

## Supporting Information

# Crosslinked Hybrid Polymer Matrices with Nanostructure Directing Abilities for Lanthanide Hydroxide Growth

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Experimental details: All hydrosilation reactions were carried out in flame dried Schlenk tubes under Ar atmosphere. The ratio between  $\alpha,\omega$ -diallyl poly(ethylene oxides) (aPEO) and PDMS-PMHS (polydimethyl-co-polymethylhydrido siloxane trimethylsilyl terminated ( $M_w = 950\text{g/mol}$ )) or PMHS (polymethylhydridosiloxane ( $M_w = 1700\text{-}3200\text{ g/mol}$ )) were adjusted to EO:Si of 4.42 and 5.68 respectively.

A typical preparation procedure was as follows: 0.950 g PDMS-PMHS (1 mmol, 1 eq) and 2.8 g aPEO (4.3 mmol, 4.3 eq) were dissolved in 7.5 mL toluene and 4.5 ml THF in a Schlenk flask. A solution of Karstedt catalyst in THF (2 mM) was prepared and 1.5 mL of this solution were added to the reaction mixture. After stirring for 18h the solvent was evaporated and the crosslinked polymer dried in vacuum.

The dried polymers were infiltrated with solutions of  $\text{La}(\text{NO}_3)_3$  in methanol (0.15 M). The samples were infiltrated under ultrasonic treatment for 3h. After infiltration the polymer samples were washed and dried.

The thus infiltrated polymer sample was put into a 0.3 M solution of  $\text{NH}_3$  in methanol and kept there for 3 h. After washing and drying under vacuum, the samples were put into an autoclave into 5ml of water. The autoclave was heated to  $120^\circ\text{C}$  and kept at that temperature for 18 h.

### Preparation of the $\text{La}(\text{OH})_3$ nanostructures

0.48 g of functionalized polymer was put into 3 ml of 0.15 M  $\text{La}(\text{NO}_3)_3$  solution (in MeOH) and kept in the ultrasonic bath for 3 h. The supernatant solution was decanted and the polymer sample washed with methanol and distilled water 2 times. 0.30 g of the infiltrated sample were put into 3 ml of a 0.3 M solution of  $\text{NH}_3$ /methanol. After 3 h the polymer was washed 3 times with methanol and distilled water and subsequently dried under vacuum. 0.12 g of this polymer was put into an autoclave filled with distilled water (5 ml). The autoclave was heated

to 120 °C and kept at that temperature for 18 h. The sample was removed and washed 3 times with distilled water.

#### Characterization based on lanthanum-doped PMHS2

Neat polymer:

ATR-FTIR:  $\nu$  = 697 (C-Si-C), 799 (C-Si-C), 843 ( $\nu$ CO, rCH<sub>2</sub>), 948, 1015 ( $\nu$ CO,  $\nu$ CC, rCH<sub>2</sub>, Si-O-Si), 1090 ( $\nu$ CO), 1259 ( $\nu$ Si-CH<sub>3</sub>, CH<sub>2</sub> twisting), 1350 (CH<sub>2</sub> wagging), 1412 (CH<sub>2</sub>), 1456 (CH<sub>2</sub> scissoring), 1951, 2867 ( $\nu$ sCH<sub>2</sub>) and 3515

<sup>13</sup>C CP/MAS (25 °C):  $\delta$  =: 71.3 (OCH<sub>2</sub>CH<sub>2</sub>O), 68.2 (OCH<sub>2</sub>CH<sub>2</sub>O), 21.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 11.3 (Si-CH<sub>2</sub>-CH<sub>2</sub>), -1.2 (Si-CH<sub>3</sub>), -2.6 (Si-CH<sub>3</sub>), -4.7 (H-Si-CH<sub>3</sub>)

<sup>29</sup>Si HPdec/MAS (25 °C)  $\delta$  = 8.0 (CH<sub>3</sub>)SiO, M<sup>1</sup>), -21.8 (OSi(CH<sub>3</sub>)<sub>2</sub>, D<sup>2</sup>), -57.6 (SiO<sub>3</sub>CH<sub>3</sub>, T<sup>2</sup>), -67.2 (SiO<sub>3</sub>CH<sub>3</sub>, T<sup>3</sup>)

Infiltrated:

