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Electronic Supplementary Information (ESI)

Novel Nanostructured Semicrystalline Ionomers by Chemoselective Sulfonation of Multiblock Copolymers of Syndiotactic Polystyrene with Polybutadiene

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1. NMR Analysis.

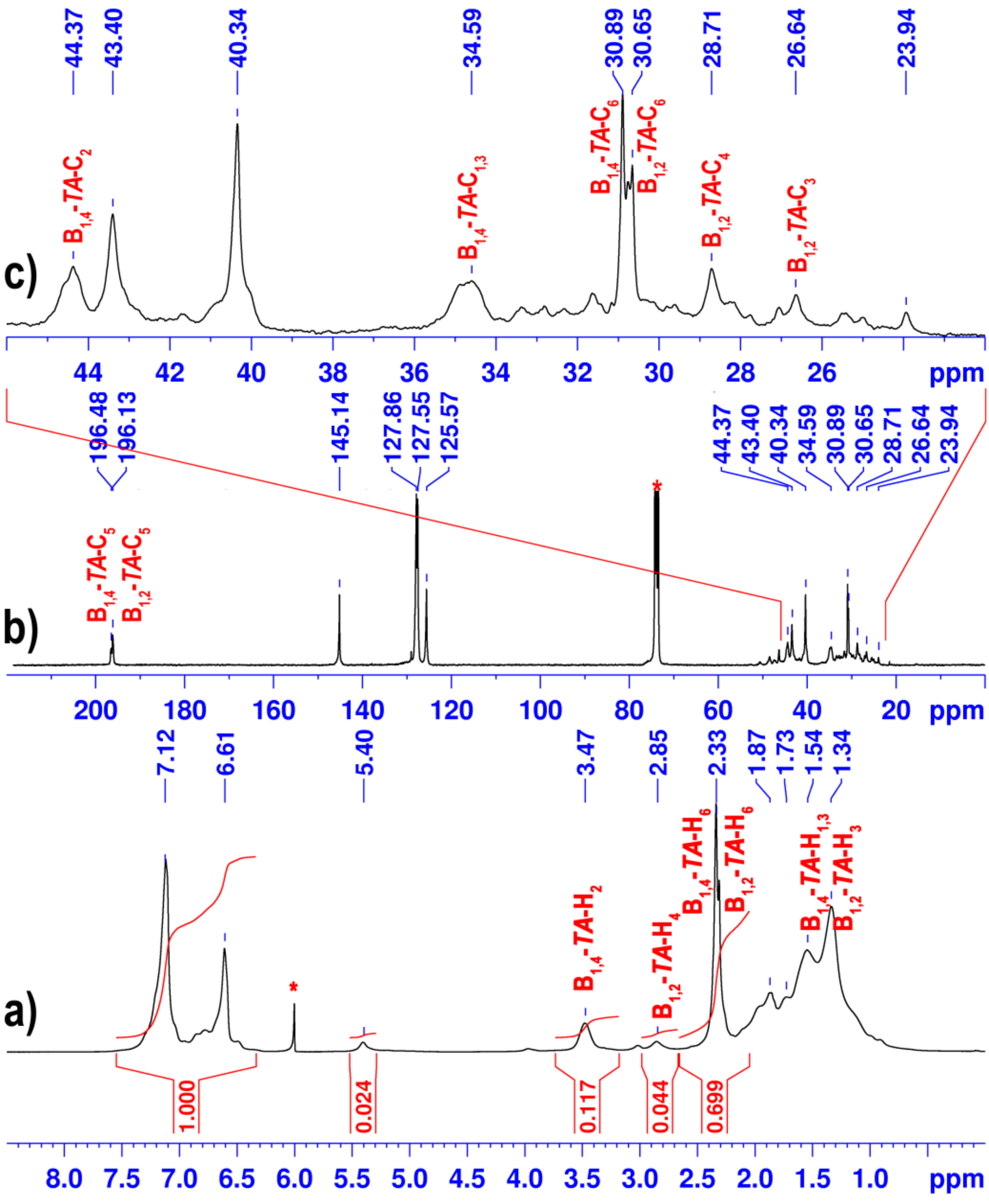


Fig. S1. NMR spectra (TCE-d_2; 25°C) of **1-*TA*** (Table 1): a) ^{1}H NMR; b) ^{13}C NMR; c) magnification of the 46-22 ppm region of ^{13}C NMR spectrum. The characteristic signals of polystyrene were not labelled for simplicity.

