Electronic Supplementary Material (ESI) for RSC Advances.

Simple and facile synthesis of water-soluble poly(phosphazenium) polymer electrolytes

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Supplementary Information

EXPERIMENTAL

NMR characterization - All NMR measurements were carried out on a Bruker Avance 360 MHz NMR spectrometer. The NMR experiments performed were as follows: 1D ^{1}H (spectra collected at 360 MHz), 1D ^{1}H decoupled phosphorus (spectra collected at 360 MHz), ^{13}C (spectra collected at 90 MHz – proton decoupled), and ^{31}P (spectra collected at 146 MHz). 2D NMR experiments included homonuclear (i.e., proton-proton) correlation spectroscopy **(**COSY), ^{1}H-^{13}C heteronuclear multiple-quantum correlation spectroscopy (HMQC), and ^{1}H-^{31}P HMQC. See Table S1 below that summarizes the 2D NMR experimental techniques. Sample preparation for NMR spectra acquisition was as follows: 20 to 30 mg of sample was dissolved in 600 μL of deuterated solvent – deuterium oxide (D_2O) for $PMCHAP^+$ and deuterated chloroform ($CDCL_3$) for PMCHAP and $CDCl_3$ for PDCP. An internal standard, tetramethylsilane, or the signal from the solvent was used for calibration of the chemical shift in the NMR spectra.

Table S1. Details and parameters for 2D NMR experiments

Technique	Details
COSY	2D homonuclear shift correlation using gradient pulses for selection Incremental resolution: 1024 x 128 Number of scans: 4
^{1}H-^{13}C HMQC	2D HMQC ^{1}H-1/X correlation via heteronuclear zero and double quantum coherence with decoupling during acquisition using gradient pulses for selection Incremental resolution: 1024 x 128 Number of scans: 10
^{1}H-^{31}P HMQC	2D HMQC ^{1}H-1/X correlation via heteronuclear zero and double quantum coherence with decoupling during acquisition using gradient pulses for selection Incremental resolution: 1024 x 128 Number of scans: 4