ATR-FTIR:  $\nu$  = 687 (C-Si-C), 735 (C-Si-C), 799, 843 ( $\nu$ CO, rCH<sub>2</sub>), 952, 1029 ( $\nu$ CO,  $\nu$ CC, rCH<sub>2</sub>, Si-O-Si), 1073 ( $\nu$ CO coordinated), 1260 ( $\nu$ Si-CH<sub>3</sub>, CH<sub>2</sub> twisting), 1301, 1350 (CH<sub>2</sub> wagging), 1453 (CH<sub>2</sub> scissoring, NO<sub>2</sub> stretching), 1650 (N=O  $\nu$ <sub>1</sub> out of plane ( $\delta$ H<sub>2</sub>O)), 1726 (C=O), 2875 ( $\nu$ sCH<sub>2</sub>) and 3413 cm<sup>-1</sup> (OH).

<sup>13</sup>C CP/MAS (25 °C):  $\delta$  = 170 (C=O), 154 (C=O), 63.6 (OCH<sub>2</sub>CH<sub>2</sub>O), 55.4 (-OCH<sub>2</sub>CH<sub>2</sub>O-coordinated), 20.5, 16.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 6.4 (Si-CH<sub>2</sub>-CH<sub>2</sub>), -6.0 ppm (Si-CH<sub>3</sub>).

<sup>29</sup>Si HPdec/MAS (25 °C):  $\delta$  = 8.2 (CH<sub>3</sub>)SiO, M<sup>1</sup>), -21.7 (OSi(CH<sub>3</sub>)<sub>2</sub>, D<sup>2</sup>), -65.2 ppm (SiO<sub>3</sub>CH<sub>3</sub>, T<sup>3</sup>).

Precipitated:

ATR-FTIR:  $\nu$  = 678, 799, 843 ( $\nu$ CO, rCH<sub>2</sub>), 950, 1022 ( $\nu$ CO,  $\nu$ CC, rCH<sub>2</sub>, Si-O-Si), 1087 ( $\nu$ CO), 1259 ( $\nu$ Si-CH<sub>3</sub>, CH<sub>2</sub> twisting), 1305, 1325, 1347 (CH<sub>2</sub> wagging), 1452 (CH<sub>2</sub> scissoring, NO<sub>2</sub> stretching), 1645 (N=O  $\nu$ <sub>1</sub> out of plane ( $\delta$ H<sub>2</sub>O)), 1949, 2867 ( $\nu$ sCH<sub>2</sub>), 3593 cm<sup>-1</sup> (OH).

<sup>13</sup>C CP/MAS (25 °C):  $\delta$  = 64.5 (OCH<sub>2</sub>CH<sub>2</sub>O), 17.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 7.6 (Si-CH<sub>2</sub>-CH<sub>2</sub>), -4.8 (Si-CH<sub>3</sub>), -6.4 ppm (Si-CH<sub>3</sub>).

$^{29}\text{Si}$  HPdec/MAS (25 °C)  $\delta = 8.5$  (( $\text{CH}_3$ ) $\text{SiO}$ ,  $\text{M}^1$ ),  $-13.4$ ,  $-20.8$  ( $\text{OSi}(\text{CH}_3)_2$ ,  $\text{D}^2$ ),  $-56.8$  ppm ( $\text{SiO}_3\text{CH}_3$ ,  $\text{T}^2$ ).

Hydrothermally treated:

ATR-FTIR:  $\nu = 683$ ,  $798$  (C-Si-C),  $844$  ( $\nu\text{CO}$ ,  $\text{rCH}_2$ ),  $949$ ,  $1015$  ( $\nu\text{CO}$ ,  $\nu\text{CC}$ ,  $\text{rCH}_2$ , Si-O-Si),  $1089$  ( $\nu\text{CO}$ ),  $1259$  ( $\nu\text{Si-CH}_3$ ,  $\text{CH}_2$  twisting),  $1350$  ( $\text{CH}_2$  wagging),  $1413$ ,  $1454$  ( $\text{CH}_2$  scissoring),  $1563$ ,  $1727$  (C=O),  $1945$ ,  $2870$  ( $\nu\text{sCH}_2$ )  $3411\text{ cm}^{-1}$  (OH).

