Triple benefits of cardanol as chain stopper, flame retardant and reactive diluent for greener alkyd coating

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1. NMR spectra

1.1 ^{1}H NMR spectra

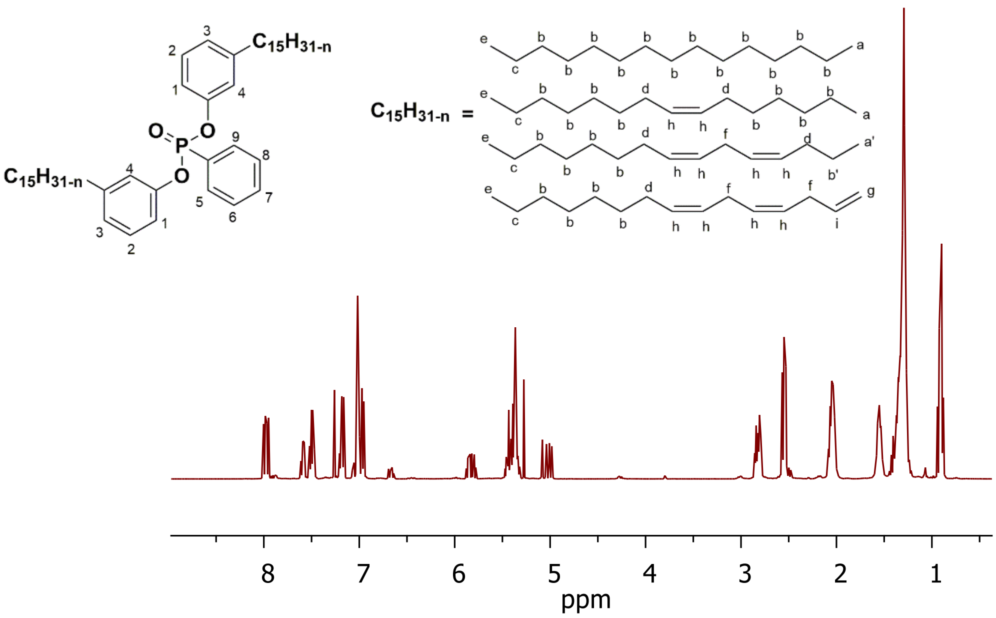

Figure S1: ^{1}H NMR spectra of phosphonate-cardanol compound

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.99 (m, 2H, aromatic protons 5 and 9), 7.59 (dt, 1H, aromatic protons 7), 7.50 (m, 2H aromatic protons 6 and 8), 7.19 (t, 2H, aromatic protons 2), 6.99 (m, 6H, aromatic protons 1, 3, and 4), 5.80–5.90 (m, 1H, CH of C_{15} chain, proton i), 5.34–5.50 (m, CH of C_{15} chain, internal double bond protons h), 4.98–5.11 (m, 2H, CH_2 of C_{15} chain, protons of the terminal double bond g), 2.82 (m, 2H, CH_2 of C_{15} chain, protons f), 2.61 (t, 2H, CH_2 of C_{15} chain, protons e), 2.00–2.15 (m, 2H, CH_2 of C_{15} chain, protons d), 1.64 (m, 2H, CH_2 of C_{15} chain, protons c), 1.20–1.50 (m, CH_2 of C_{15} chain, protons b, b'), 0.92 (m, 3H, CH_3 of C_{15} chain, terminal –CH_3, protons a, a').

