Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supplementary information

SI 1 Evaluation of swelling volume of the homo and co-polymer membranes

For calculating swelling volume, two pieces of the dried membranes were taken and are immersed in 85 % (CHTA-0, CHTA-10, CHTA-30 and CHTA-50) and 68 % (CHTA-90 and CHTA-100) phosphoric acid for 3 days. After 3 days, the membranes were taken out, wiped with tissue paper to remove excess acid and the dimensions (length, breadth and thickness) were taken. Swelling volume is calculated by using the relation.

$$\text{Swelling volume} = \frac{V2 - V1}{V1} \text{ x } 100\% \quad (1)$$

where V_2 and V_1 are the volumes (length x breadth x height) of doped and dried membrane respectively.

SI 2 Determination of oxidative stability (Fenton's test)

Oxidative stability of the membranes was determined by using Fenton's test. For this, two pieces of the dried membranes were taken, immersed in freshly prepared Fenton's reagent (3% H_2O_2 solution containing 4 ppm Fe^{2+}) and kept at 70 °C for 120 h. The integrity and weight loss of the membranes after definite time interval is the measure of oxidative stability. The membranes were taken periodically at an interval of 24 h, washed thoroughly with deionized water 5 to 6 times and dried in a vacuum oven at 120 °C for 15 h. After drying, by recording the weight of membranes, weight loss can be calculated. From weight loss, oxidative stability is calculated using the equation:

$$\text{Oxidative stability} = \frac{Wf - Wi}{Wi} \text{ x } 100\% \quad (2)$$

where W_f and W_i are the weight of membrane after and before Fenton's test.

SI 3 Determination of acid doping

The amount of acid doped is usually expressed as number of moles of phosphoric acid doped per repeating unit (N_{PA}/RU). It can be calculated as:

$$\text{Number of moles of } H_3PO_4 \text{ doped} = \frac{W_2 - W_1}{W_1} \frac{W_{PBI}}{M_{H_3PO_4}} \text{ moles / repeating unit } H_3PO_4 \quad (3)$$

where W_2 and W_1 are the weight of doped and dried membrane, W_{PBI} is the molecular weight of PBI repeating unit and $M_{H_3PO_4}$ is the molecular weight of phosphoric acid respectively.

SI 4 Calculation of molecular mass of co-polymers

Mark-Houwink Equation

$$[\eta] = K (M_w)^a \quad (4)$$

$K = 1.94 \times 10^{-4}$ and $a = 0.791$

Co-polymer	Inherent viscosity (dL/g)	Molecular mass (kDa)
CHTA-0	3.46	237
CHTA-10	2.74	176
CHTA-30	2.13	128
CHTA-50	3.56	246
CHTA-90	3.24	218
CHTA-100	1.50	082

SI 5 Calculation of co-polymer composition

For 100% terephthalic acid based PBI (homopolymer, CHTA-0), integral value of terephthalic acid part is 5.5 (f-marked in NMR spectra). For 100% cyclohexane dicarboxylic acid based PBI (homopolymer, CHTA-100), integral value corresponding to cyclohexane part is 16 (g+h+i - marked in NMR spectra).

In the co-polymer compositions, the integral value of diaminobenzidine part is kept as constant (10.7, c+d+e - shown in NMR spectra) and then compared the integral values of terephthalic acid part (aromatic) and cyclohexane part (aliphatic).

For example- In CHTA-10, co-polymer

Integral of terephthalic part = 5.1

Integral value of cyclohexane part = 1.5

% of cyclohexane part in the co-polymer = 1.5/ (1.5+5.1) = 22.7

% of terephthalic part = 5.1/ (5.1+1.5) = 77.3

Similarly, compositions of other co-polymers were calculated. Table given below gives the integral values and actual compositions of all co-polymers.