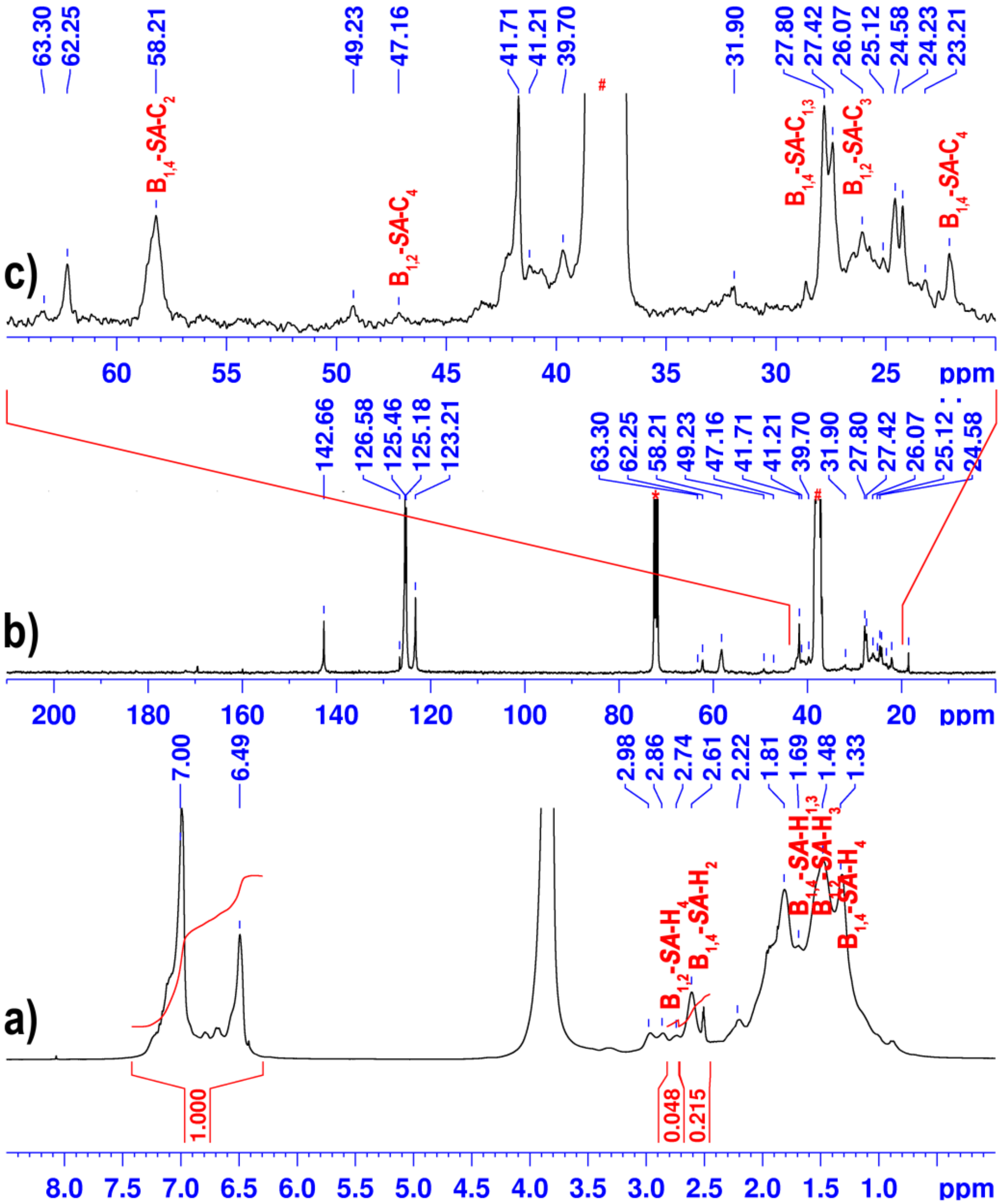
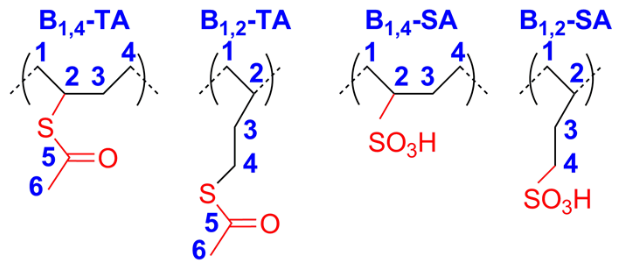