Characterization of PMHS1:

Neat Polymer:

ATR-FTIR: ( $\text{cm}^{-1}$ )  $771$  (C-Si-C),  $794$  (C-Si-C),  $842$  ( $\nu\text{CO}$ ,  $\text{rCH}_2$ ),  $948$ ,  $1026$  ( $\nu\text{CO}$ ,  $\nu\text{CC}$ ,  $\text{rCH}_2$ , Si-O-Si),  $1093$  (shoulder,  $\nu\text{CO}$ ),  $1260$  ( $\nu\text{Si-CH}_3$ ,  $\text{CH}_2$  twisting),  $1349$  ( $\text{CH}_2$  twisting),  $1411$  ( $\text{CH}_2$  wagging),  $1455$  ( $\text{CH}_2$  scissoring),  $1667$ ,  $2150$  (Si-H),  $2866$  ( $\nu\text{sCH}_2$ ) and  $3524$  (OH)

$^{13}\text{C}$  CP/MAS (25 °C):  $\delta = 67.0$  ( $\text{OCH}_2\text{CH}_2\text{O}$ ),  $64.2$  ( $\text{OCH}_2\text{CH}_2\text{O}$ ),  $16.9$  ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ),  $7.1$  (Si- $\text{CH}_2$ - $\text{CH}_2$ ),  $-4.7$  (( $\text{Si-CH}_3$ ) $_3$ ),  $-6.9$  (Si- $\text{CH}_3$ ),  $-9.5$  (H-Si- $\text{CH}_3$ )

$^{29}\text{Si}$  HPdec/MAS (25 °C)  $\delta = 8.4$  ( $\text{CH}_3$ ) $\text{SiO}$ ,  $\text{M}^1$ ),  $-21.6$  ( $\text{OSi}(\text{CH}_3)_2$ ,  $\text{D}^{2\text{o}}$ ),  $-37.1$  ( $\text{OSi}(\text{CH}_3)\text{H}$ ,  $\text{D}^{\text{H}}$ ),  $-57.9$  ( $\text{SiO}_3\text{CH}_3$ ,  $\text{T}^2$ ),  $-66.5$  ( $\text{SiO}_3\text{CH}_3$ ,  $\text{T}^3$ )