Co-polymer	CH integral	DAB integral	TA integral	Composition based on ^{1}HNMR (%)	
				CH part	TA part
CHTA-0	0	10.7	5.5	0	100
CHTA-10	1.5	10.7	5.1	23	77
CHTA-30	6	10.7	4	60	40
CHTA-50	8.6	10.7	3.2	73	27
CHTA-90	14	10.7	0.05	100	0
CHTA-100	16	10.7	0	100.0	0

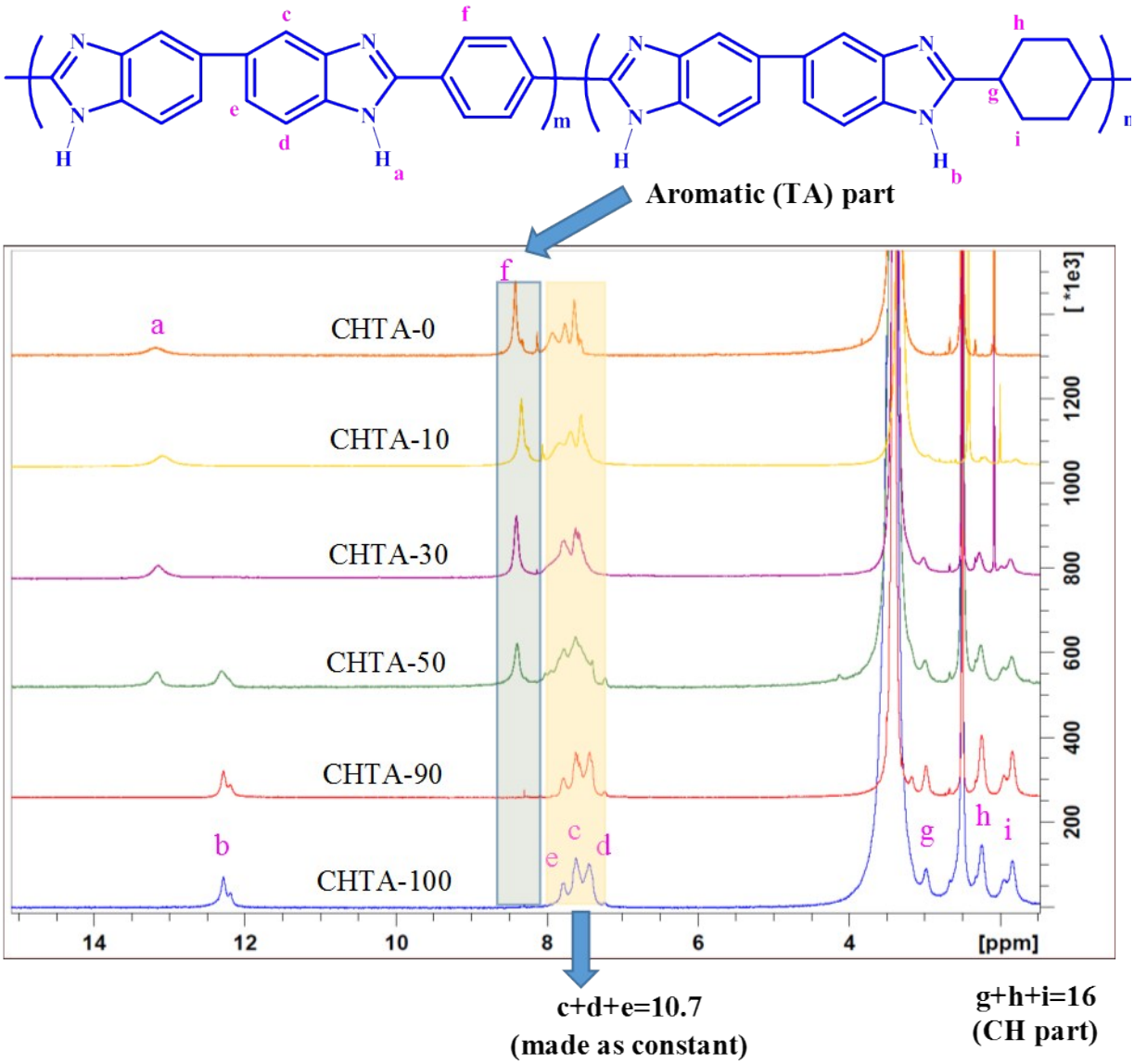


Figure shows NMR spectra of the co-polymers

SI 6 Calculation for finding out the d-spacing of co-polymers

The d-spacing of the materials calculated from PXRD measurements using Bragg's equation

$$n \lambda = 2 d \sin \theta \quad (5)$$

(Wavelength of CuKα line is 1.5419 Å)