RESULTS

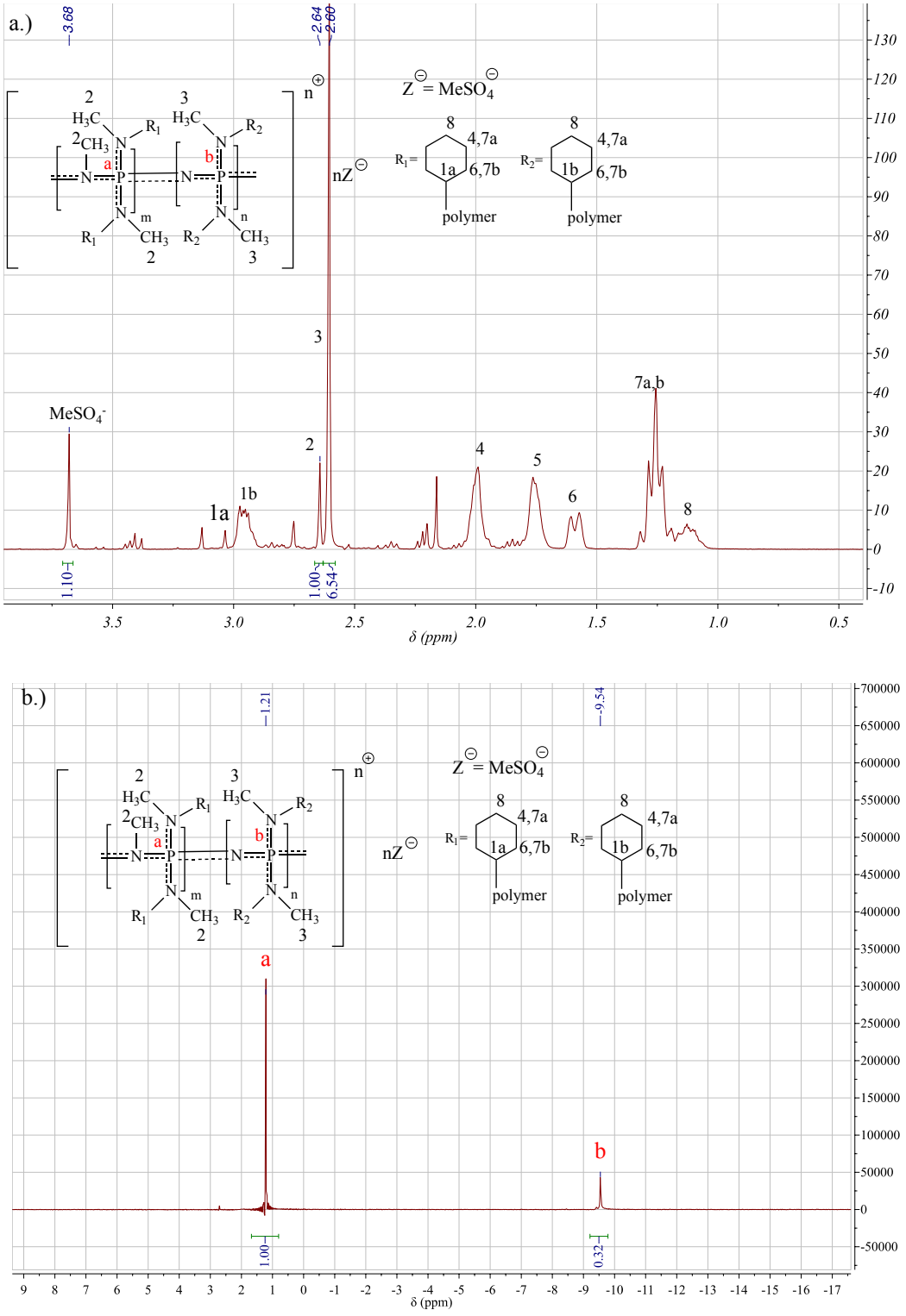

Fig. S1. a.) Integrated ^{1}H NMR spectra of PMCHAP^{+} batch #2. b.) Integrated ^{31}P NMR spectra of PMCHAP^{+} batch #1. Both spectra used D_2O as the NMR solvent.

Degree of methylation (i.e., average number of methylated repeat units) determined by integrating the ^{1}H NMR and the ^{31}P NMR

By ^{1}H NMR:

$$DF = \frac{Area(\delta = 2.64\ ppm)}{Ratio\ of\ protons \cdot Area(\delta = 2.60\ ppm)}$$

Note: Ratio of protons is equal to 1.5 because the signal at 2.65 ppm corresponds to 9 protons, while the signal at 2.60 ppm corresponds to 6 protons.

By ^{31}P NMR:

$$DF = \frac{Area(\delta = -9\ ppm)}{Area(\delta = -9\ ppm) + Area(\delta = 1\ ppm)}$$

Table S2. Degree of methylation of PMCHAP^{+} obtained by integrating ^{1}H and ^{31}P NMR spectra

Batch	DF from ^{1}H NMR	Std. error	DF from ^{31}P NMR	Std. error
1	0.104	0.005	0.214	0.034
2	0.099	n/a	0.115	n/a

Std. error calculated from n=3 samples. Better agreement between the integrated ^{1}H and ^{31}P NMR spectra was observed for batch #2.