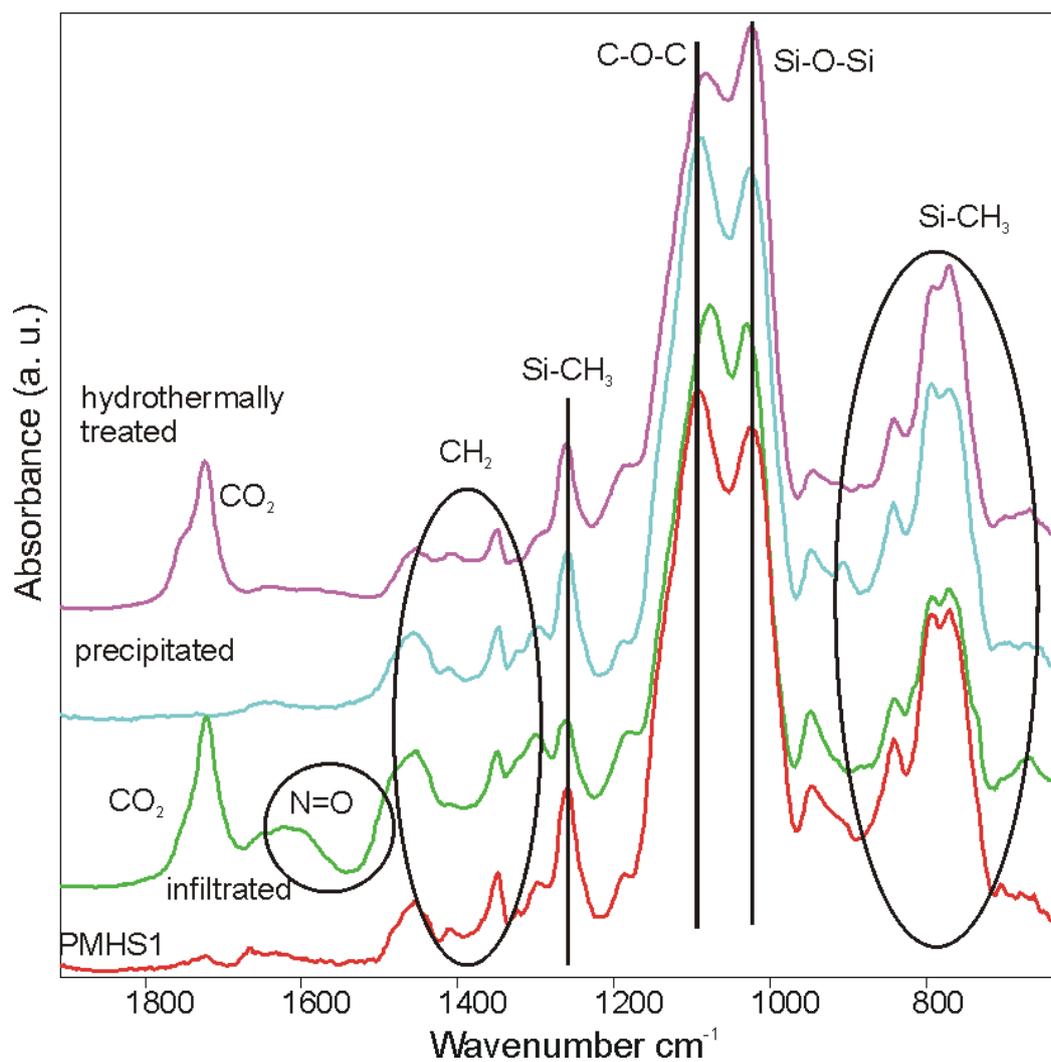


Figure I: FT-IR of neat PMHS1 and La-doped PMHS1 following the nanoparticle preparation

