Supporting information

Influence of experimental parameters on the side reactions of hydrosilylation of allyl polyethers studied by a fractional factorial design

A. Bouvet-Marchand,[a,b] C. Chatard,[a] A. Graillot,[a*] G. Boutevin,[a] C. Loubat,[a] D. Grosso[b]*

[a]SPECIFIC POLYMERS, 34160 Castries, France

[b]Aix-Marseille University, IM2NP, 13397 Marseille, France

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S 1. Methodology of the fractional factorial design

More details on the elaboration of the fractional factorial design and its analysis are presented here.

To afford the reduction of experimental runs in fractional factorial design, some main factors need to be aliased, *ie.* main factors had to be confounded with the estimate of an interaction. This loss of information is *a price one must pay for choosing a smaller design*.[1] Here, the factors X_4 and X_5 were respectively aliased with the interactions X_1X_2 and X_1X_3.. Using the Box notation, for which the column of the factor X_n is noted **n,** these two relations can be written : **4**=**12** and **5**=**13**. This implies that the signs of the column 4 and 5 are respectively the

results of the multiplications of the column 1 and 2' signs and column 1 and 3'signs. With I denoting the column of all +'s, the relations can be noted as I≡124 and I≡135. These expressions are called the generators of the design and the equation **I=124=135** is called the defining relation, giving the complete confounding pattern for this design of resolution III. As a consequence of aliasing two factors, the set of experiments was reduced to 8 runs ($2^{5-2}=2^3=8$).

By ignoring the third and fourth-factor interactions, the equation of the matrix response can be described as follows :

$$y = b_0 + b_1X_1 + b_2X_1 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_4 + b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 + b_{45}X_4X_5$$

To reduce the number of unknown parameters, 8 contrasts are introduced as estimators of the aliased coefficients. These contrasts are built from the defining relation. For example, the estimator β_1 was obtained by multiplying each term of the generating relation by **1**, *ie.* **1**.**I**=**1**=**1**.**124**=**1**.**135**, leading to the relation $\beta_1 = b_1 + b_{24} + b_{35}$.

The new model is then reduced to 8 unknown parameters :

$$y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_5X_5 + \beta_{23}X_{23} + \beta_{34}X_{34}$$

By replacing the vector X_n by their signs for each run, 8 equations can be obtained. Their resolution conduct to the expression of the contrasts. As for example, β_1 can be calculated as follows with y_n, the response for each run :

$$\beta_1 = \frac{-y_1 + y_2 - y_3 + y_4 - y_5 + y_6 - y_7 + y_8}{8} = b_1 + b_{24}$$

However, a DOE with a resolution III only enables the estimation of the contrasts βn and is therefore not sufficient to evaluate the effect of each factor (b_n). By building the opposite

design of experiments with the following defining relation I=-124=-135=2345 and the respective contrasts β'n, it was then possible to attain a design of experiments of resolution IV. The number of experiments were therefore doubled. The different equations connecting β_n and β'_n to b_n were resolved to deduce the estimation of each coefficient b_n, giving valuable information on the effect of each factor.

The final design of experiments with a resolution IV is presented in Table 2 (see manuscript). Because different results can be obtained from the same experiment, replicated runs were carried out in order to estimate the experimental error of this DOE, representing its dispersion of results.

S 2. Characterization of the PEG hydrogenated form

2D-COSY and 2D-HSQC coupled with DEPT 135 analyses were required in complement to the ^{1}H NMR to identify the hydrogenated form of the PEG. Indeed, the signals corresponding to the CH_2 of the hydrogenated PEG were overlapped by the signals of the polyether and the different by-products and were not visible in ^{1}H NMR. However, the signal of the methyl of the hydrogenated form was clearly observed at 0.9 ppm (N°15). It was demonstrated at first by 2D- COSY that the peak N°15 was correlated to another signal at 1.62 ppm (N°16, see Figure S1).