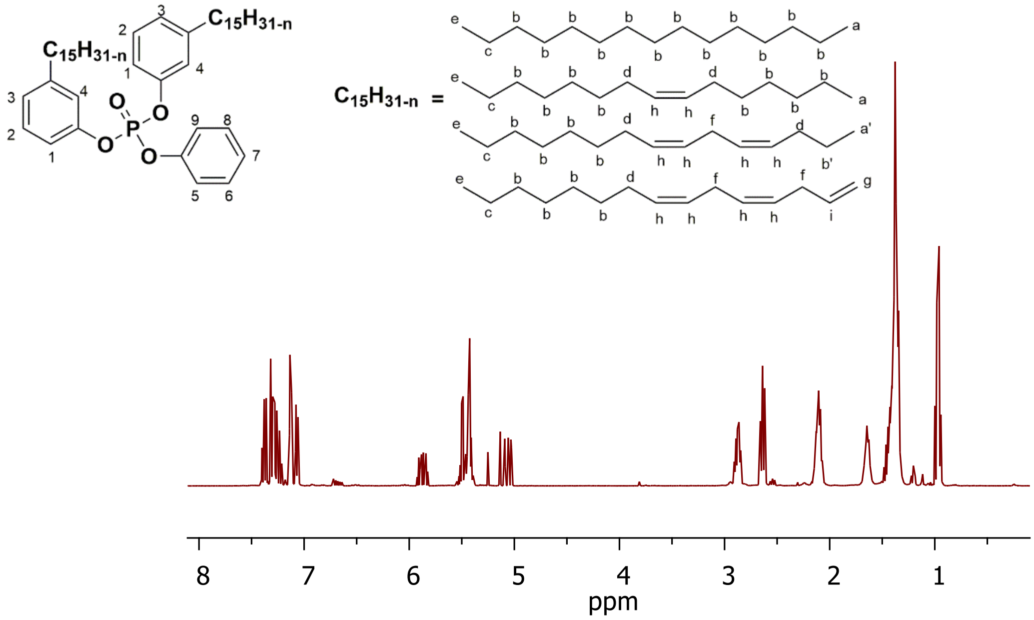

Figure S2: [1]H NMR spectra of phosphate-cardanol compound

[1]H NMR (400 MHz, $CDCl_3$, ppm): δ: 7.37 (m, 2H, aromatic protons 5 and 9), 7.24-7.28 (m, 3H, aromatic protons 6, 7 and 8), 7.19-7.24 (m, 2H, aromatic proton 2), 7.05 (m, 6H, aromatic protons 1, 3, and 4), 5.80–5.90 (m, 1H, CH of C_{15} chain, proton i), 5.34–5.50 (m, CH of C_{15} chain, internal double bond protons h), 4.98–5.11 (m, 2H, CH_2 of C_{15} chain, protons of the terminal double bond g), 2.82 (m, 2H, CH_2 of C_{15} chain, protons f), 2.61 (t, 2H, CH_2 of C_{15} chain, protons e), 2.00–2.15 (m, 2H, CH_2 of C_{15} chain, protons d), 1.64 (m, 2H, CH_2 of C_{15} chain, protons c), 1.20–1.50 (m, CH_2 of C_{15} chain, protons b, b'), 0.92 (m, 3H, CH_3 of C_{15} chain, terminal –CH_3, protons a, a').

1.2 [31]P NMR spectra

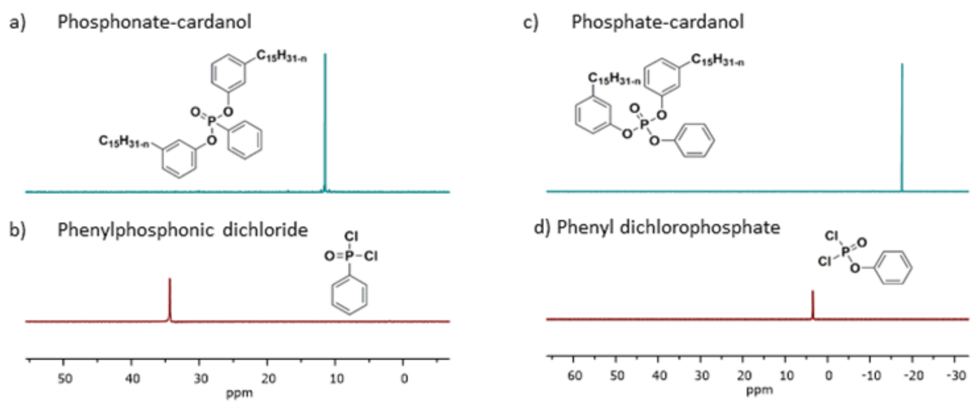

Figure S3: [31]P NMR spectra of (a) phosphonate- and (b) phosphate-cardanol compounds and their (c and d) initial phosphory-lated reagents.