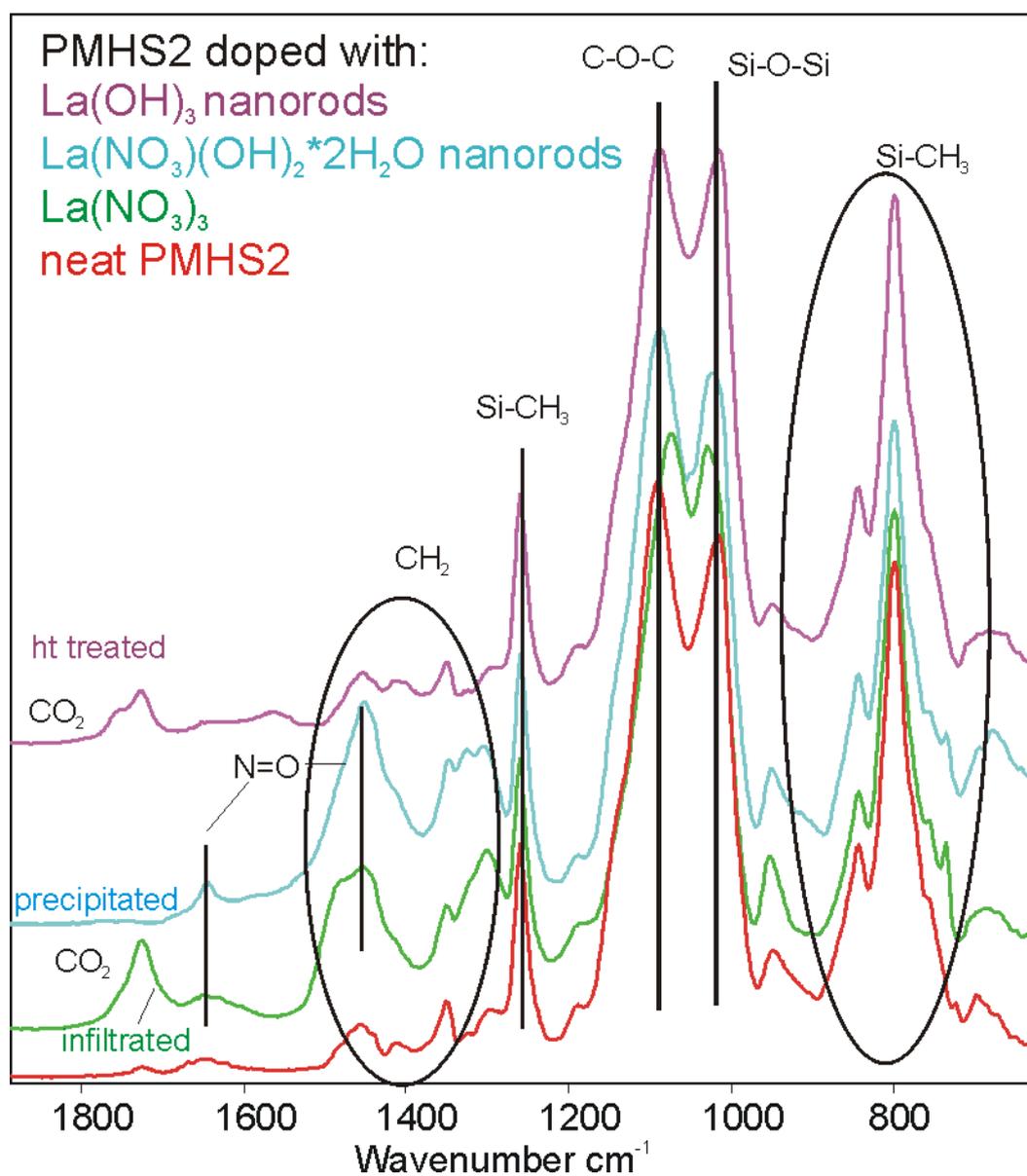
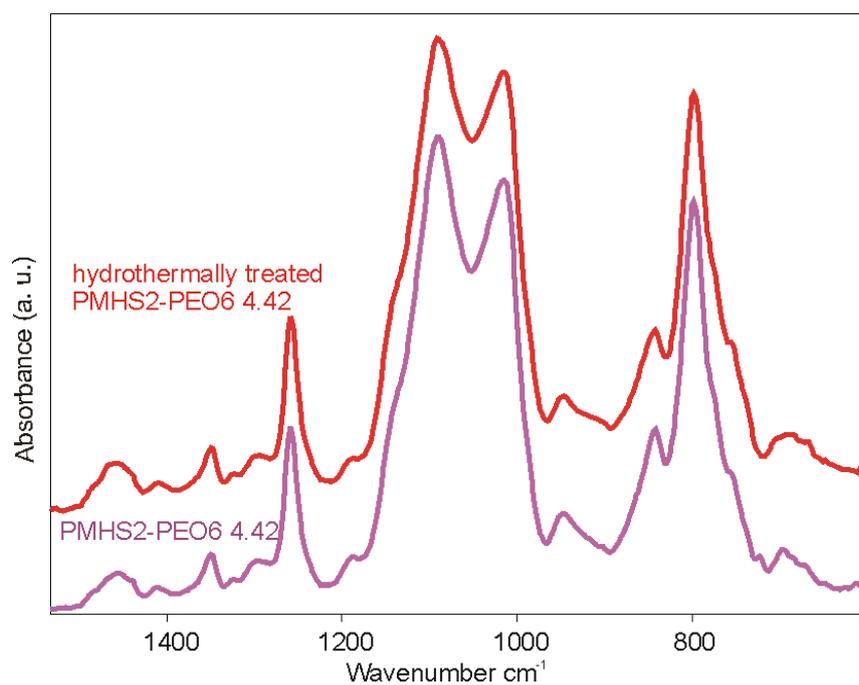
