PIEZOELECTRIC POLY(LACTIDE) STEREOCOMPLEXES WITH A CHOLINIUM ORGANIC IONIC PLASTIC CRYSTAL

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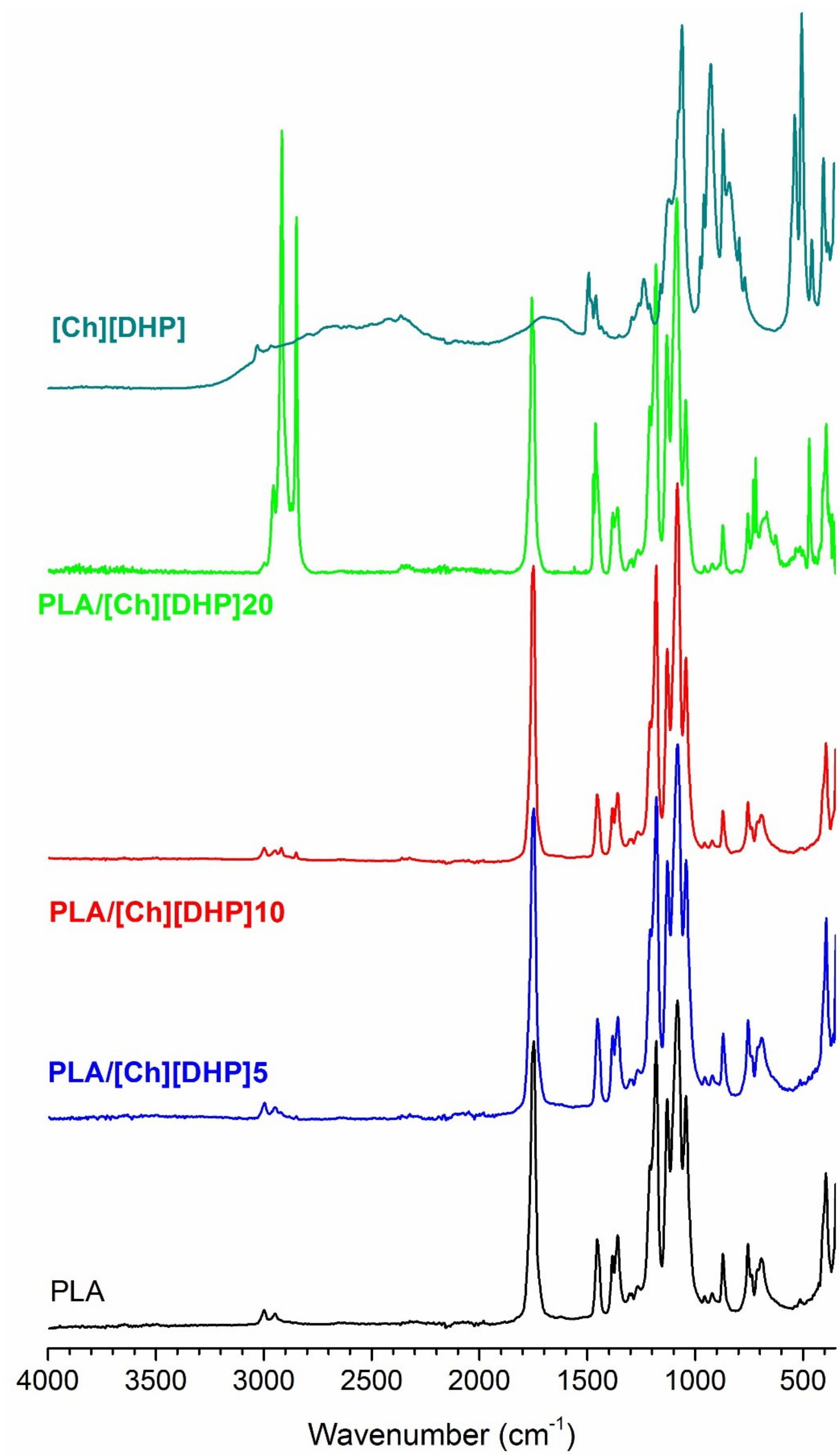

Figure S1. FTIR-ATR spectra of [Ch][DHP], PLA and PLA/[Ch][DHP] blend membranes.

