatography measurements were done in a GC-14A (Shimadzu) chromatograph equipped with flame ionization detector (FID) and an integrator (Shimadzu C-R6A Chromatopac). The column was a BP624 (from SGE analytical science) of 50 m, inner diameter of 0.53 mm and film thickness of 3.0 µm. Table S.5 shows the gas chromatography conditions.

Table S.5. Gas chromatography conditions for the quantification of VTMS and VTES.

Injector temperature	170 °C
Injector operation mode	Splitless
Injection volume	0.5 µl
Carrier gas	Helium
Column	BP624
Operation mode	Constant pressure
Injector pressure	0.5 kg/cm^2
Detector temperature	250 °C
Temperature program	

Different monomer/water ratios and amounts of silane were used, and the concentration of the silane was determined in the water phase. The compositions used are presented in Tables 2.3 to 2.6 for VTMS, and VTES.

Table S.6. Composition of the mixtures for the calculation of the partitioning coefficient of VTMS in water.

	VAc/H_2O	VTMS [wt%]*
Sample 1	30/70	1.0
Sample 2	50/50	1.0
Sample 3	30/70	2.0
Sample 4	50/50	1.5
Sample 5	20/80	0.5

*With respect to VAc.

Table S.7. Composition of the mixtures for the calculation of the partitioning coefficient of VTES in water.

	VAc/H_2O	VTES [wt%]*
Sample 1	30/70	1.0
Sample 2	30/70	2.0
Sample 3	50/50	1.0
Sample 4	50/50	1.0
Sample 5	20/80	1.5
Sample 6	10/90	2.0

*With respect to VAc.

b) Vinyl silanetriol

The vinyl silanetriol (VSTO) could not be quantified in the gas chromatograph. Instead, its concentration was determined gravimetrically by allowing the full polycondensation reactions to go on (thus forming a nonvolatile solid). The protocol was the following:

The VSTO was obtained in the moment by hydrolyzing VTMS right before the measurement. For that, the necessary amount of VTMS was mixed with 12 g of 0.01 N HCl aqueous solution and strongly agitated for 3 minutes until optical clarity of the mix was achieved. After adding 40 g of pH 6 buffered water and 20 g of VAc, the mixture was strongly agitated for 1 minute and left 5 minutes to rest to allow phase separation. After separating both phases, they were left to evaporate at 100 ºC and vacuum and the solid that was formed in each phase was weighted. Table S.8 shows the ratios that were used for this set of experiments.

Table S.8. Composition of the mixtures for the calculation of the partitioning coefficient of VSTO in water.

	VAc/H_2O	VSTO [wt%]*
Sample 1	30/70	1.0
Sample 2	30/70	3.0
Sample 3	30/70	5.0
Sample 4	30/70	7.0
Sample 5	30/70	10.0

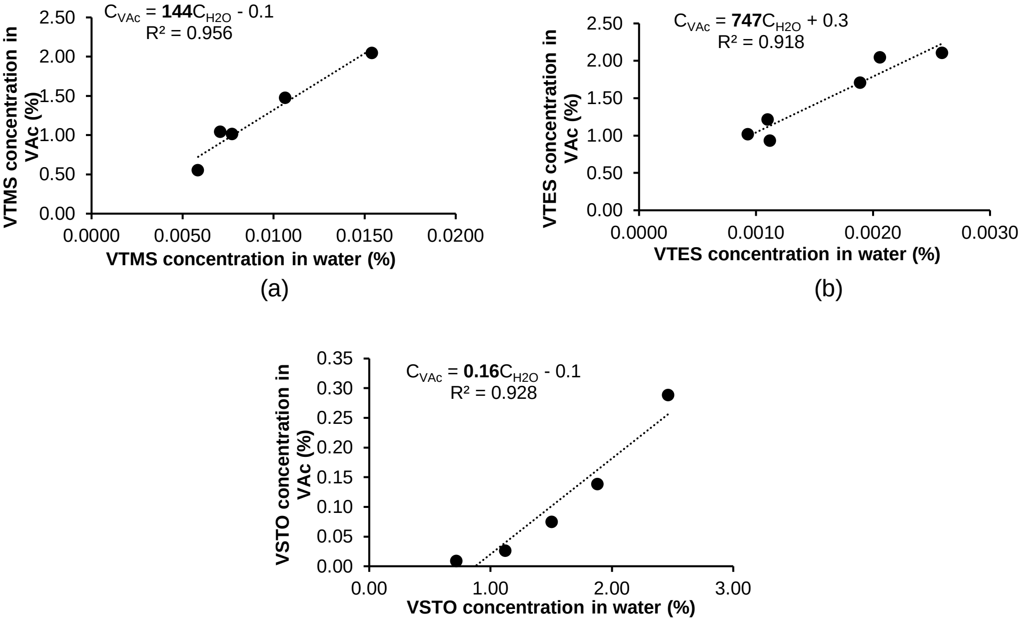
*With respect to VAc.

B. Results

The partitioning coefficient is defined as the ratio of the solute concentration between the organic and aqueous phases. Therefore, the concentration of the silane in the organic phase was plotted over its concentration in the aqueous phase using different compositions. The partition coefficient was obtained from the slope of the curve as presented in Figure S.12.

Table S.9 shows the partitioning coefficients calculated from Figure S.12, and the calculation of the percentage of silane in each phase considering a monomer/water ratio of 30/70. As observed, there is a very significant difference between the non-hydrolyzed silanes (VTMS, VTES) and the hydrolyzed VSTO. The non-hydrolyzed silanes are almost completely in the monomer phase (although not in the same amount), while the VSTO is mostly in the water phase.

The differences in the organic phase of the non-hydrolyzed silanes are nearly negligible, but the concentration in the water phase presents significant differences.



(a) (b)

(c)

Figure S.12. Calculation of the partition coefficient of VTMS (a), VTES (b) and VSTO (c) between VAc and water.

Table S.9. Partitioning coefficients of the silanes.

	VTMS	VTES	VSTO
Partitioning coefficient	144	747	0.161
Silane in monomer phase (%)*	98.41	99.69	6.46
Silane in water phase (%)*	1.59	0.31	93.54

*When the VAc/H_2O ratio is 30/70 wt%

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