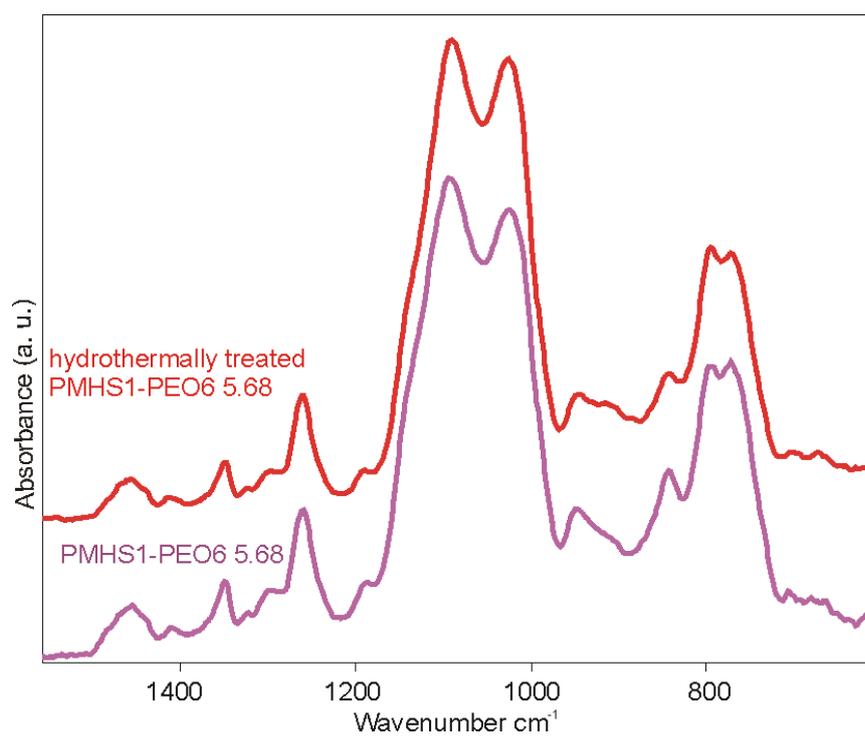