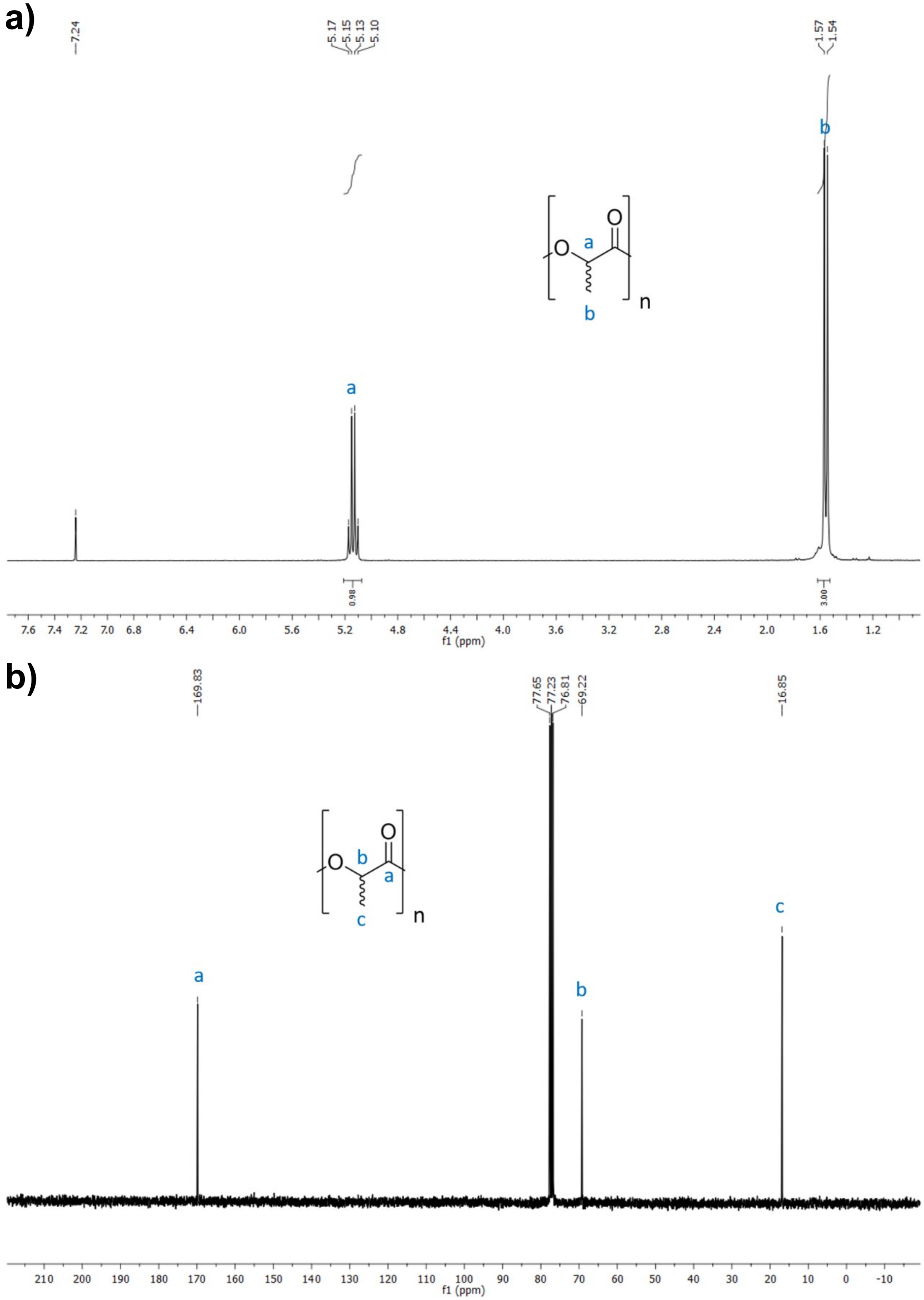

Figure S2. ^{1}H NMR a) and ^{13}C NMR b) spectra of PLA (300.13 MHz, 75.47 MHz, solvent $CDCl_3$).

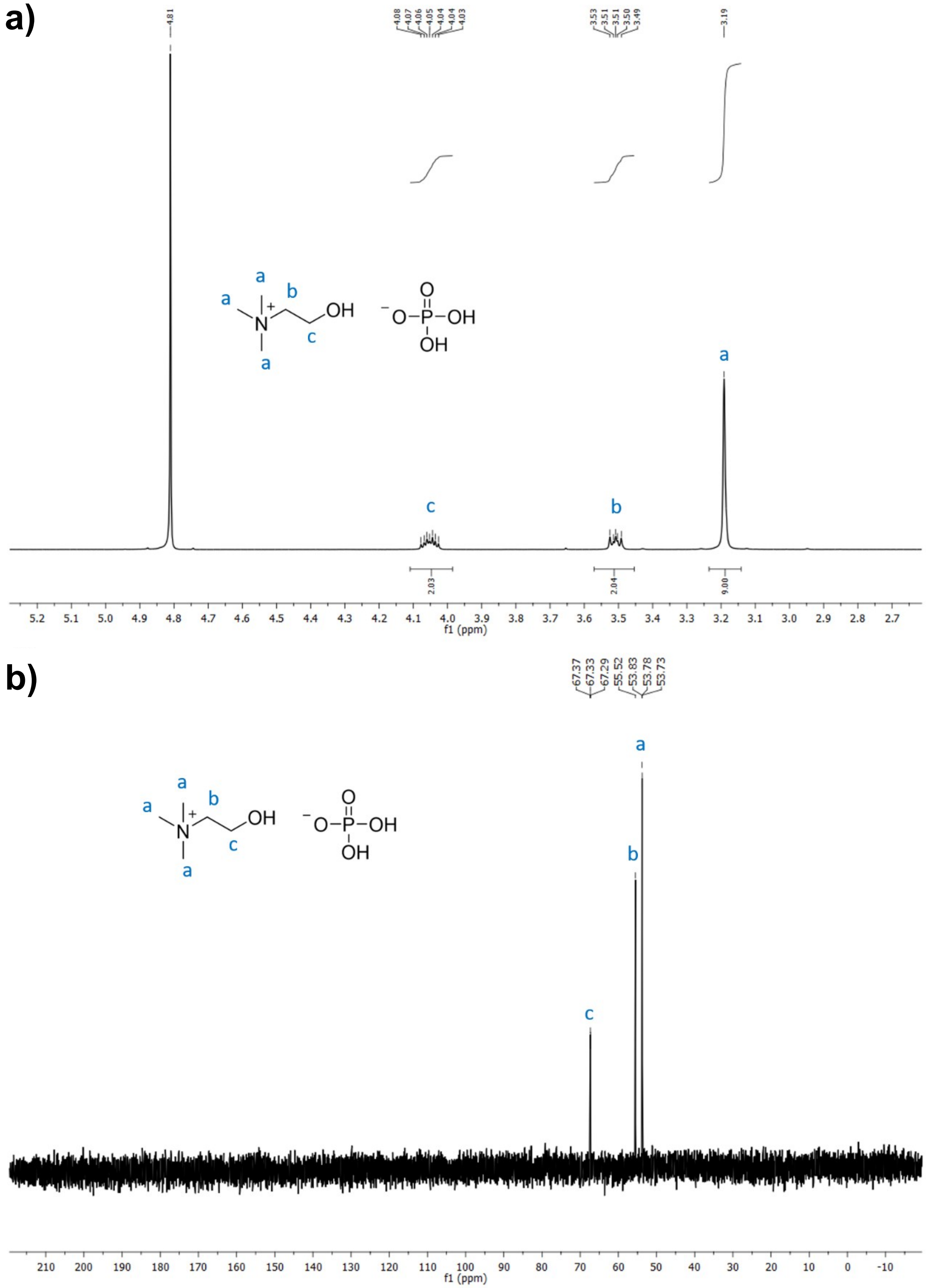

Figure S3. ^{1}H NMR a) and ^{13}C NMR b) spectra of [Ch][DHP] (300.13 MHz, 75.47 MHz, solvent D_2O).