For CHTA-100, the value of 2θ = 19.8° and d = 4.48A°

For CHTA-90, the value of 2θ = 19.9° and d = 4.46 A°

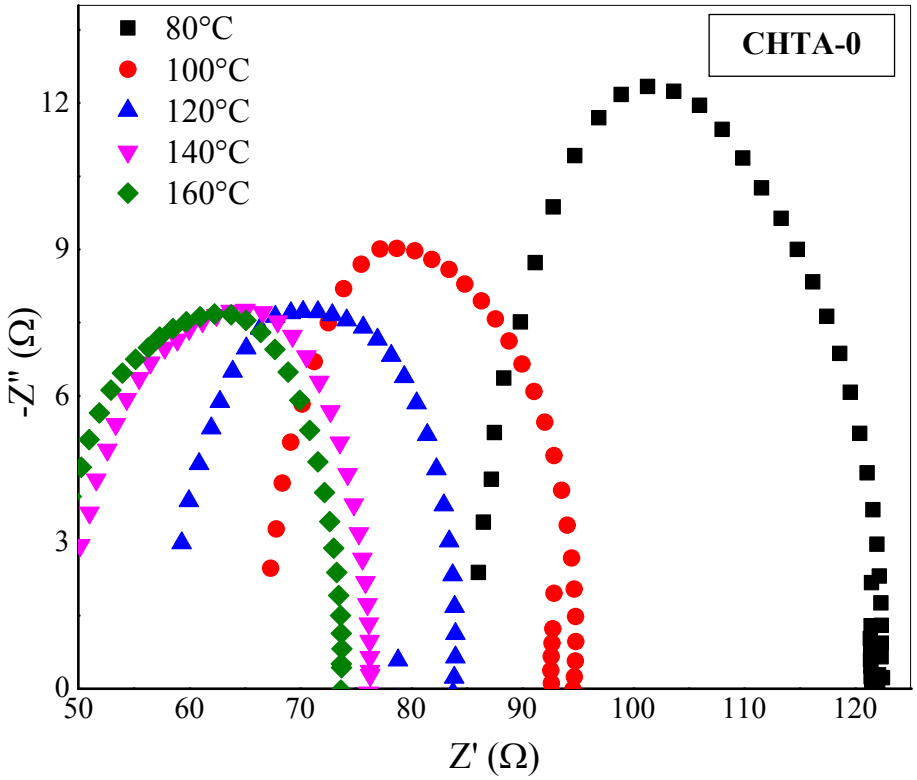
For CHTA-50, the value of 2θ = 21.0° and d = 4.23 A°

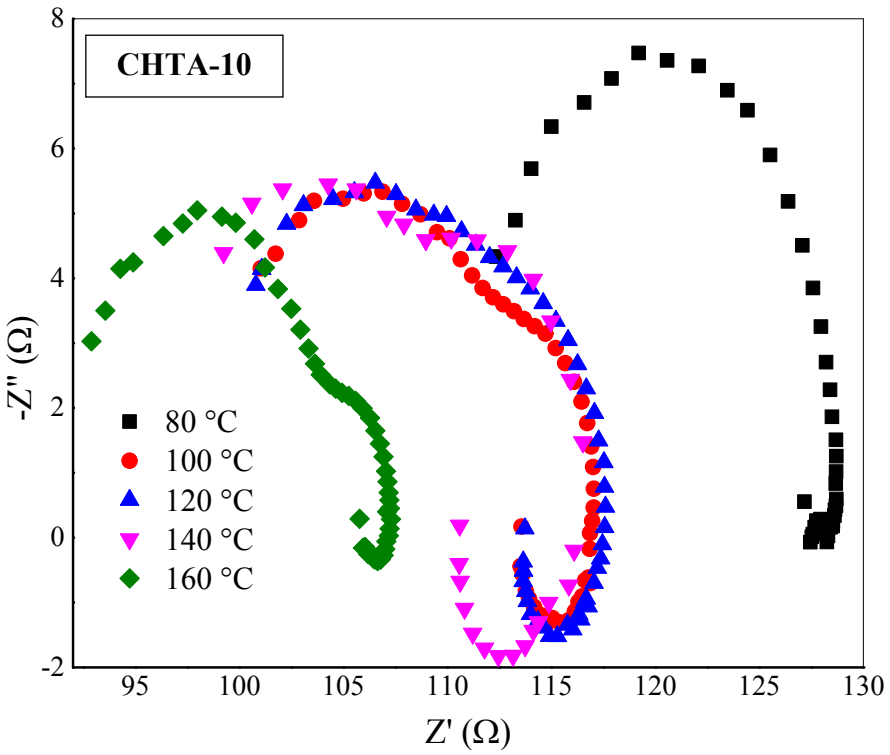
For CHTA-30, the value of 2θ = 24.5° and d = 3.63 A°