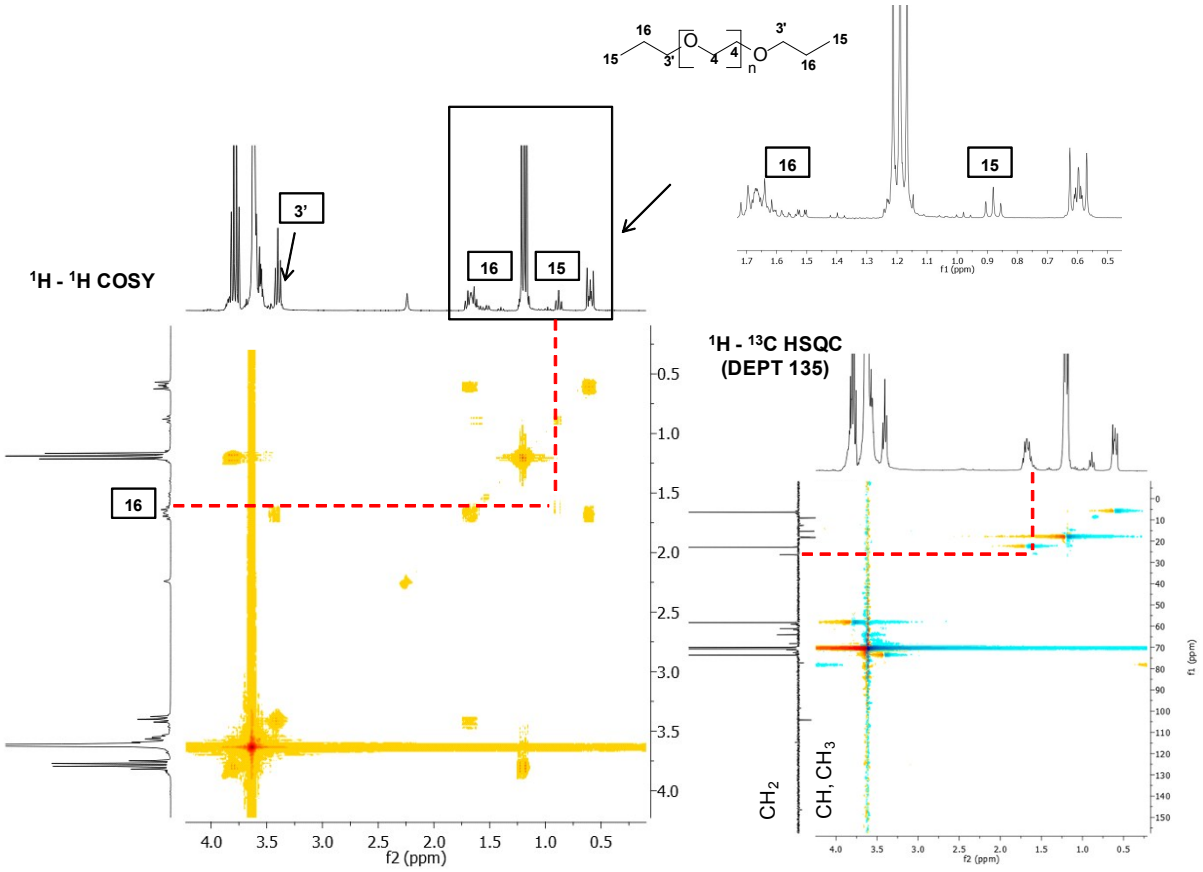

Figure S1. 2D-COSY and HSQC-DEPT 135 spectra of the run N°10 after treatment.

By HSQC-DEPT 135, this peak 16 was proved to correspond to a methylene. However, the CH_2 in alpha of the oxygen (N°3'), expected at 3.4 ppm, was not visible neither by COSY nor by HSQC because its intensity was overly low compared to the CH_2 of the polyether repetitive motifs. Even though this signal was not observed, the presence of a CH_3-CH_2 saturated bond at these chemical shifts clearly indicates that these peaks correspond to the hydrogenated form of the PEG.

S 3. Quantification of the side reactions by ^{1}H NMR

After complete conversion of the allyl-ether functions (Figure S2), characteristic peaks of the PEG-functionalized alkoxysilane and of the different by-products were integrated in the ^{1}H NMR spectrum obtained for each run.