Fig. S2. NMR spectra (TCE-d_2/DMSO-d_6, v/v = 1/1, 90°C) of **1-*SA*** (Table 1): a) ^{1}H NMR; b) ^{13}C NMR; c) magnification of the 65-20 ppm region of ^{13}C NMR spectrum. The characteristic signals of polystyrene were not labelled for simplicity.

Table S1. ^{1}H and ^{13}C NMR diagnostic signals for sPS(B−*TA*) and sPS(B−*SA*).



Units		**sPS(B−*TA*)**[b]		**sPS(B−*SA*)**[c]	
	H or C	**^{1}H (ppm)**	**^{13}C (ppm)**	**^{1}H (ppm)**	**^{13}C (ppm)**
	1,3	1.5	34.59	1.6	27.80
	2	3.47	44.37	2.61	58.21
$B_{1,4}$	4	*n.r*[a]	*n.r.*[a]	1.36	22.11
	5	–	196.48	–	–
	6	2.33	30.89	–	–
	3	1.4	26.64	1.69	27.8−26.0
$B_{1,2}$	4	2.85	28.71	2.74	47.16
	5	–	196.13	–	–
	6	2.33	30.65	–	–

[a] *n.r.* = not resolved; [b] tetrachloroethane-d_2, 25 °C; [c] tetrachloroethane-d_2/dimethylsulfoxide-d_6, v/v = 1/1, 100 °C.