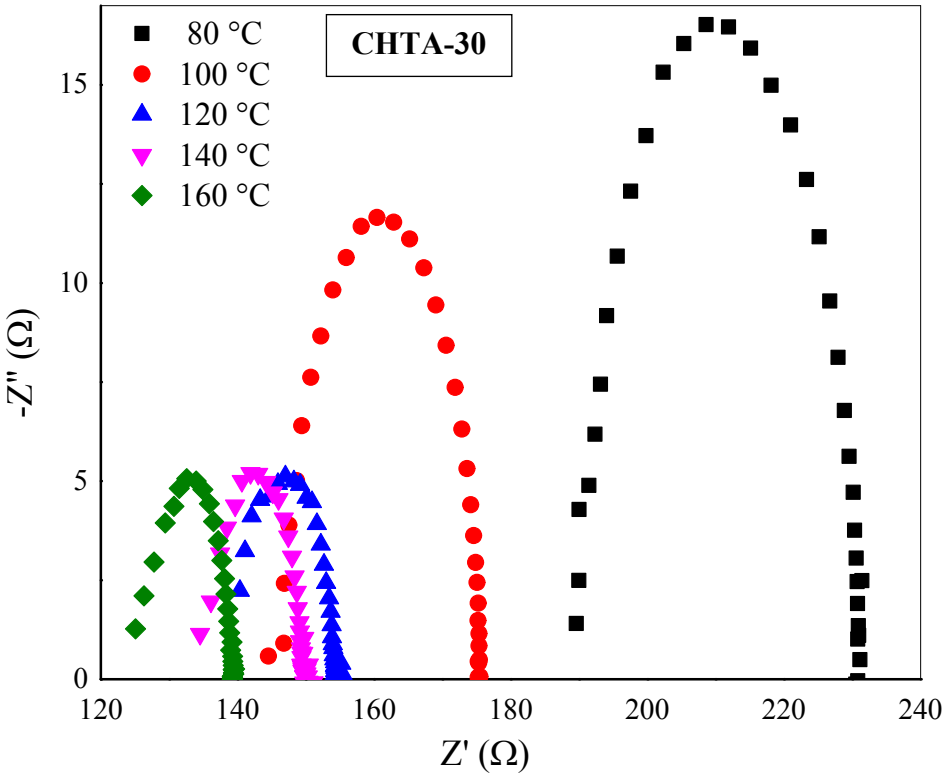
For CHTA-10, the value of 2θ = 25.0° and d = 3.56 A°

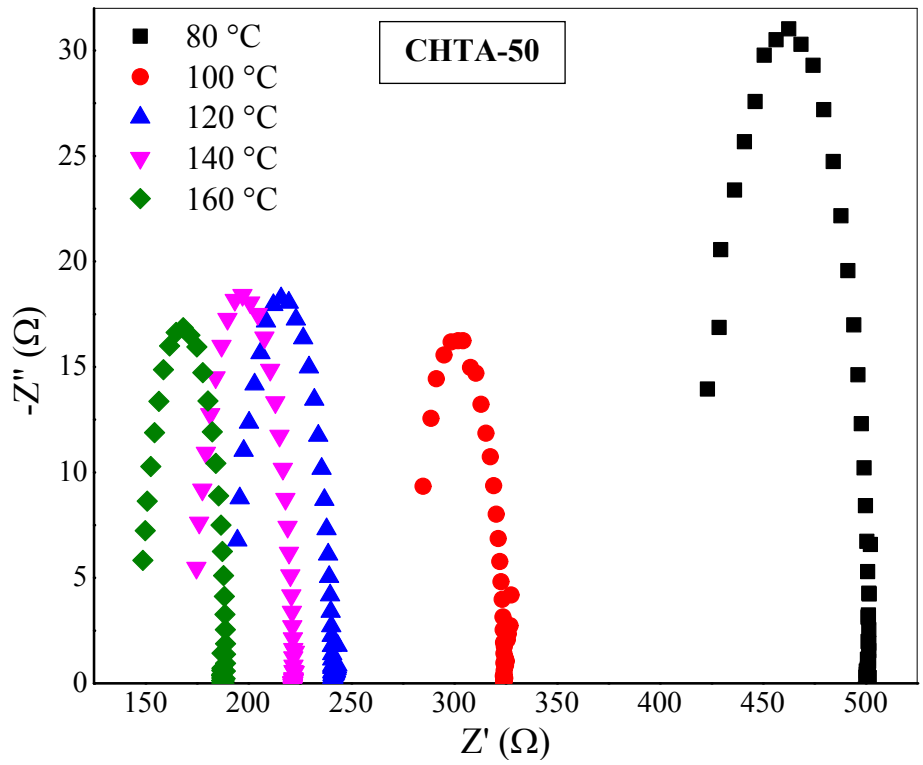
For CHTA-0, the value of 2θ = 25.6° and d = 3.48 A°