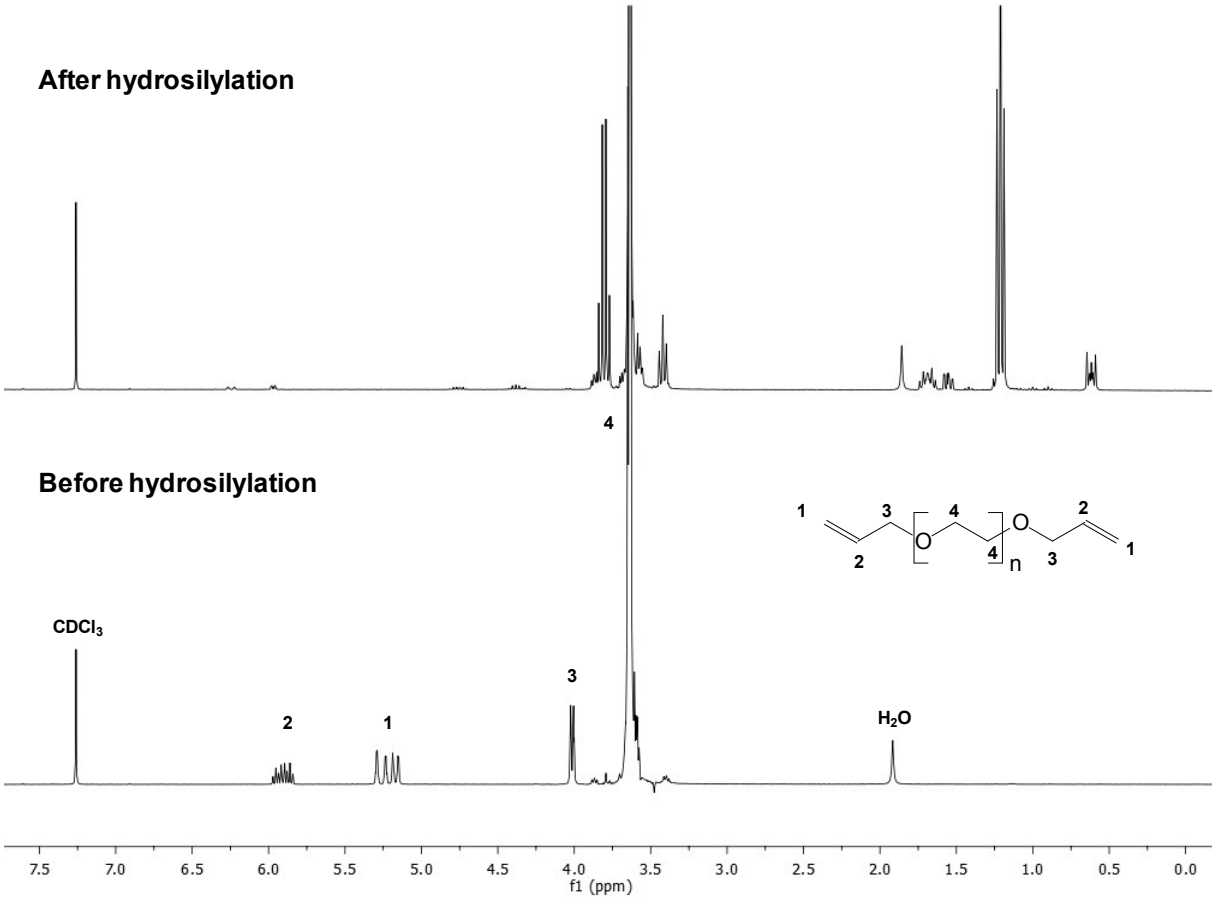

Figure S2. Superimposed spectra of the PEG terminated allyl-ether (bottom spectrum) with the spectrum of the treated product after hydrosilylation (top spectrum)

The proportions of each by-product were then determined by calculating the ratio between the integral of 2 protons of the corresponding side-product on the sum of the integrals of 2 protons of each product formed (see equations below). $^{I_{CH_2(1)}}$ is the integral of the C**H₂**-Si of the PEG-terminated alkoxysilane. $^{I_{CH_{(7)}}}$ and $^{I_{CH_{(8)}}}$ correspond respectively to the integrals of the *trans*-C**H**-O and *cis*-C**H**-O of the PEG-terminated propenyl-ether. $^{I_{CH_2(13)}}$ is the integral of the C**H₂** of the propanal formed during the cleavage and $^{I_{CH_3(15)}}$ the integral of the C**H**$_3$ of the hydrogenated form of the PEG.

$$\%_{iso} = \frac{2 \times (I_{CH_{(7)}} + I_{CH_{(8)}}) \times 100}{I_{CH_{2(1)}} + 2 \times \left(I_{CH_{(7)}} + I_{CH_{(8)}}\right) + I_{CH_{2_{(13)}}} + (\frac{2}{3}) \times I_{CH_{3(15)}}}$$

$$\%_{cl} = \frac{I_{CH_{2(13)}} \times 100}{I_{CH_{2(1)}} + 2 \times \left(I_{CH_{(7)}} + I_{CH_{(8)}}\right) + I_{CH_{2_{(13)}}} + (\frac{2}{3}) \times I_{CH_{3(15)}}}$$

$$\%_{hyd} = \frac{(\frac{2}{3}) \times I_{CH_{3(15)}} \times 100}{I_{CH_{2(1)}} + 2 \times \left(I_{CH_{(7)}} + I_{CH_{(8)}}\right) + I_{CH_{2_{(13)}}} + (\frac{2}{3}) \times I_{CH_{3(15)}}}$$

S 4. ANOVA analysis of each side reactions

The analysis of variance for all three responses are presented in Table S 1, S 2 and S 3.

Table S 1. Analysis of variance for the isomerization response

Factor	Sum of squares	Df	Mean square	F	p-value
X_2	17.22	1	17.22	5.85	0.032
X_4	11.90	1	11.90	4.04	0.067
X_5	10.89	1	10.89	3.70	0.078
Residual	35.30	12	2.94		
Total (corrected)	75.31				

Table S 2. Analysis of variance for the cleavage response

Factor	Sum of squares	Df	Mean square	F	p-value
X_3	2.25	1	2.25	1.71	0.22
X_4	4.62	1	4.62	3.52	0.09
X_5	2.10	1	2.10	1.60	0.23
X_{23}	5.52	1	5.52	4.21	0.07
X_{24}	4.0	1	4.0	3.05	0.11
Residual	13.12	10	1.31		
Total (corrected)	31.62				

Table S 3. Analysis of variance for the hydrogenation response

Factor	Sum of squares	Df	Mean square	F	p-value
X_4	1.27	1	1.27	4.61	0.05
X_5	1.76	1	1.76	6.39	0.025
Residual	3.57	13	0.27		
Total (corrected)	6.59				

References

1. Wu, C.-F.; Hamada, M., *Experiments : planning, analysis, and optimization*. 2nd ed.; Wiley: Hoboken, N.J., 2009; p xxix, 716 p.