2. Gel Permeation Chromatography.

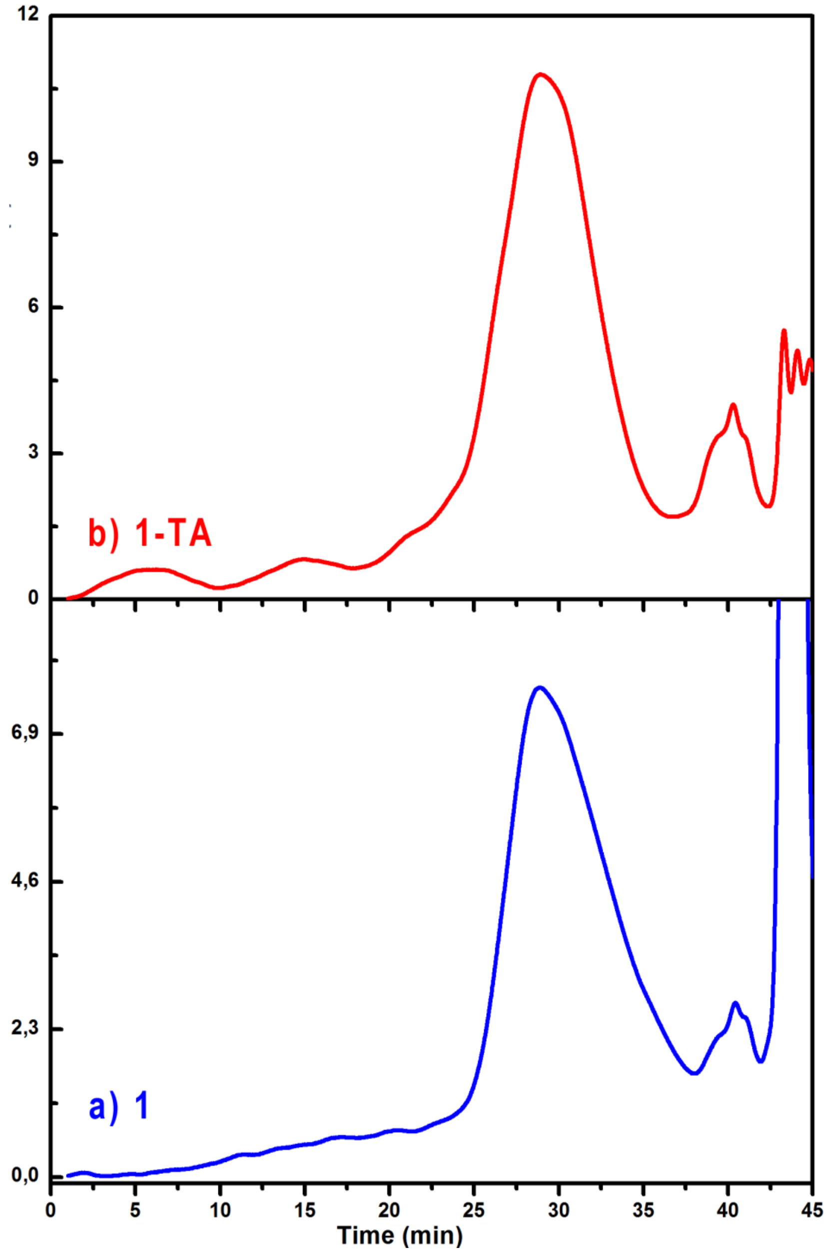


Fig. S3. GPC chromatograms of the samples: a) **1**; b) **1−*TA*** (Table 1).