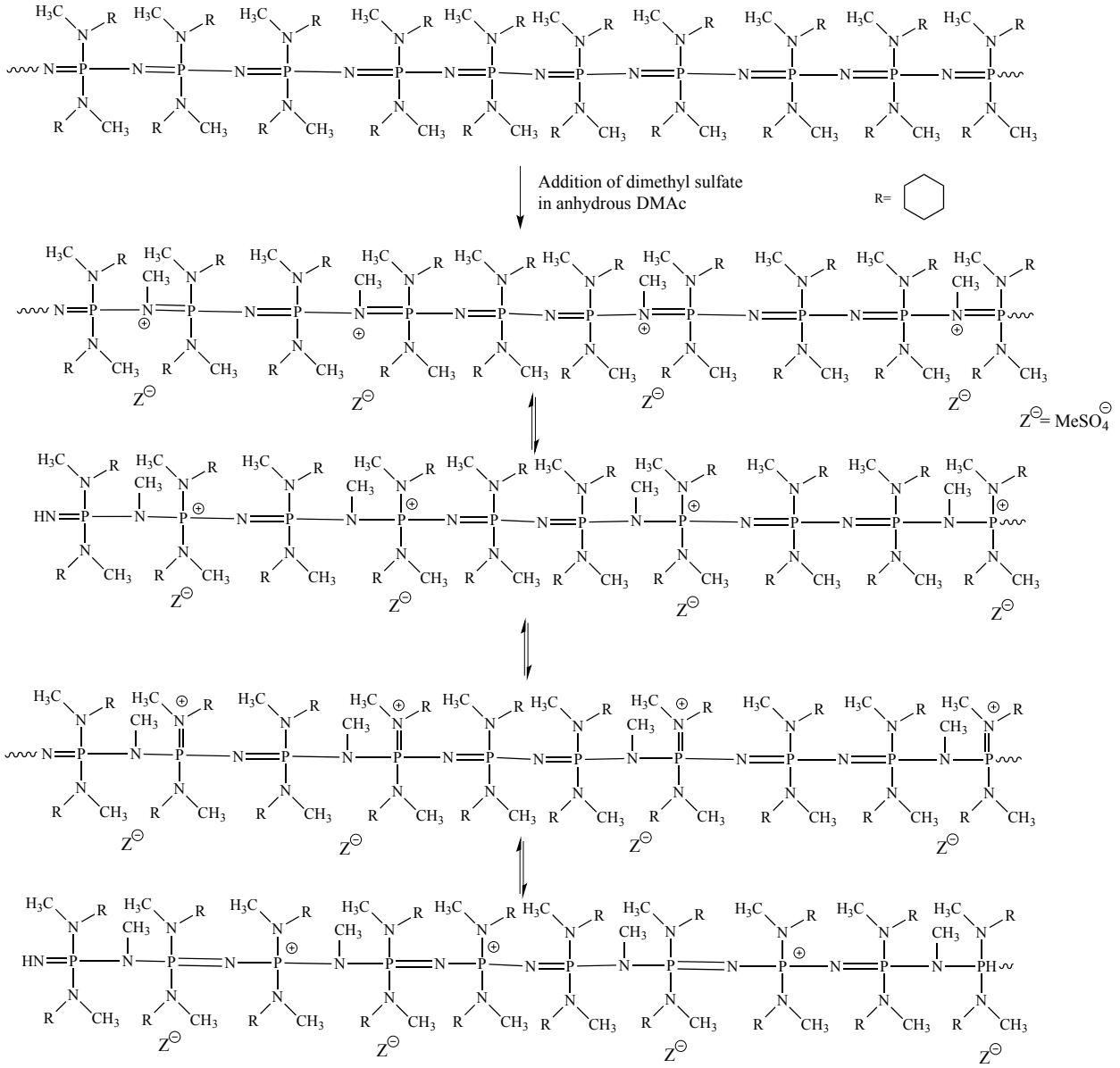

Fig. S2. The synthesis of PMCHAP^{+} using dimethyl sulfate (DMS). A polymer chain with 4 of the 10 repeat units has been methylated. Alternative resonance structures are illustrated.