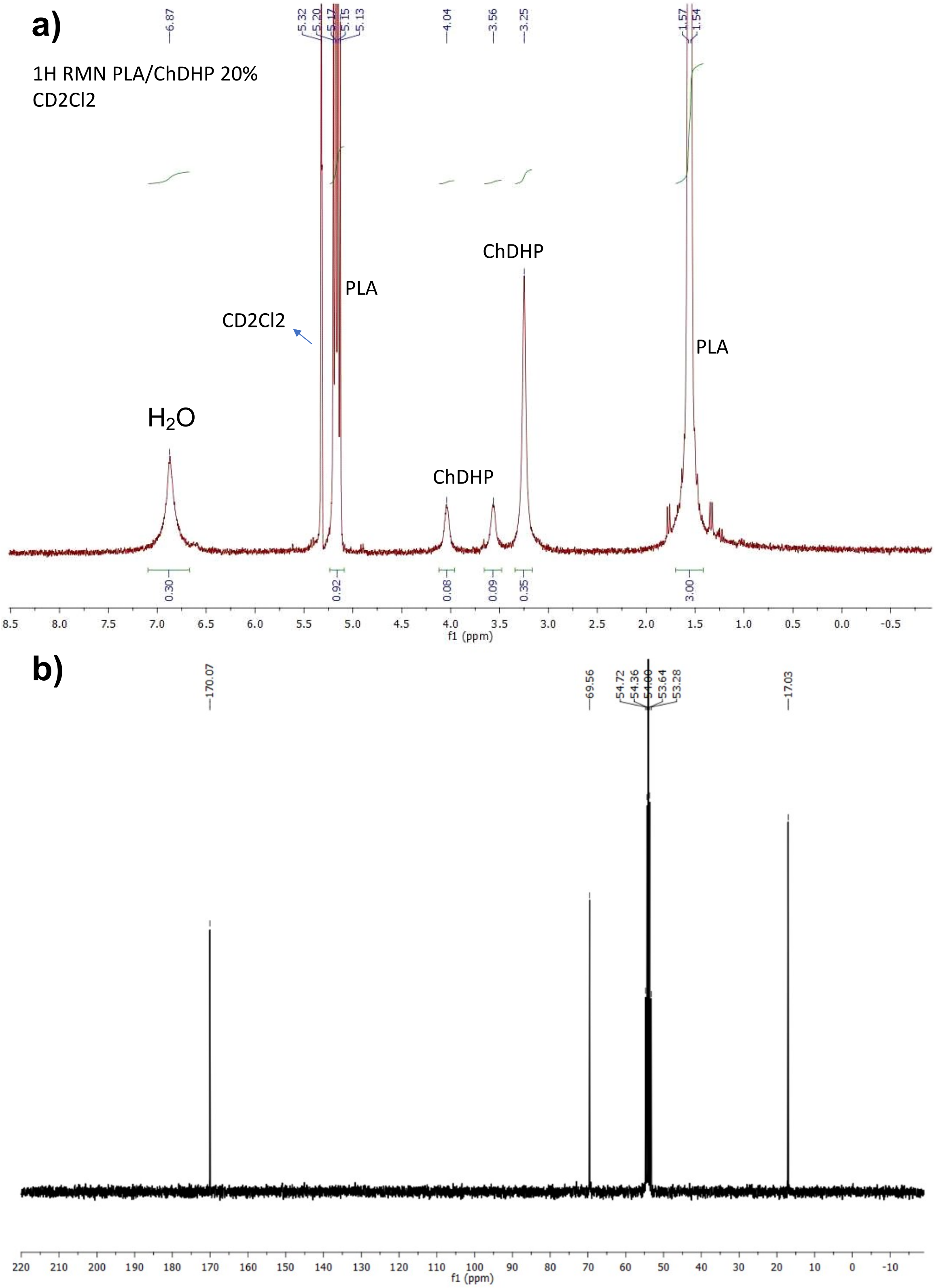

Figure S4. ^{1}H NMR a) and ^{13}C NMR b) spectra of PLA/[Ch][DHP]20 composition (300.13 MHz, 75.47 MHz, solvent CD_2Cl_2).