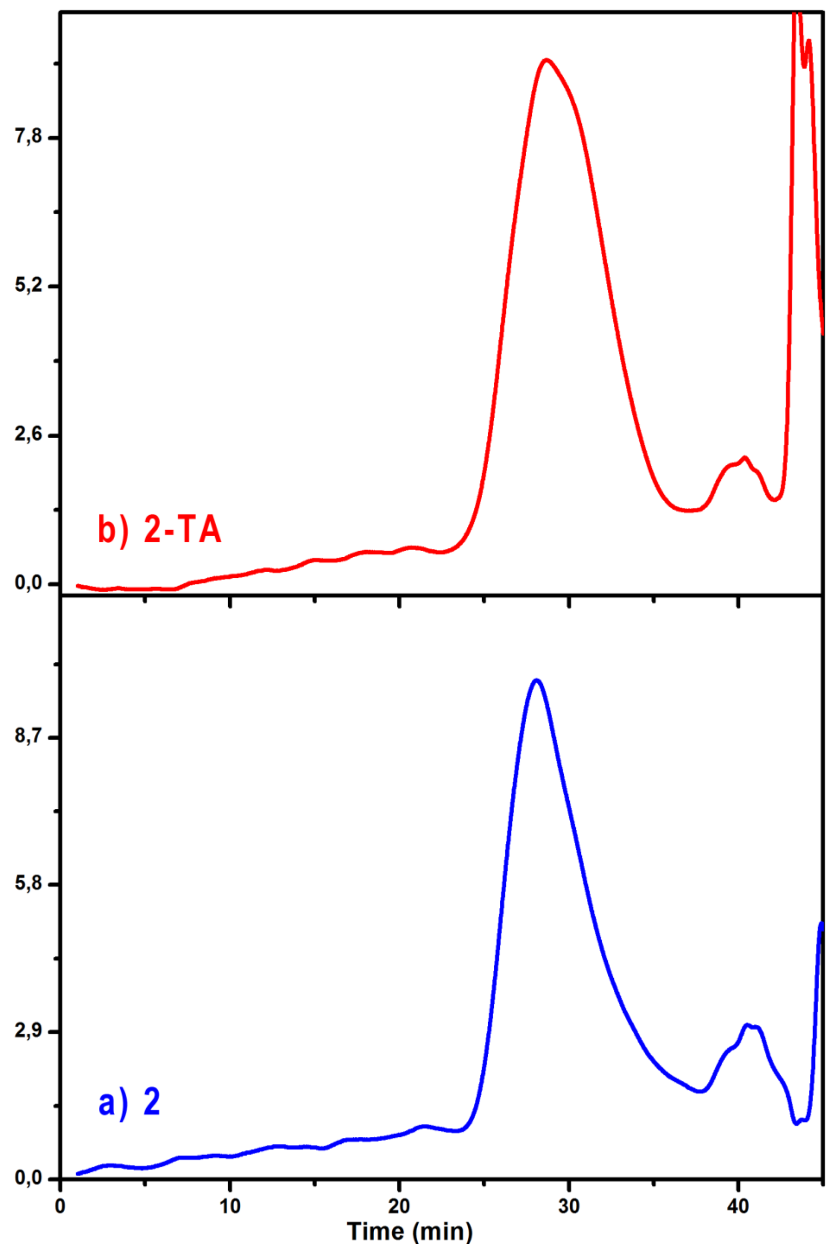


Fig. S4. GPC chromatograms of the samples: a) **2**; b) **2−*TA*** (Table 1).

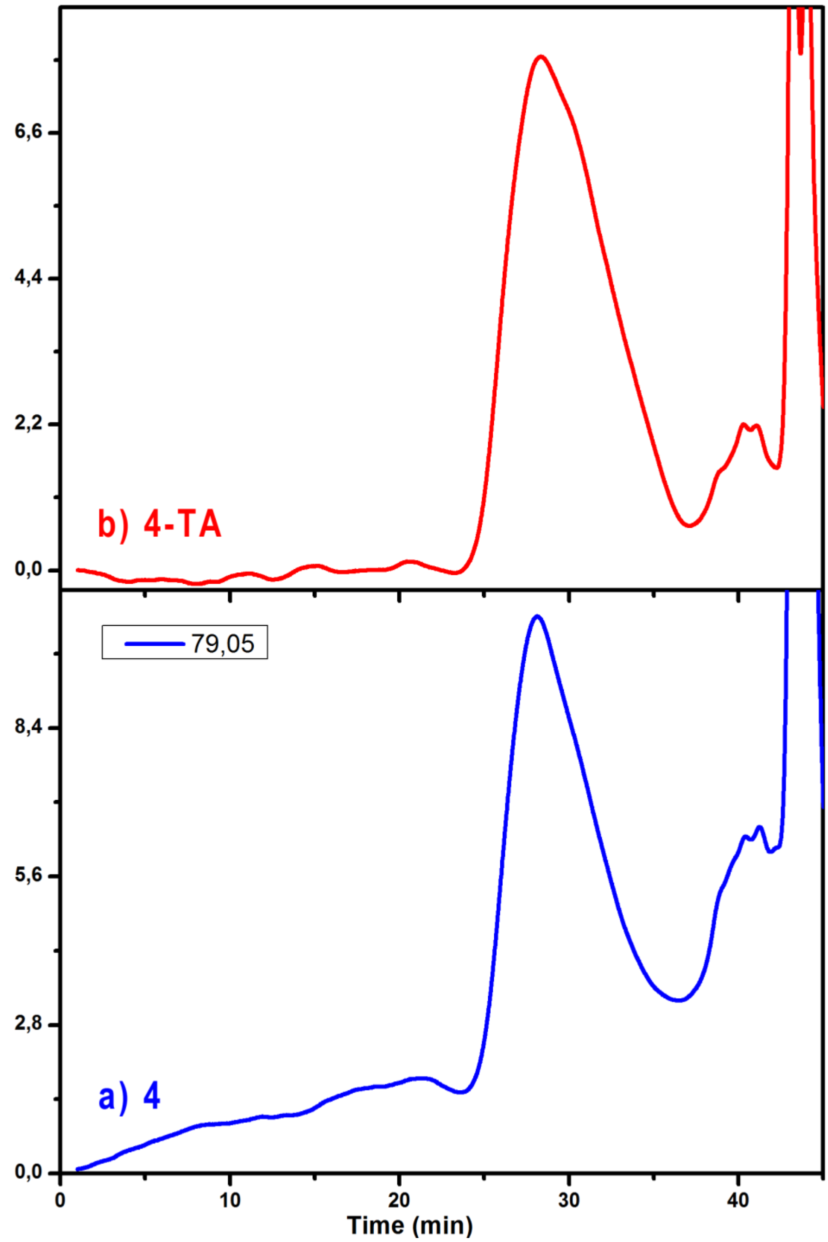


Fig. S5. GPC chromatograms of the sample: a) **4** and b) **4−*TA*** (Table 1).