1.3 [1]H NMR spectra

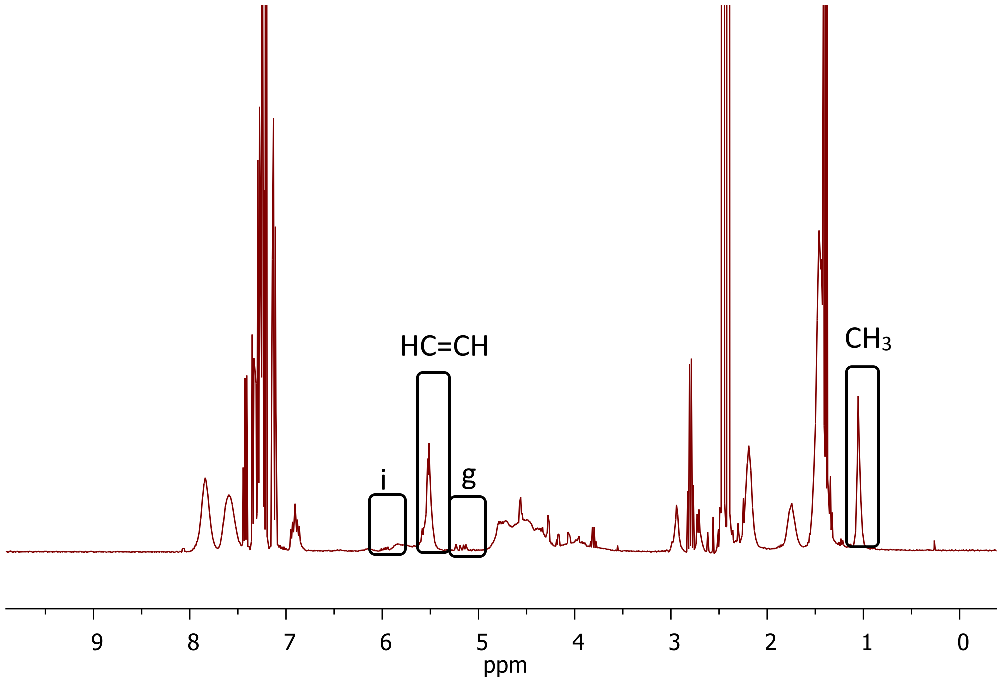

Figure S4: [1]H NMR spectrum of reference alkyd resin before curing

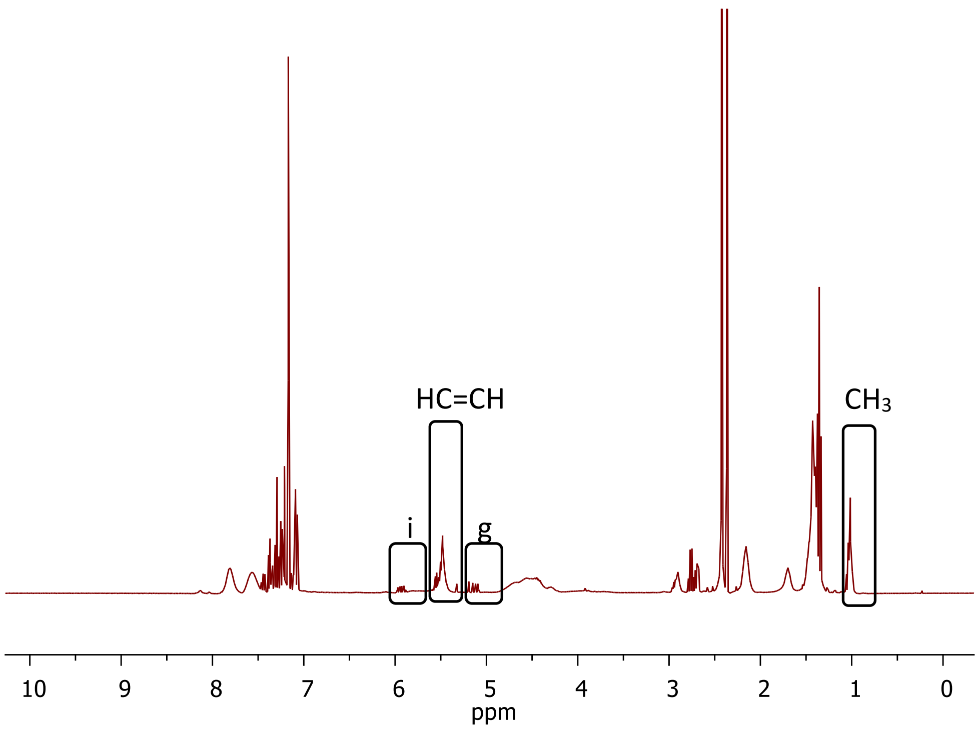

Figure S5: [1]H NMR spectrum of 1wt % P PO_3CR alkyd resin before curing

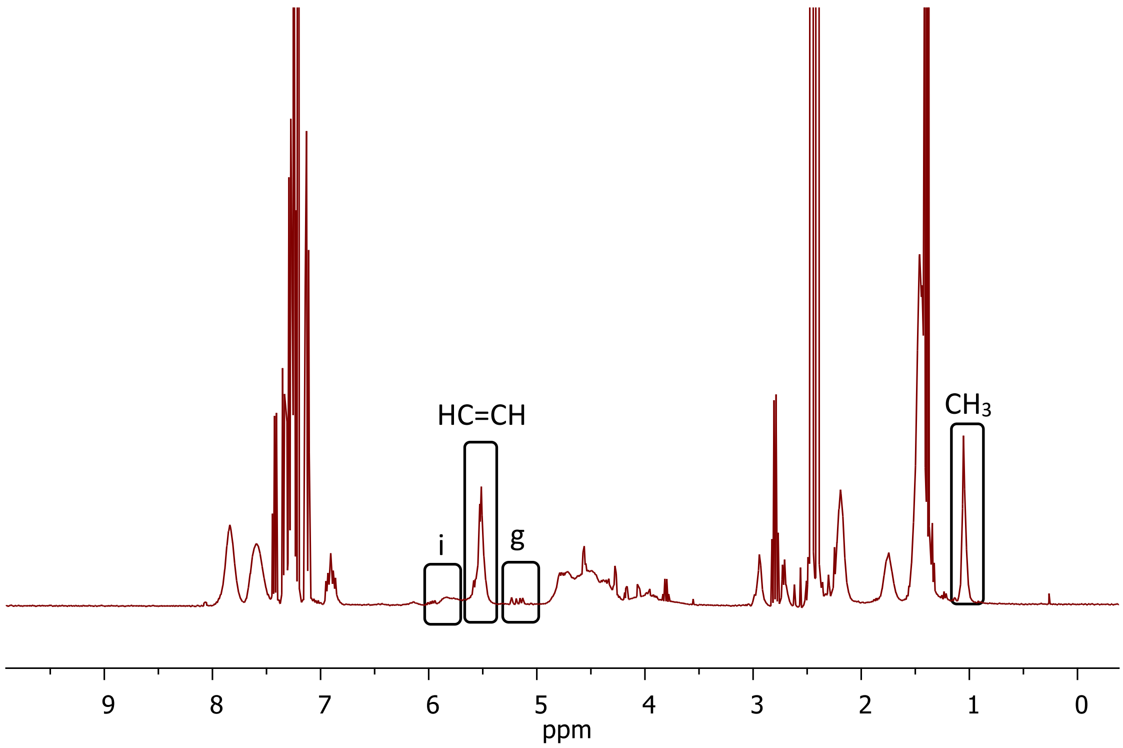

Figure S6: [1]H NMR spectrum of 2wt % P PO_3CR alkyd resin before curing

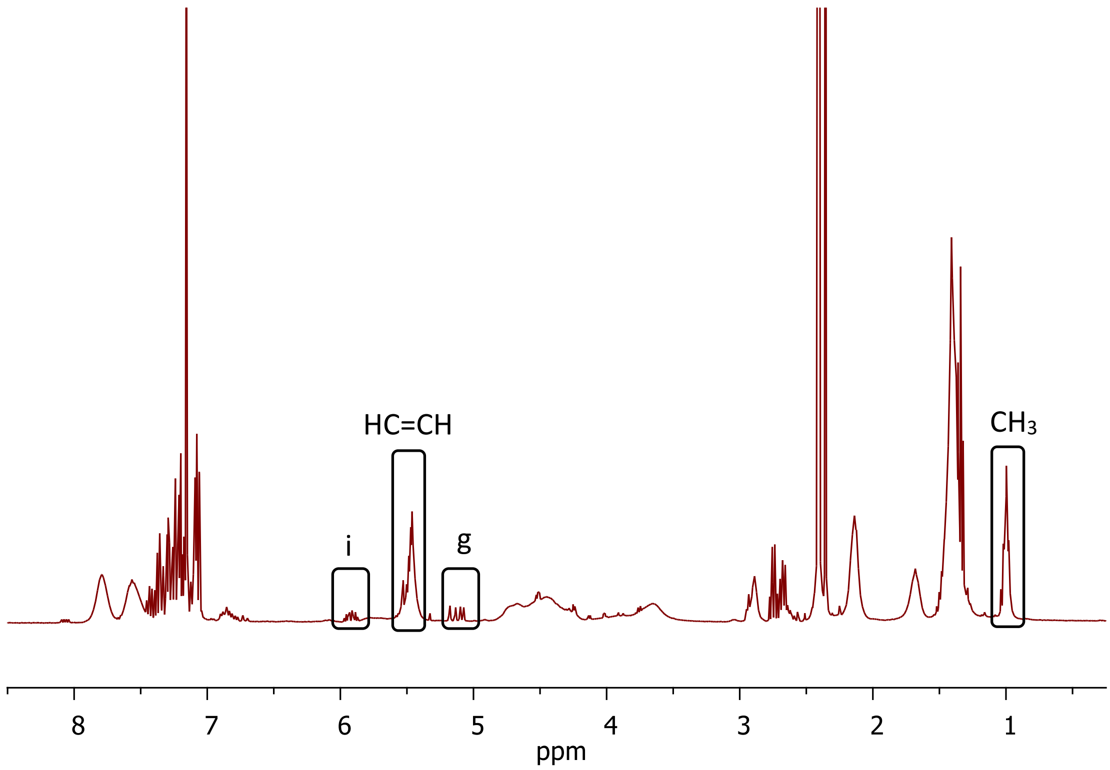

Figure S7: [1]H NMR spectrum of 1wt % P PO_4CR alkyd resin before curing

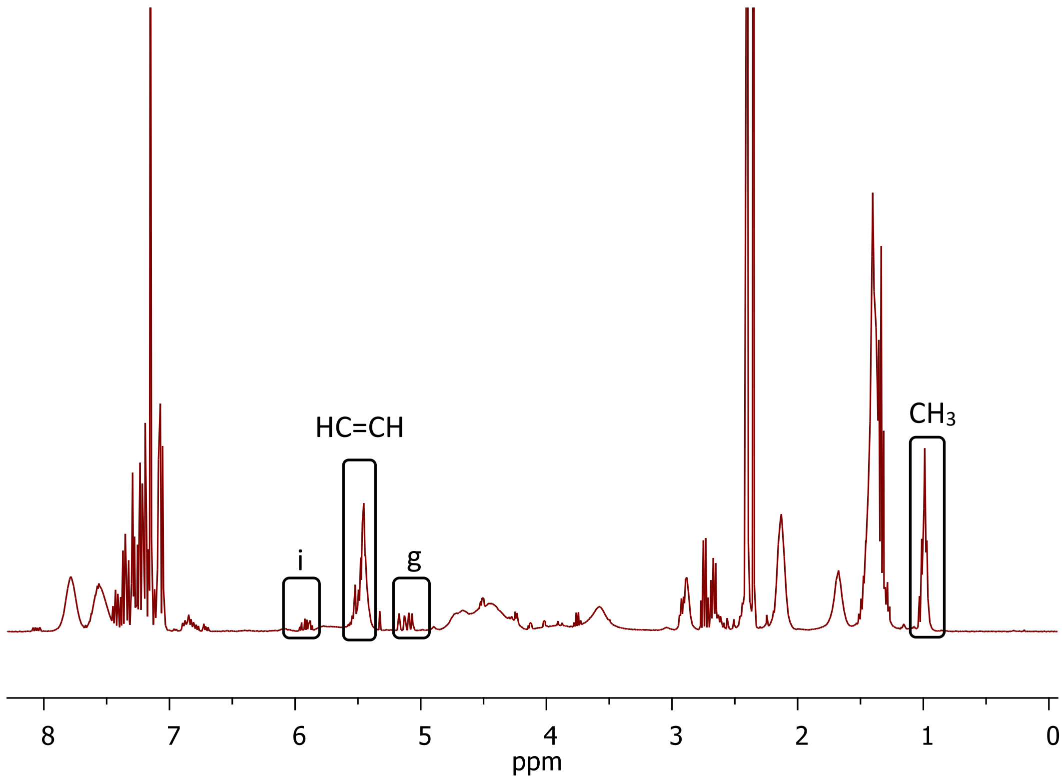

Figure S8: ^{1}H NMR spectrum of 2wt % P PO_4CR alkyd resin before curing

1.4 ^{1}H HRMAS NMR spectra

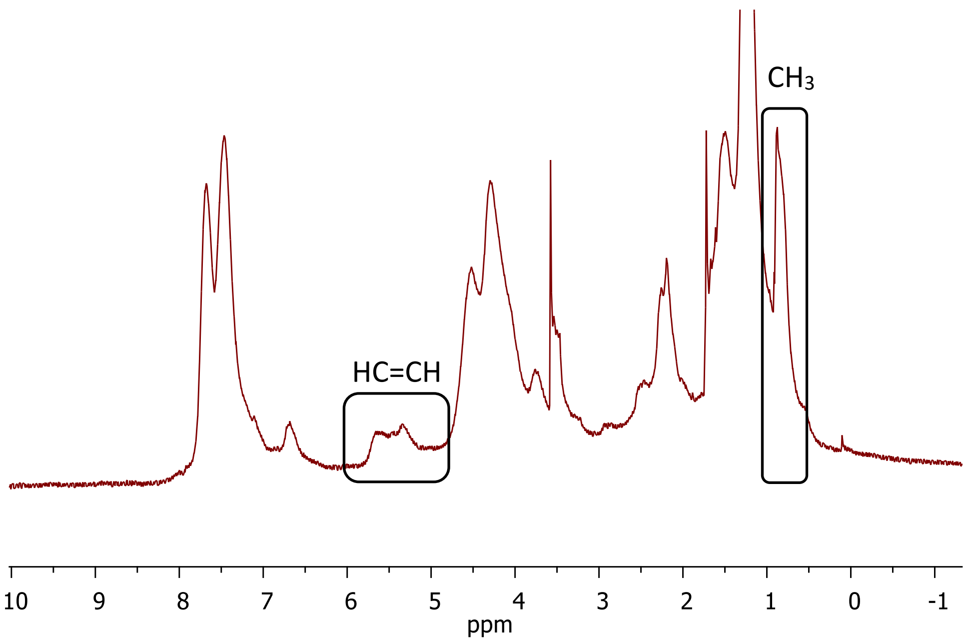