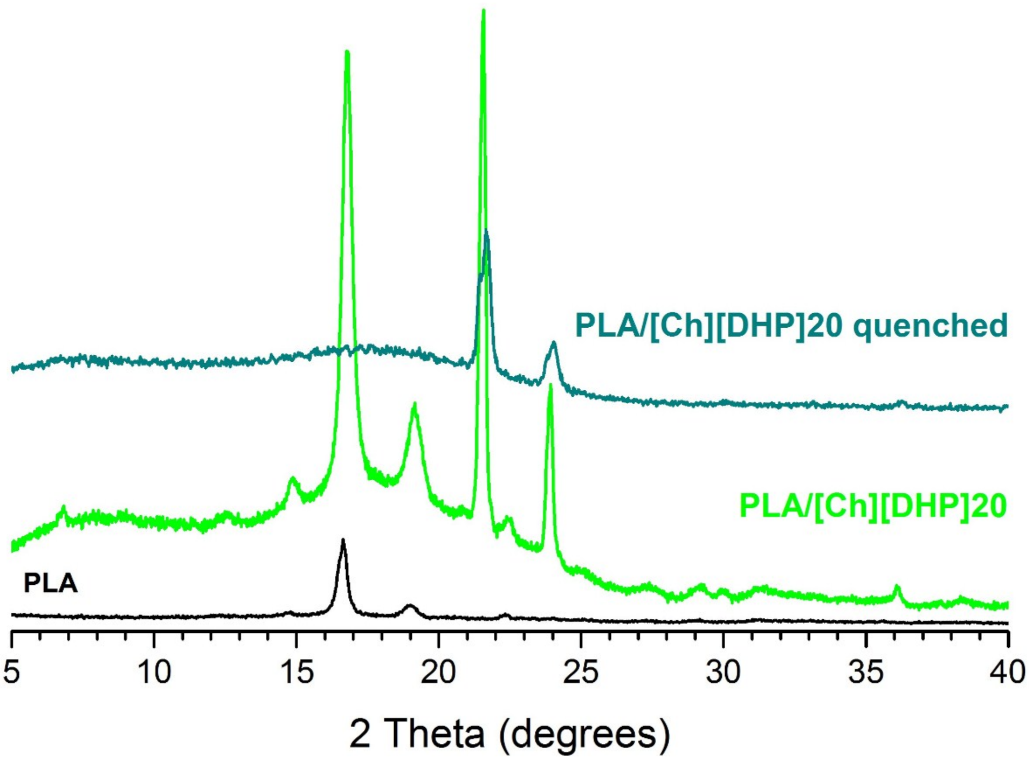

Figure S5. X-ray diffraction profiles of pure PLA, PLA/[Ch][DHP]20 and PLA/[Ch][DHP]20 quenched in liquid nitrogen from 250 °C.

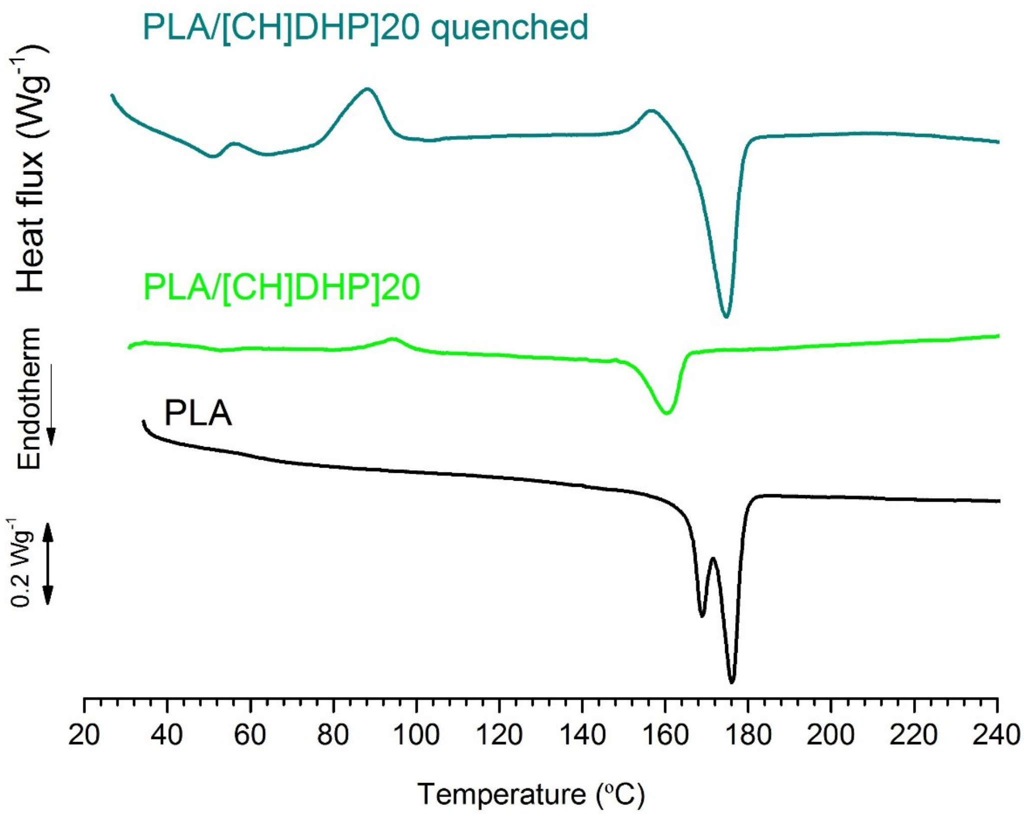

Figure S6. DSC thermograms of pure PLA, PLA/[Ch][DHP]20 and PLA/[Ch][DHP]20 quenched in liquid nitrogen from 250 °C. The small peak observed at 55 °C for the quenched sample is probably related with the stabilization of the DSC equipment.