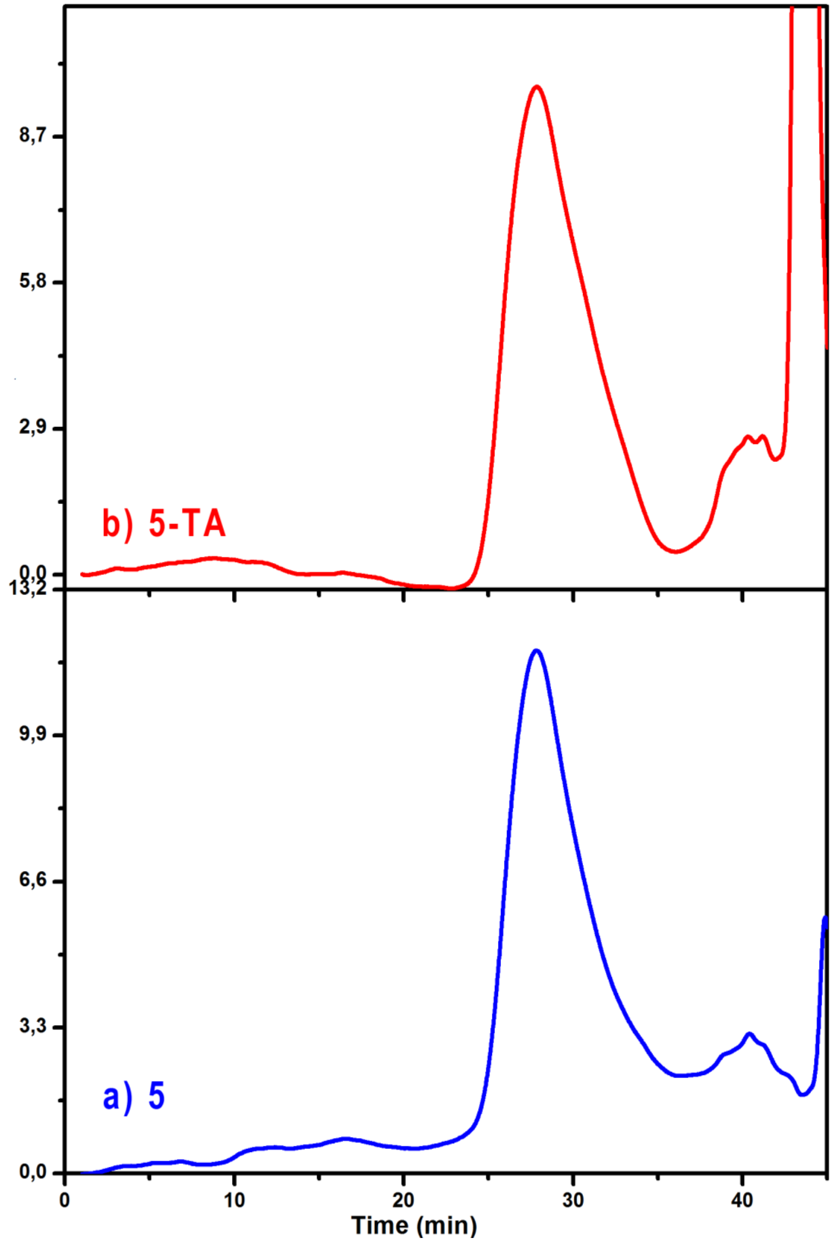


Fig. S6. GPC chromatograms of the samples: a) **5**; b) **5−*TA***.

3. Solubility Properties of Thioacetylated and Sulfonated sPSB Copolymers.

Table S2. Room Temperature Solubility of sPS(B−*TA*) and sPS(B−*SA*).