Figure S9: ^{1}H NMR spectrum of reference alkyd resin after curing

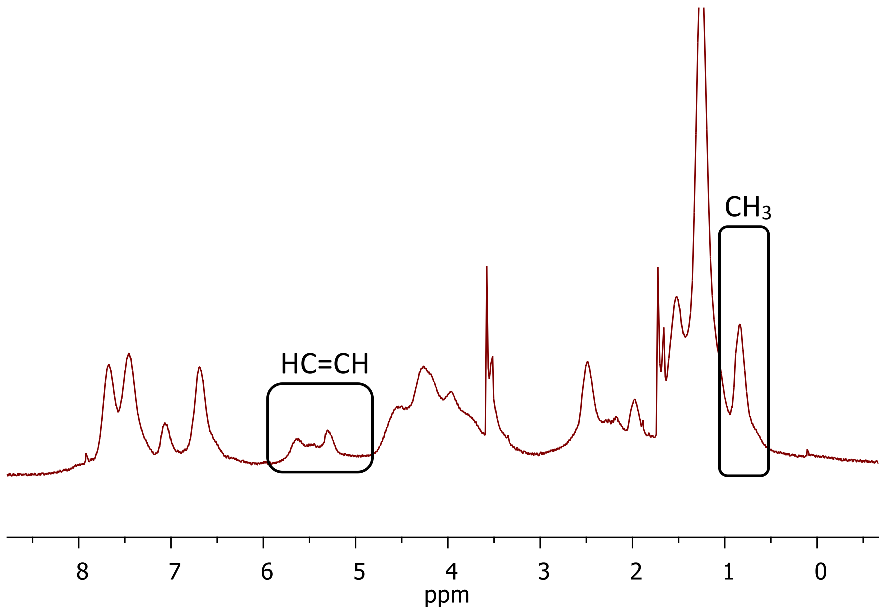

Figure S10: ^{1}H NMR spectrum of 1wt % P PO_3CR alkyd resin after curing

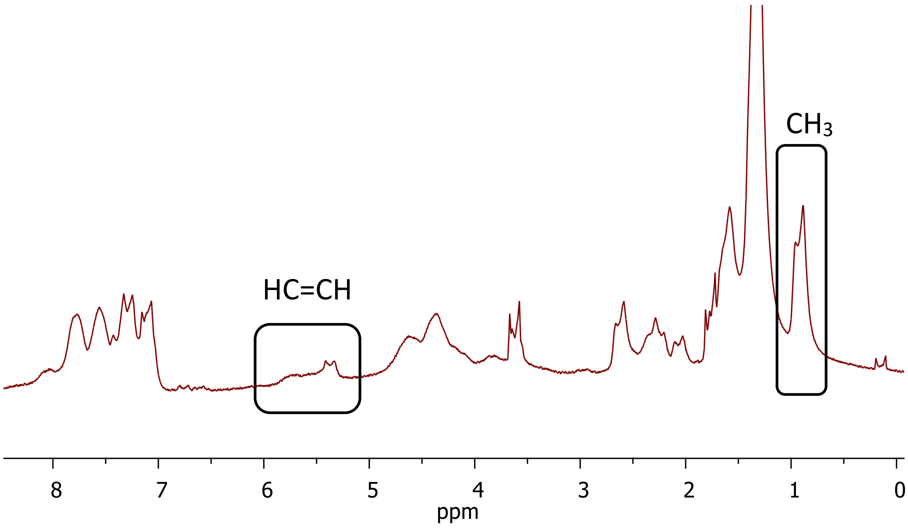

Figure S11: ^{1}H NMR spectrum of 2wt % P PO_3CR alkyd resin after curing

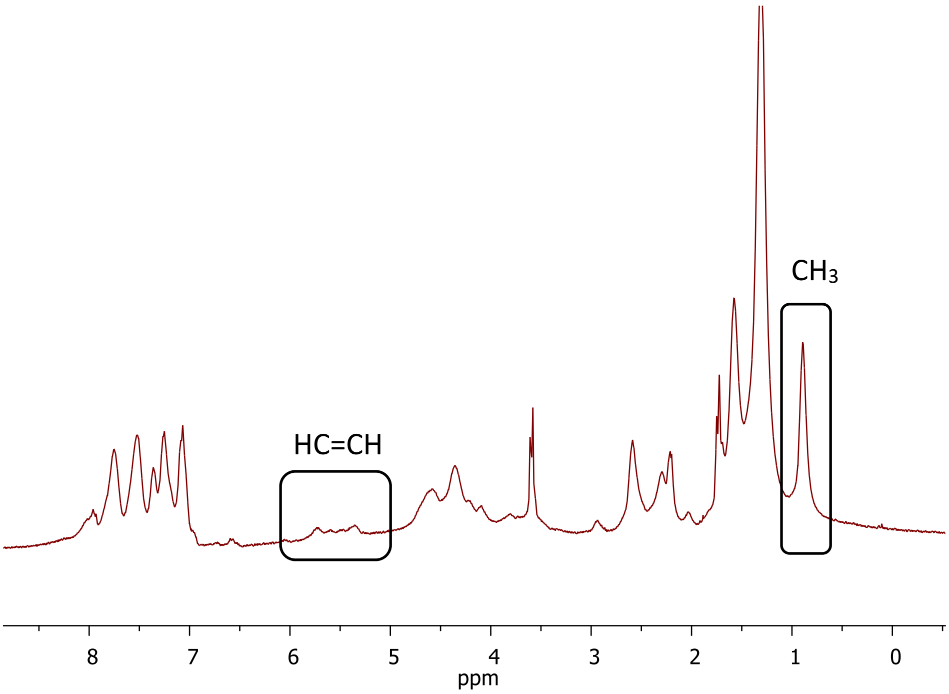

Figure S12: [1]H NMR spectrum of 1wt % P PO_4CR alkyd resin after curing

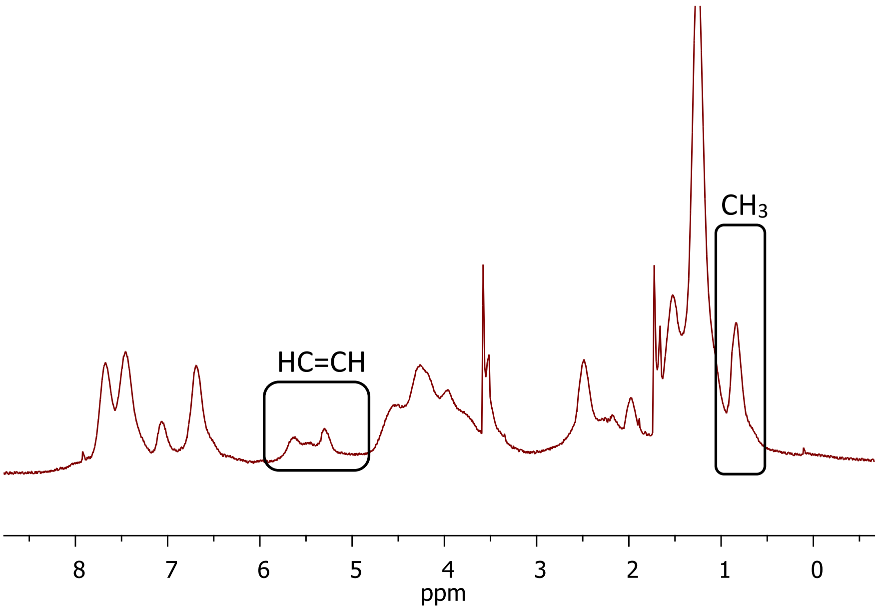

Figure S13: [1]H NMR spectrum of 1wt % P PO_4CR alkyd resin after curing

2. Standards

2.1 ISO 2409:2020 : adhesion test