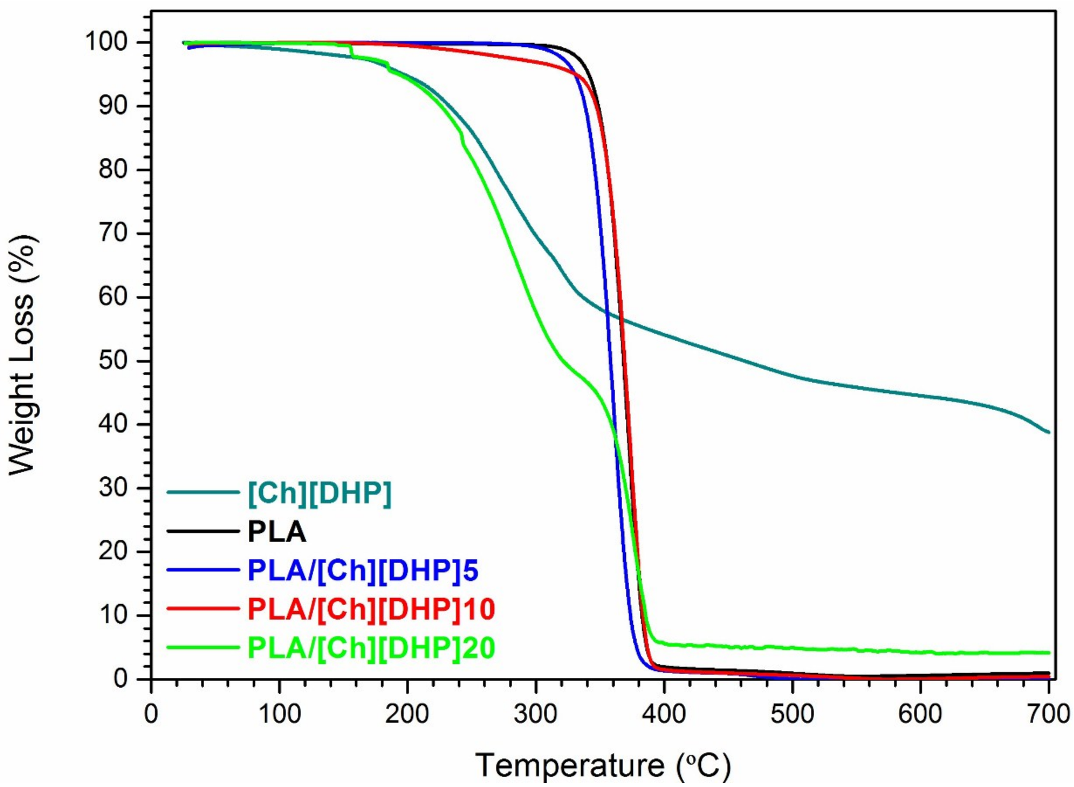

Figure S7. Thermogravimetric curves of [Ch][DHP], PLA and PLA/[Ch][DHP] blend membranes.

The membranes produced were found to be thermally stable up to 200 °C.

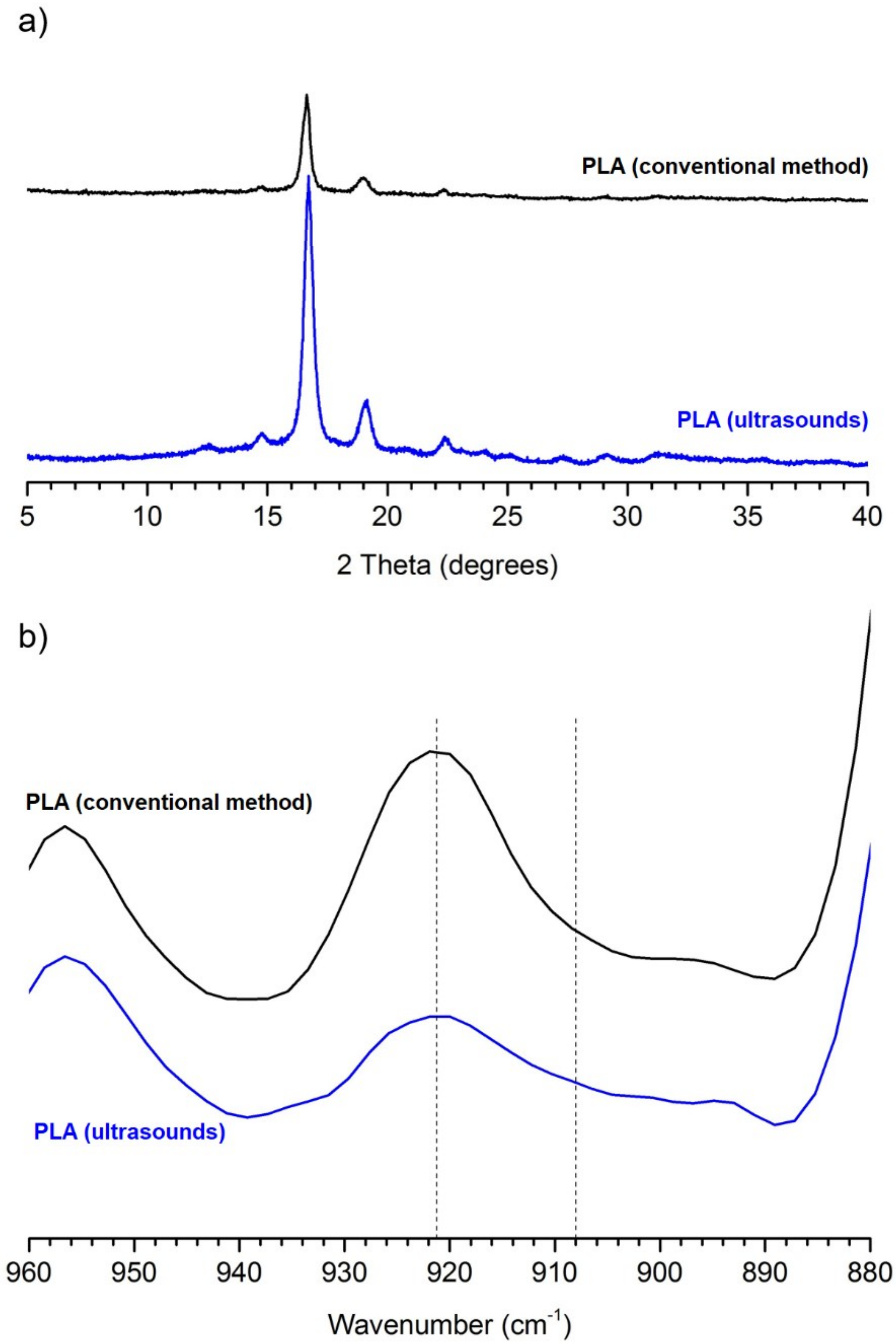

Figure S8. XRD profiles a) and expanded FTIR-ATR spectra b) of aged PLA membrane prepared using extensive ultrasounds and pure PLA membrane prepared by conventional method.