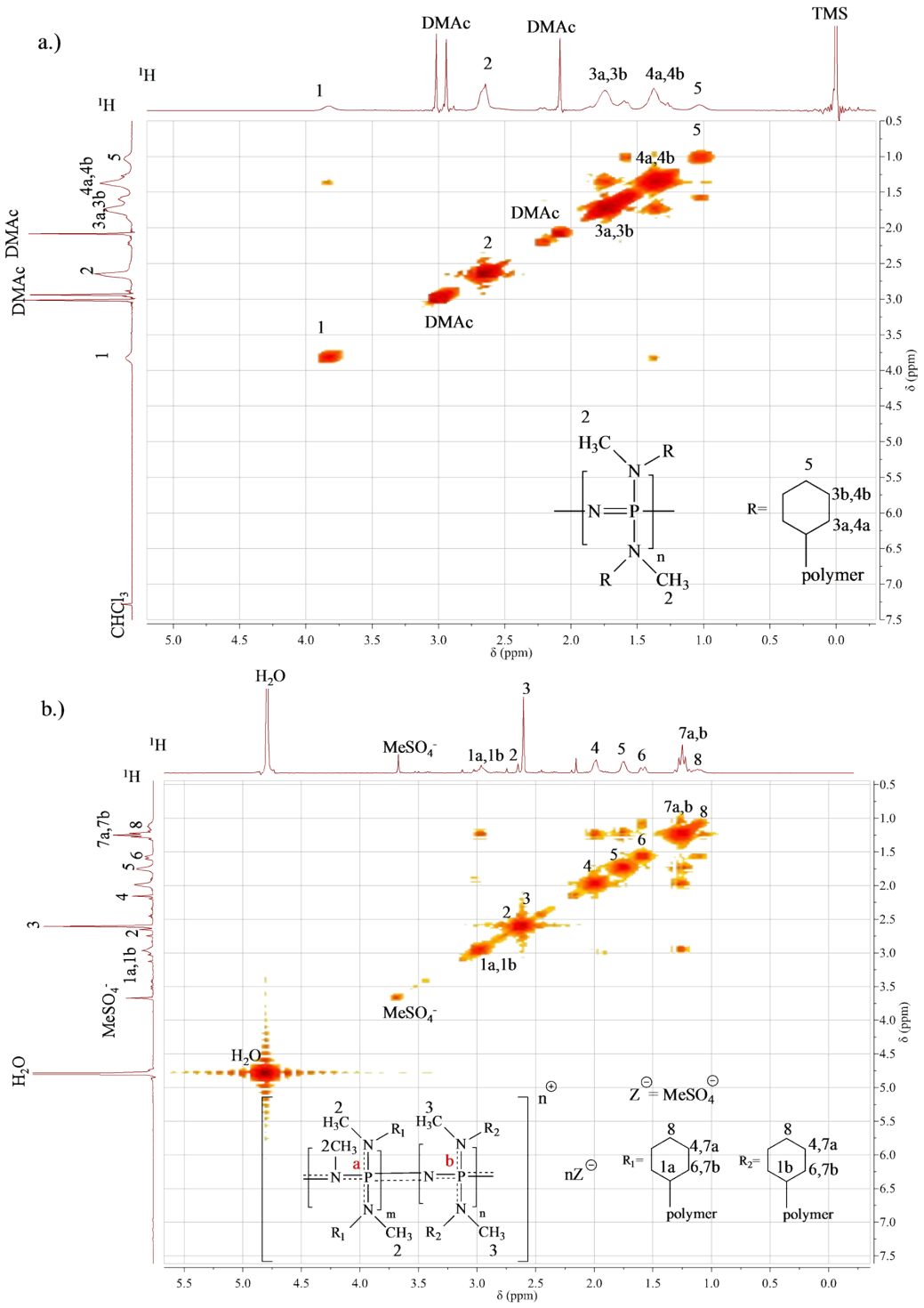

Fig. S3. COSY spectra of a.) PMCHAP and b.) PMCHAP^{+}. a.) used $CDCl_3$ as the NMR solvent while b.) used D_2O as the NMR solvent.