This standard is used to determine the resistance of coating to be separated from its support. A grid is cut through the coating by incisions which reach the surface of the support. Depending on the coating thickness, the space between the cutting tool blades is different as listed in Table 1.

Table S1: Cutting tool blades depending on the coating thickness

Coating thickness	*Space between the blades*
0 - 60 µm	1 mm
60 - 120 µm	2 mm
>120 µm	3 mm

A grid is obtained by using the appropriate cutting tool blades on the coating. Then, a scotch tape is stuck and removed five times. The grid is examined and depending on the damages, a class from 0 to 5 is given (Table 2).

Table S2: Damages depending on the ISO 2409:2020 class

ISO 2409 :2020 class	*ASTMD3359 class*	*Pictures of damages*	*Evaluation criteria*
0	5B		Edges of the cuts are completely smooth; none of the squares of the grid is detached.
1	4B		Small flakes of the coating are detached at intersections; less than 5 % of the area is affected.
2	3B		Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the grid.
3	2B		The coating has flakes along the edges and on parts of the squares. The area affected is 15 to 35 % of the grid.
4	1B		The coating has flaked along the edges of cuts in large ribbons and whole squares have detaches. The area affected is 35 to 65 % of the grid.
5	0B		The area affected is more than 65 % of the grid.

2.2 ISO 1522:2006 : hardness

The ISO 1522:2006 is used to determine the damping of a pendulum on a coating. The test consists of measuring the damping time (or number of oscillations before damping) of a pendulum resting on the coating by mean of two steal balls. The pendulum is spread at an angle 12 ° from vertical, then released. The pendulum is considered to be damped when the maximum angle amplitude of the pendulum is less than or equal to 4 °. One oscillation corresponds to one second.

2.3 ISO 2813: 2014 : gloss

The ISO 2813:2014 (similar to ASTM D 523) is used to determine the gloss of a coating according to a determined measurement angle. Firstly, the gloss level