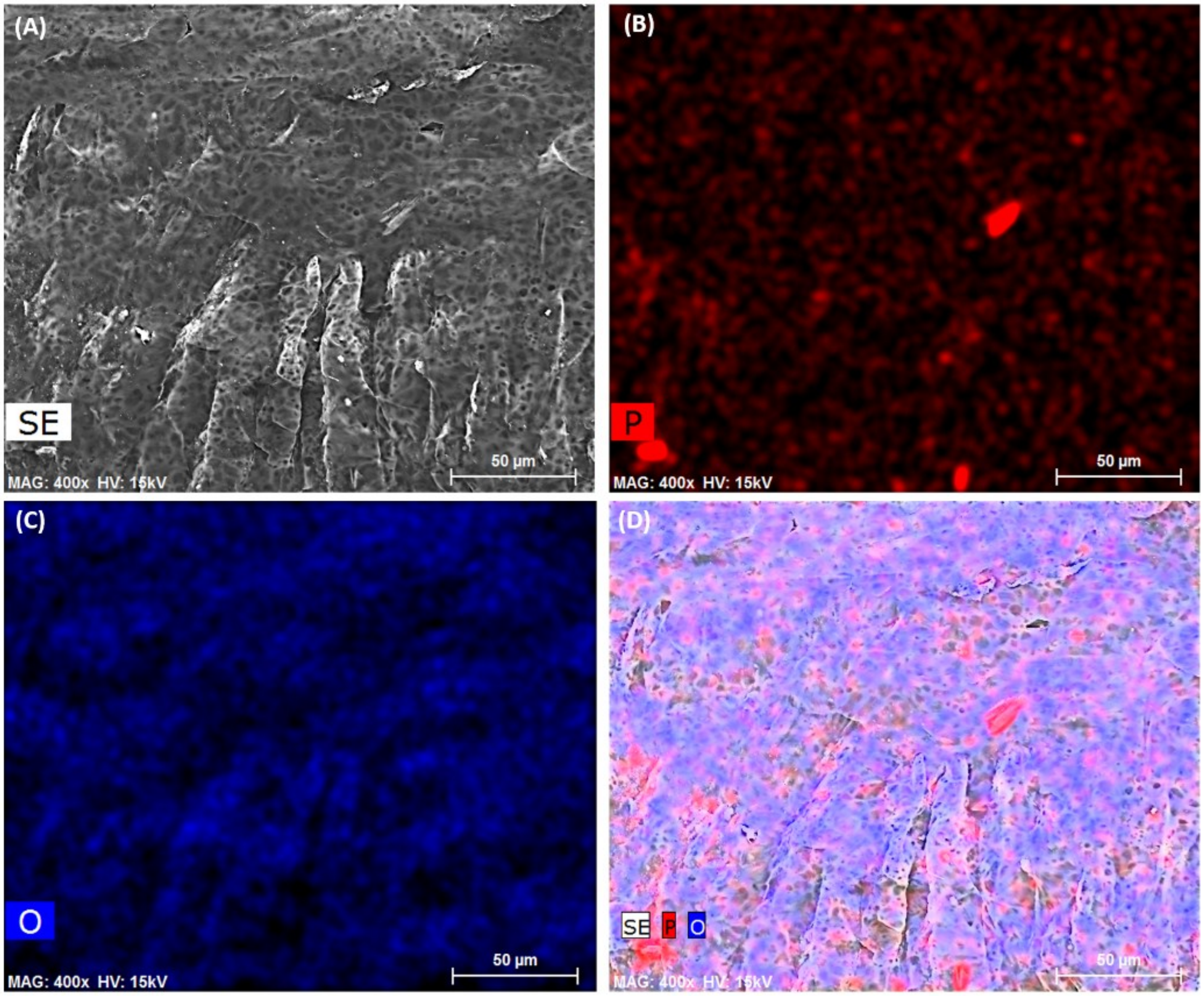

Figure S9. (A) SEM micrograph and (B, C and D) matching phosphorous and oxygen EDS maps obtained on the top surface of a PLA/[CH][DHP]5 membrane.