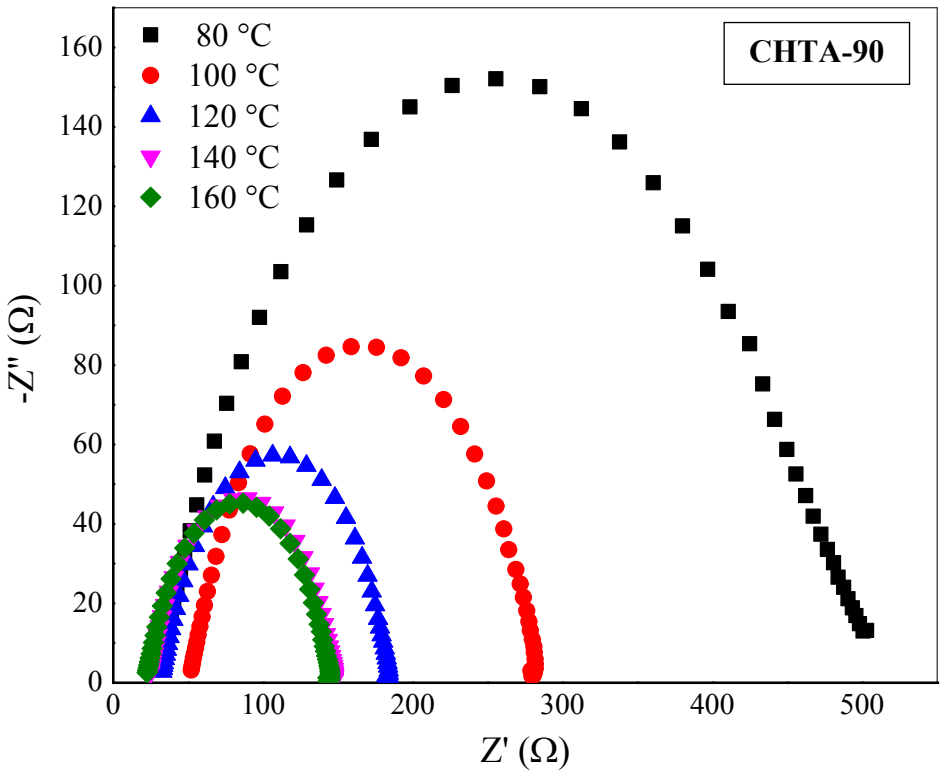
SI 7 Nyquist plot of the membranes.