is determined with a measurement at 60 °. If the value is inferior to 10 gloss unit (GU), the coating is considered matt and the measurement should be made at 85 °; if the value is included between 10 to 70 GU, then the coating presents a medium value of gloss. Finally, if the value is superior to 70 GU at 60°, the coating is considered highly brilliant and the measurement should be made at 20 °.

2.4 Gardner color scale

The Gardner color scale is a one-dimensional scale used to measure the shade of the color yellow. The values are comprised between 1 and 18 as presented in Figure S11.

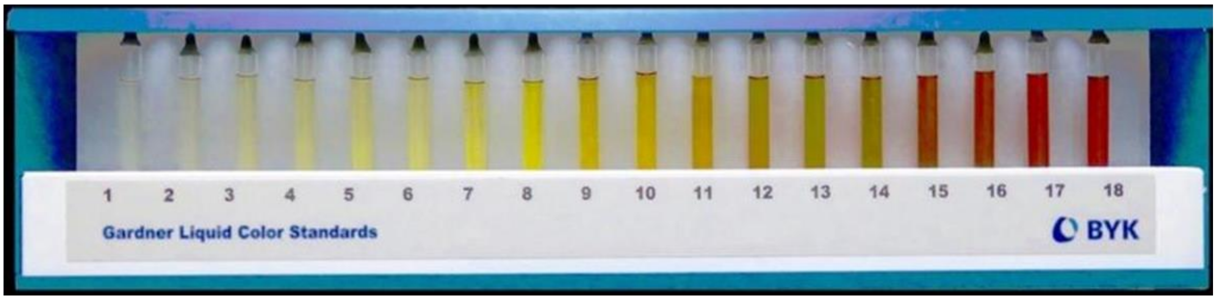

Figure S14: Gardner color scale