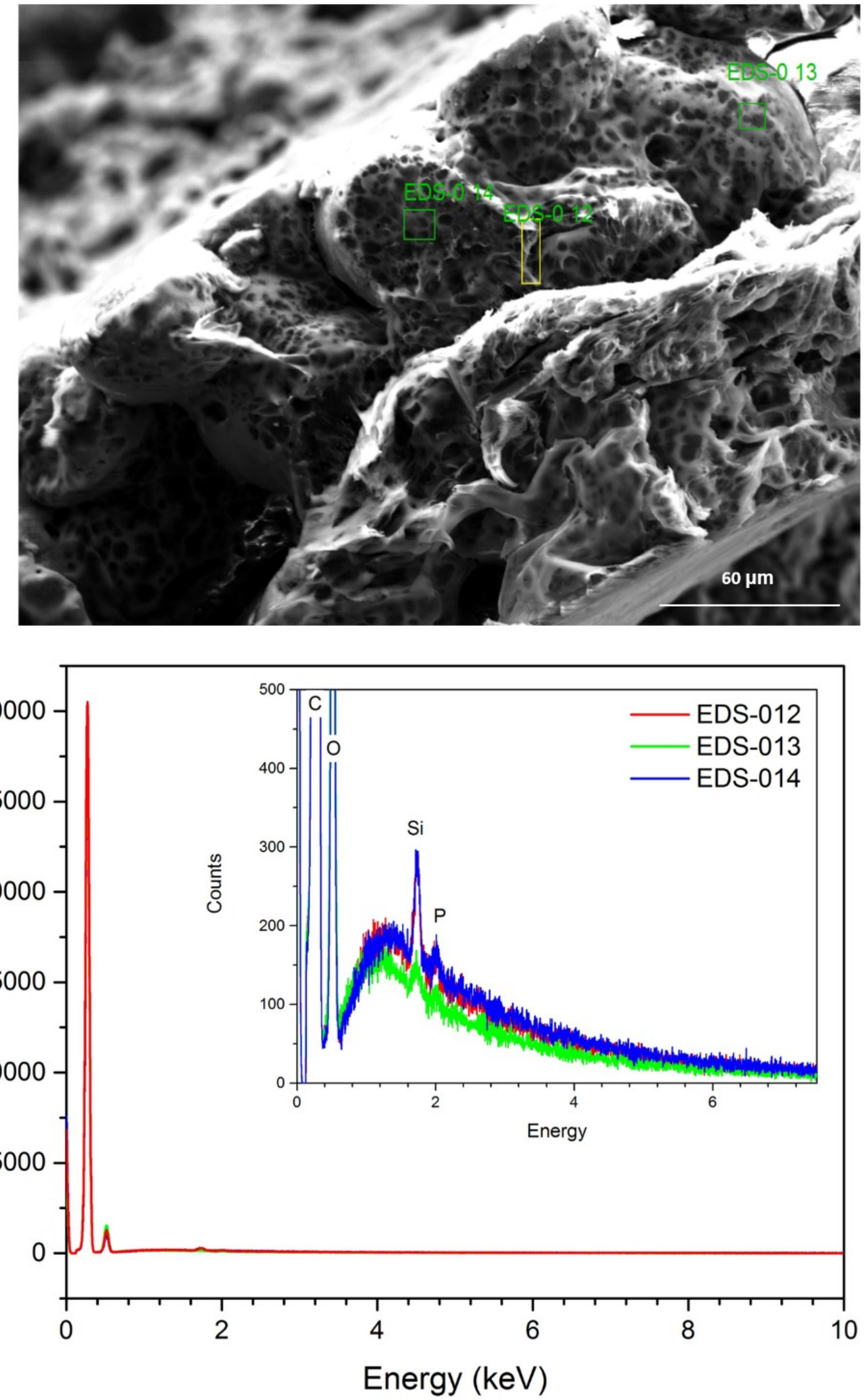

Figure S10. EDS spectra of PLA/[CH][DHP]10 taken at 3 different locations of the cross-section.

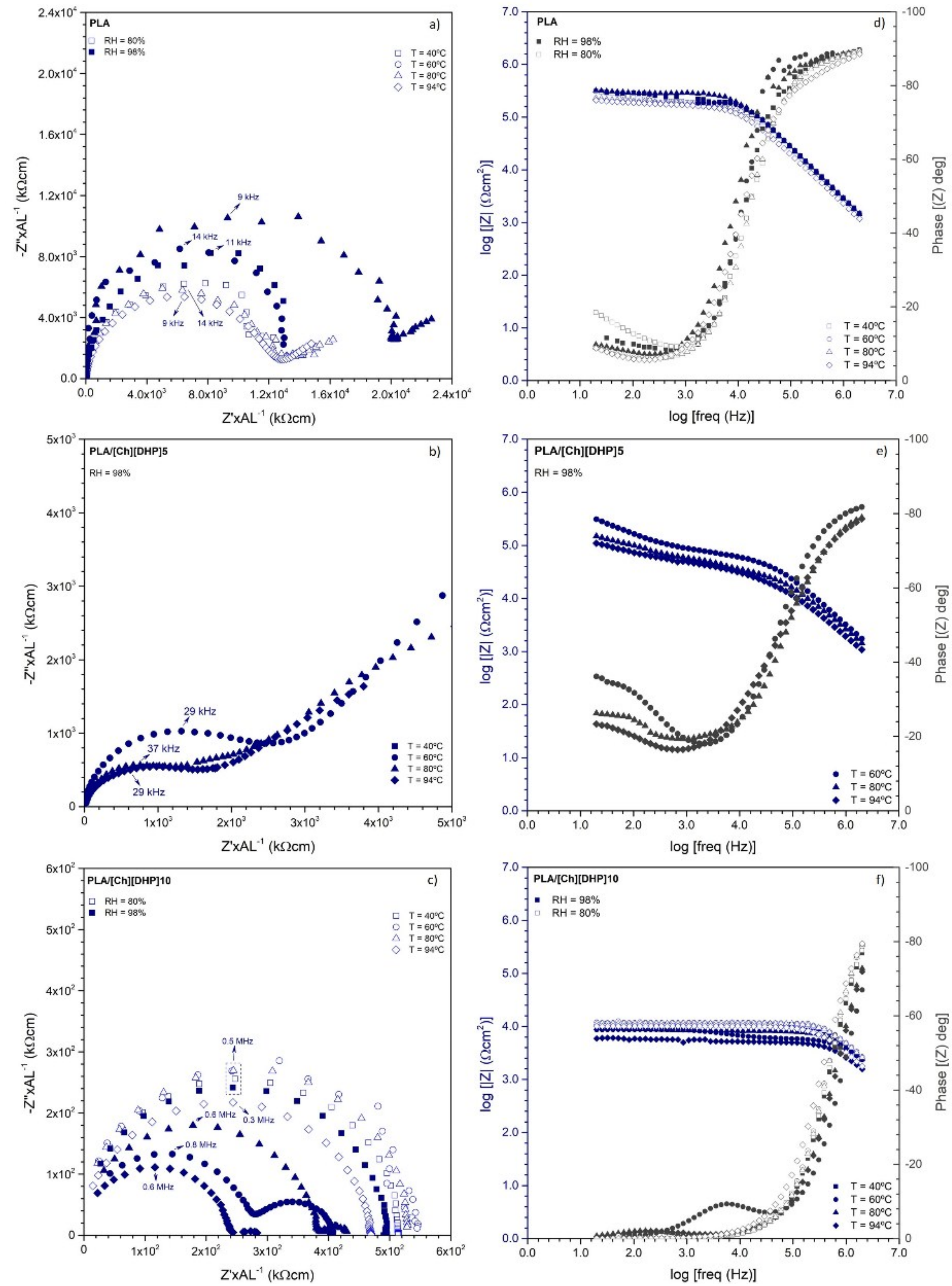

Figure S11 a) to c) shows the Nyquist plots of PLA and PLA/[Ch][DHP] blend membranes at variable relative humidity (60% to 98%) for temperatures ranging from 40 °C up to 94 °C.