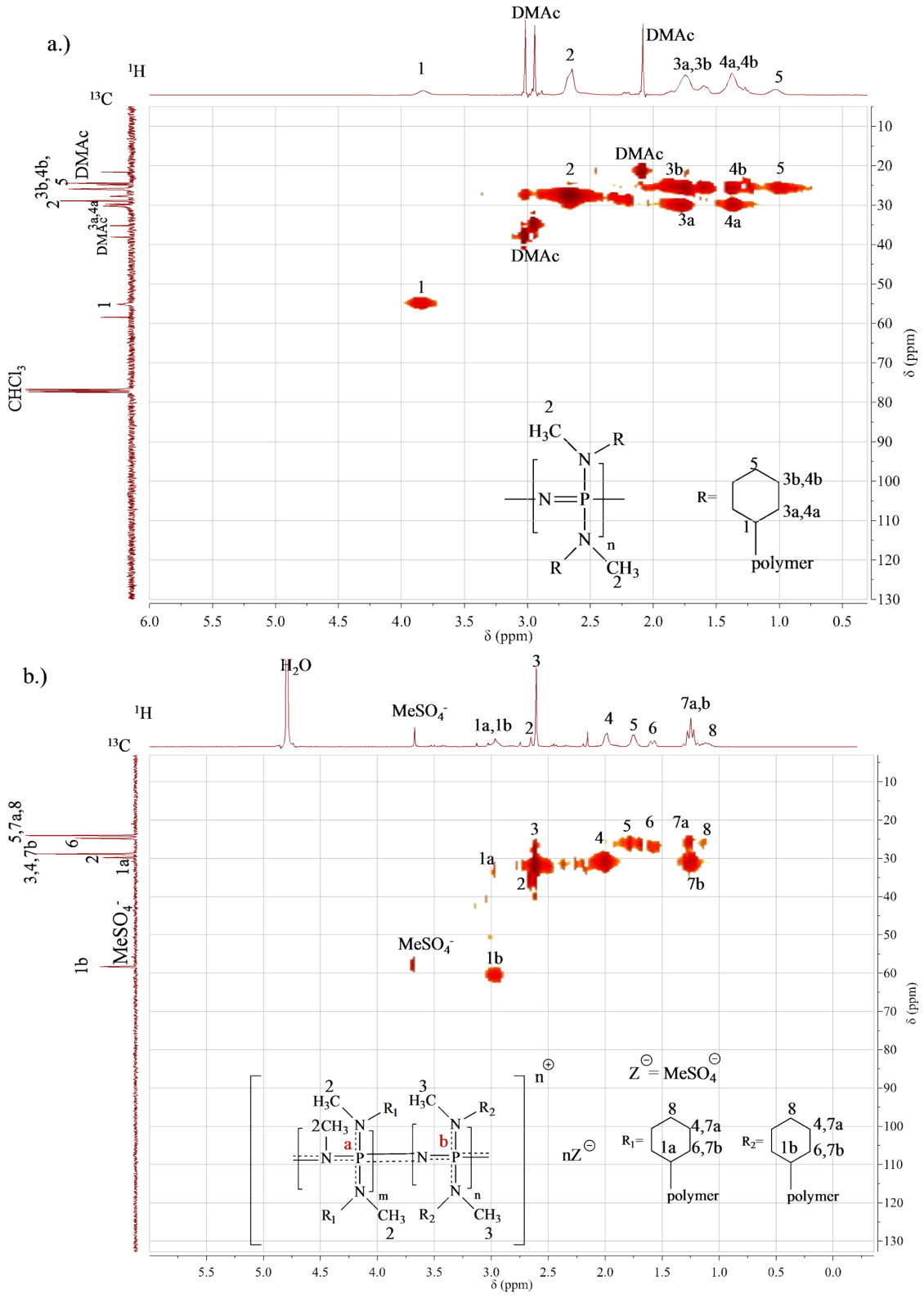

Fig. S4. ^{1}H-^{13}C HMQC spectra of a.) PMCHAP and b.) PMCHAP^{+}. a.) used $CDCl_3$ as the NMR solvent while b.) used D_2O as the NMR solvent.

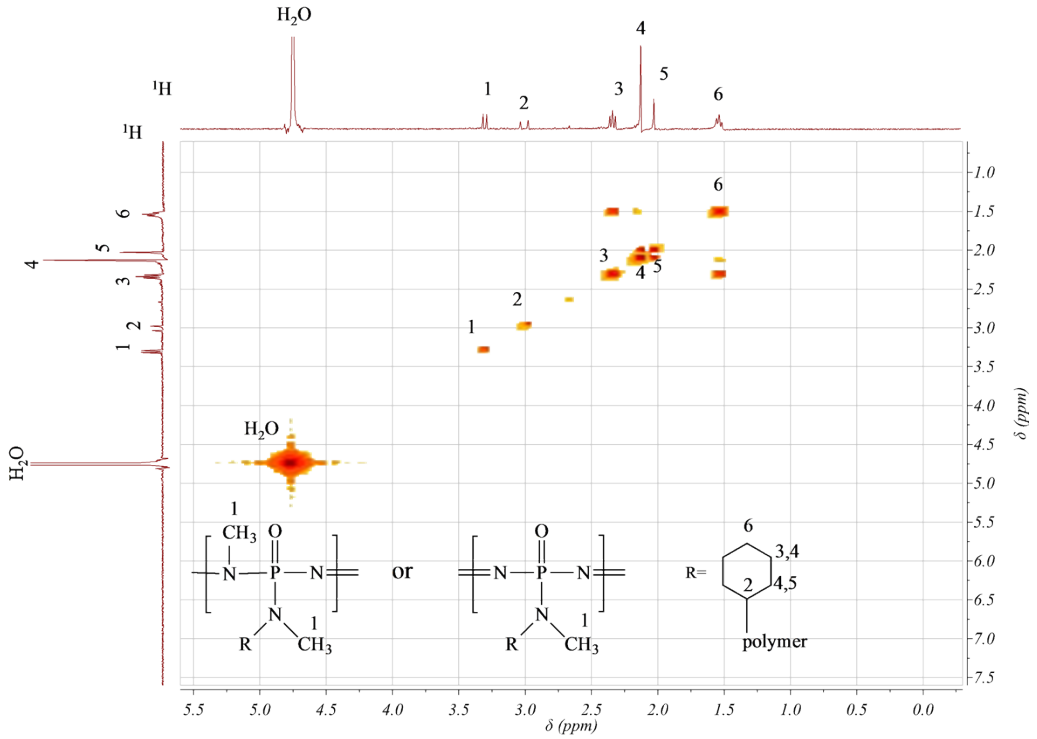

Fig. S5. COSY spectrum of PMCHAP$^+$ after exposure to 1 M NaOD in D_2O for 3 days at 60 °C. NMR solvent for this sample was D_2O.