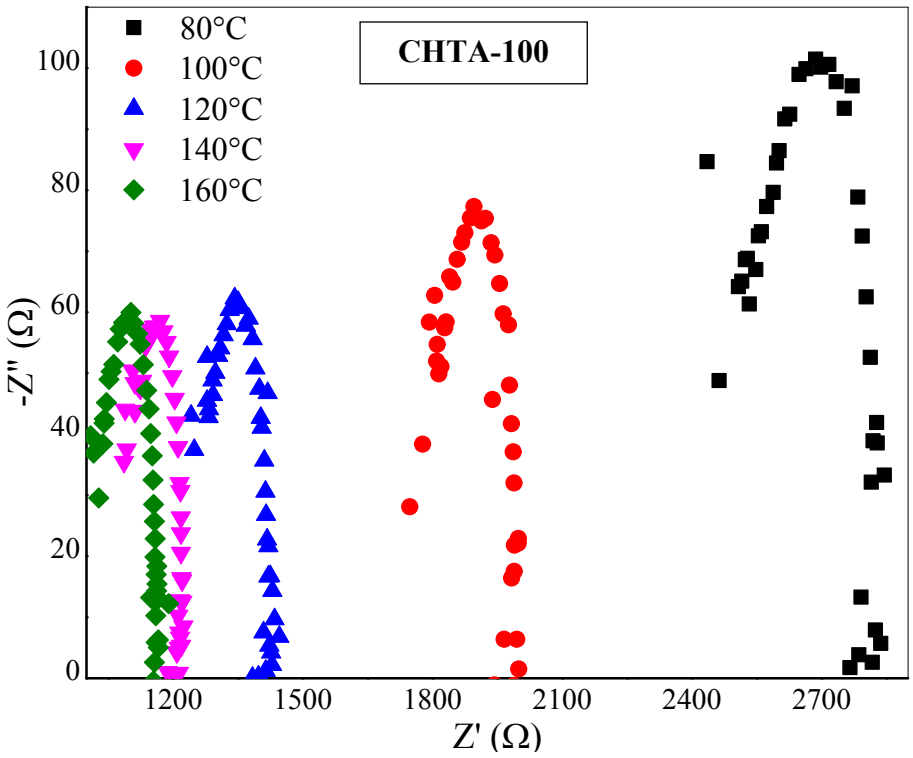



CHTA-10
80 °C
100 °C
120 °C
140 °C
160 °C
-Z'' (Ω)
Z' (Ω)
8
6
4
2
0
-2
95
100
105
110
115
120
125
130

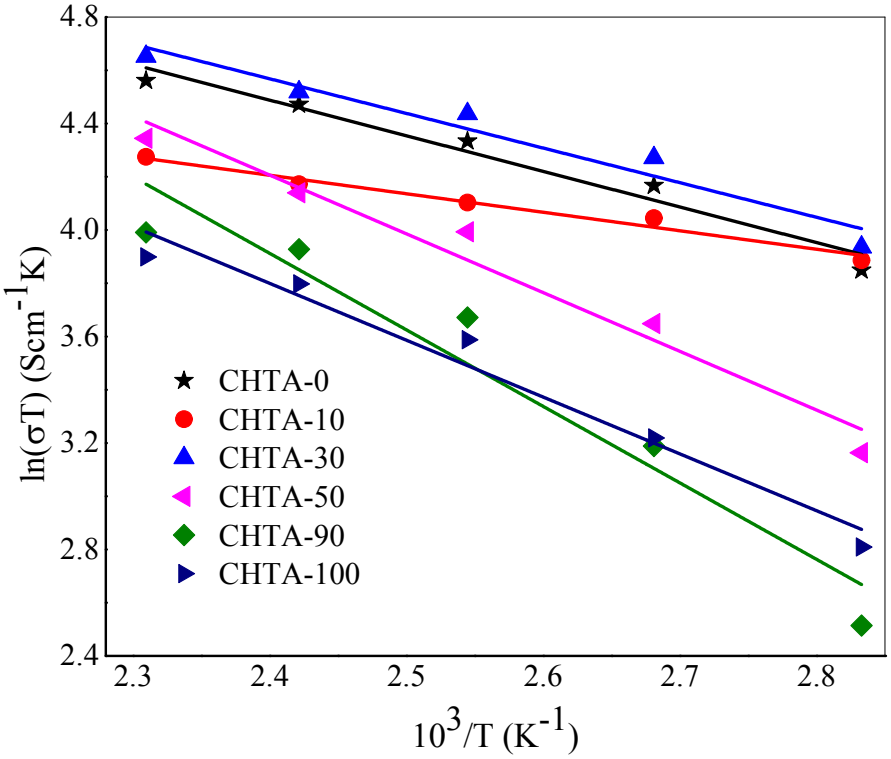

CHTA-30
80 °C
100 °C
120 °C
140 °C
160 °C
-Z'' (Ω)
Z' (Ω)
15
10
5
0
120
140
160
180
200
220
240


CHTA-50
80 °C
100 °C
120 °C
140 °C
160 °C
-Z'' (Ω)
Z' (Ω)
0
5
10
15
20
25
30
150
200
250
300
350
400
450
500


CHTA-90
80 °C
100 °C
120 °C
140 °C
160 °C
-Z'' (Ω)
Z' (Ω)
0
20
40
60
80
100
120
140
160
0
100
200
300
400
500



SI 8 Arrhenius plots of homo and co-polymers to describe the kinetics and proton conduction mechanism.



SI 9 Thermo gravimetric profiles of homo and co-polymers.