Figure II: FT-IR spectra of PMHS2 and La-doped PMHS2

a)



**Figure III: FT-IR spectra of (a) neat and hydrothermally treated PMHS1-PEO6 5.68 and (b) neat and hydrothermally treated PMHS2-PEO4 4.42**

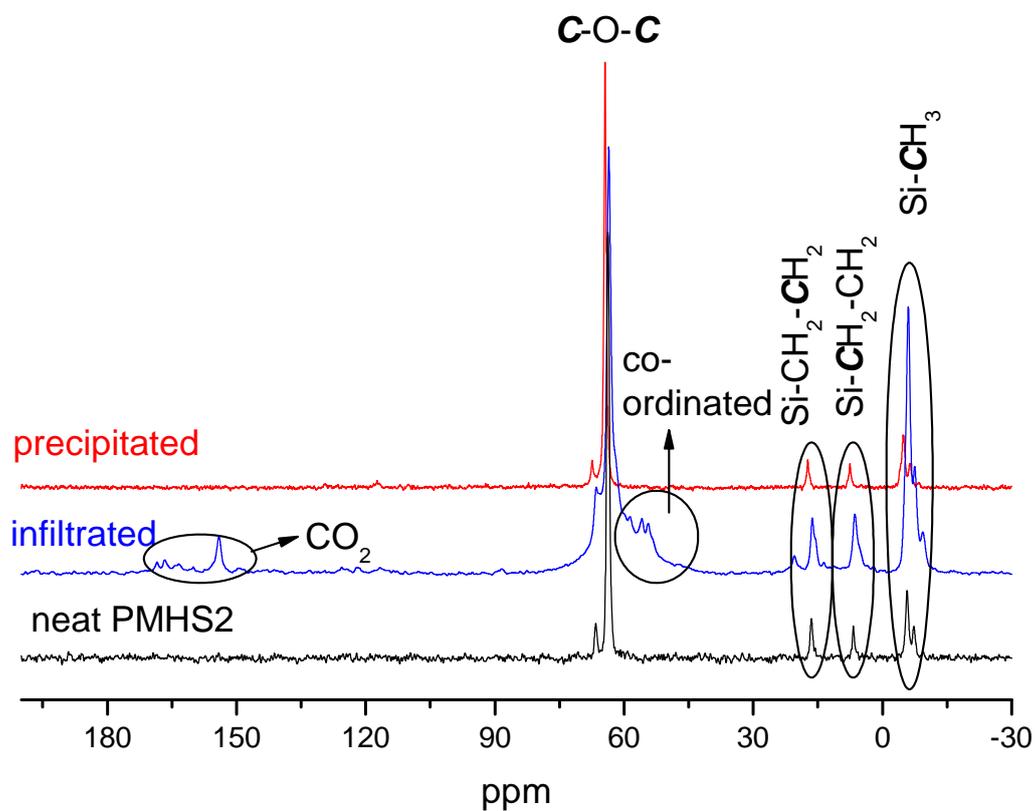
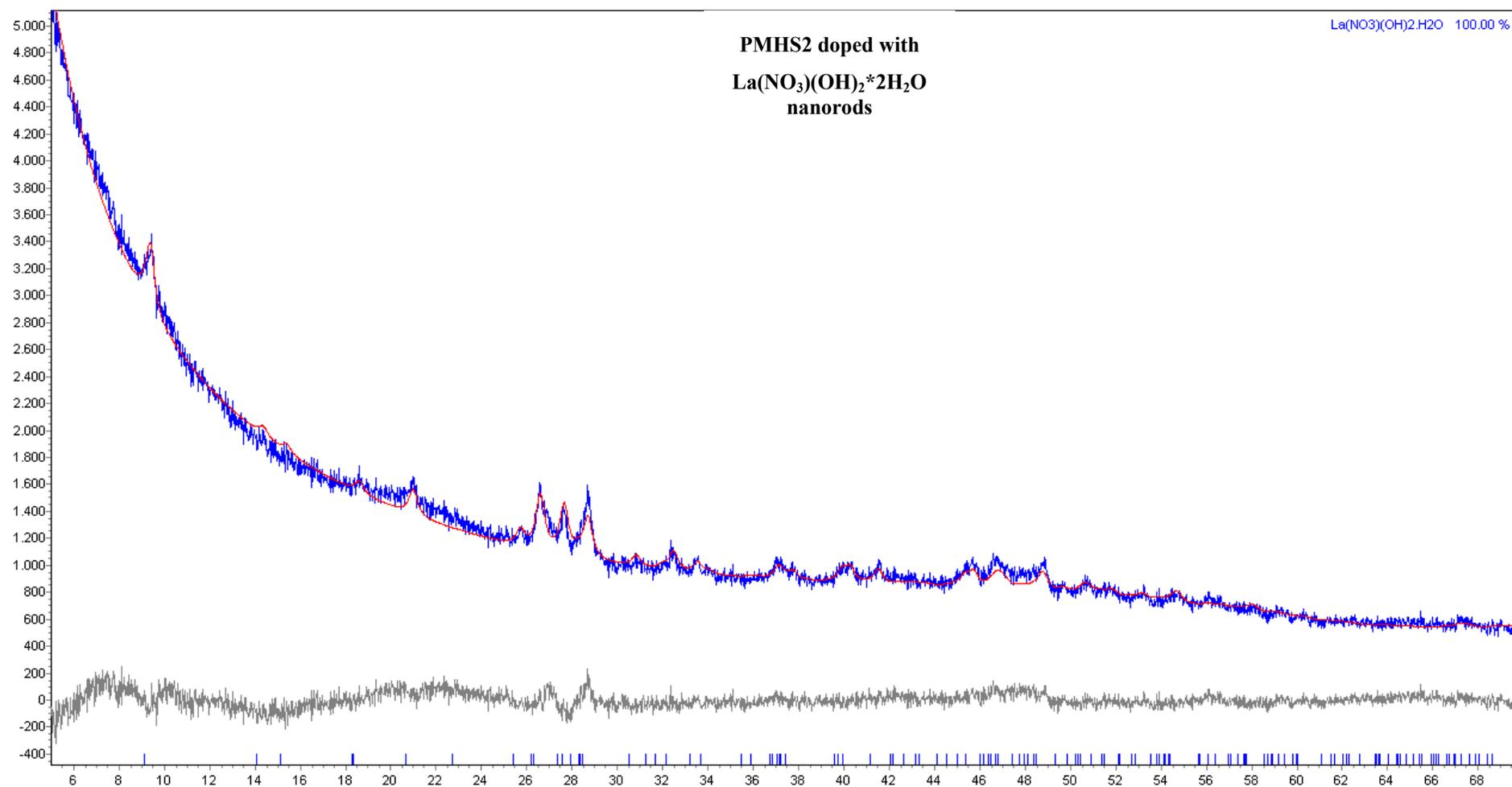
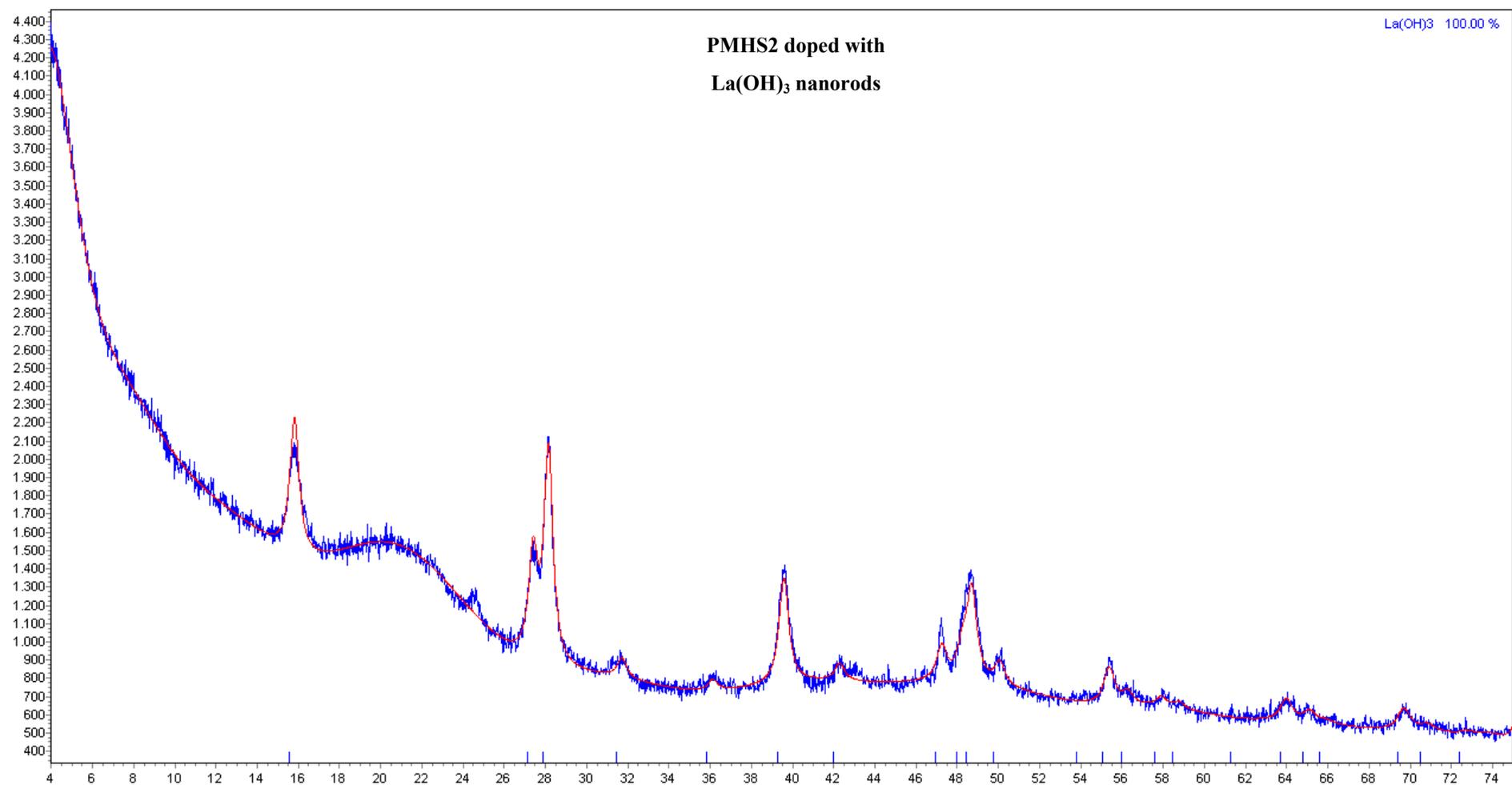


Figure IV:  $^{13}\text{C}$ -HPdec/MAS-NMR of neat PMHS2, infiltrated with  $\text{La}(\text{NO}_3)_3$  and precipitated with ammonia resulting in  $\text{La}(\text{NO}_3)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  nanorod containing PMHS2. No changes in the polymer matrix, like formation of carboxylates, were observed.



**Figure V: XRD pattern of precipitated PMHS2 (PMHS2 doped with  $\text{La}(\text{NO}_3)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  nanorods) and the fitted pattern textured in 100 directions of  $\text{La}(\text{NO}_3)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (red line)**



**Figure VI:** XRD pattern of La-doped PMHS2 after ht treatment (PMHS2 doped with  $\text{La(OH)}_3$  nanorods) and the fitted pattern textured in 100 directions of  $\text{La(OH)}_3$  (red line)