The impedance spectra are in most cases dominated by one single relaxation with a peak frequency at *ca*. 10 kHz, 30 kHz and 300 kHz for pure PLA, PLA/[Ch][DHP]5 and PLA/[Ch][DHP]10, respectively. Such variation can be understood in simple terms considering the usual parallel RC equivalent circuit with relaxation frequency proportional to $(RC)^{-1}$, since the resistance decreases by orders of magnitude with increasing choline fraction and the capacitance is much less affected by composition (the dielectric constant should be typical of ionic conductors, varying from about 10 to 100). There is also a capacitive tale (or a second semicircle in the case of the most conductive sample PLA/[Ch][DHP]10) at low frequency which is ascribed to the membrane electrode interface. The Bode diagrams corresponding to the Nyquist plots are presented in Fig. 11 c) e) and f) illustrate of the frequency dependence of the impedance. The maximum phase angle is in the range 80° - 90º from 2 MHz down to 100 kHz for pure PLA, then sharply decreasing to around 10° at 1 kHz, which is the frequency that marks the transition between the bulk relaxation and the electro/membrane interface capacitance regime, which accompanied by a slight increase in the phase angle. The addition of increasing amounts of choline to PLA decreases progressively the phase angle at high frequencies, and increases the frequency at the transition between the bulk and the electrode relaxations (about 10 kHz for PLA/[Ch][DHP]5 and 100 kHz for PLA/[Ch][DHP]10). The ohmic resistance of the samples is taken as the amplitude of the high frequency semicircle in the Nyquist plots.

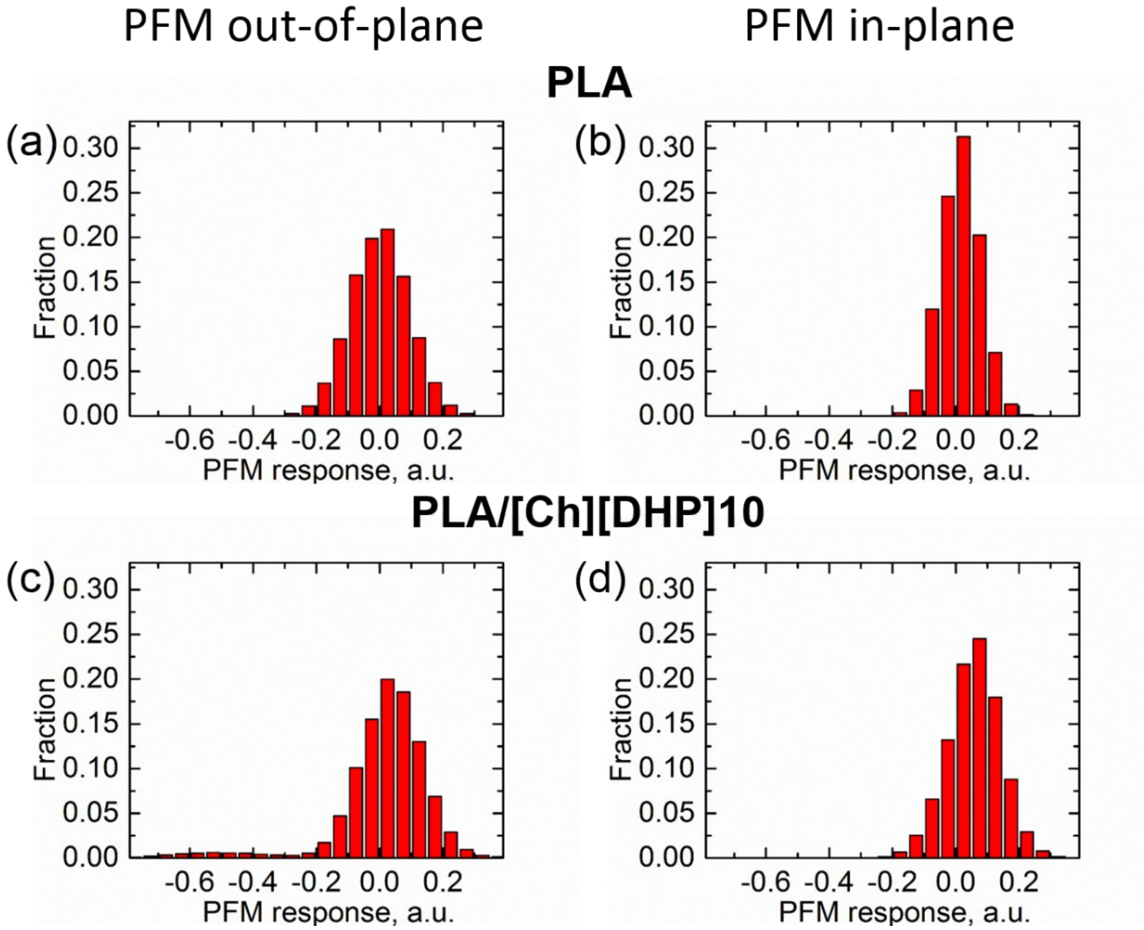

Figure S12. Piezoelectric histograms of both vertical and lateral piezoresponses shown in Fig. 8. Only out-of-plane histogram shows significant piezoresponse in the negative part.

Table S1. Contact angles (α) of pure PLA and PLA/[Ch][DHP]10 membranes with water, along with the respective standard deviations (s).

Sample	$\alpha \pm s$ (degree)
PLA	80.07±1.21
PLA/[Ch][DHP]10	97.73±2.27

Table S2. Effective d_{33} piezoelectric coefficients derived by the comparison with the standard periodically pooled $LiNbO_3$ (PPLN) sample (d_{33}=7.5 pm V^{-1}).

Sample	Effective d_{33} (pm V^{-1})	Ratio of PLA/PPLN responses
PLA	2.1	0.28
PLA/[Ch][DHP]10	4.8	0.61
PPLN	7.5	1