Solvent / Polymer	Toluene	Chloroform	Acetonitrile	TCE[a]/DMSO[b] (v/v = 1/1)	DMSO[b]	DMAc[c]	DMF	Water
sPS(B−*TA*)	Soluble	Soluble	Insoluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble
sPS(B−*SA*)	Insoluble	Insoluble	Insoluble	Soluble	Soluble (T > 80°C)	Soluble (T > 80°C)	Soluble (T > 80°C)	Insoluble

[a] 1,1,2,2-tetrachloroethane; [b] dimethylsulfoxide; [c] *N,N*-dimethylacetamide.

4. Thermal Analysis.

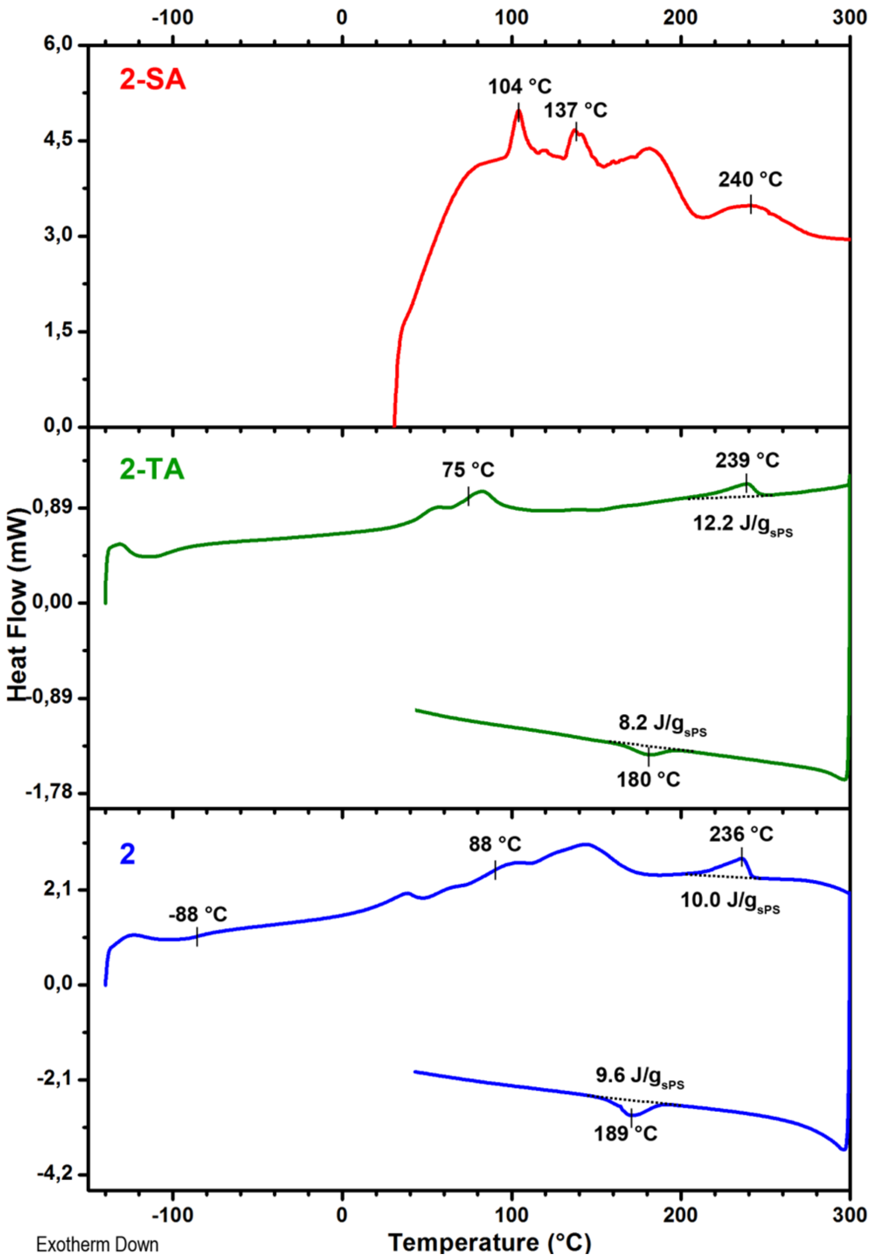


Fig. S7. DSC thermograms of the samples **2**, **2−*TA*** and **2−*SA***.

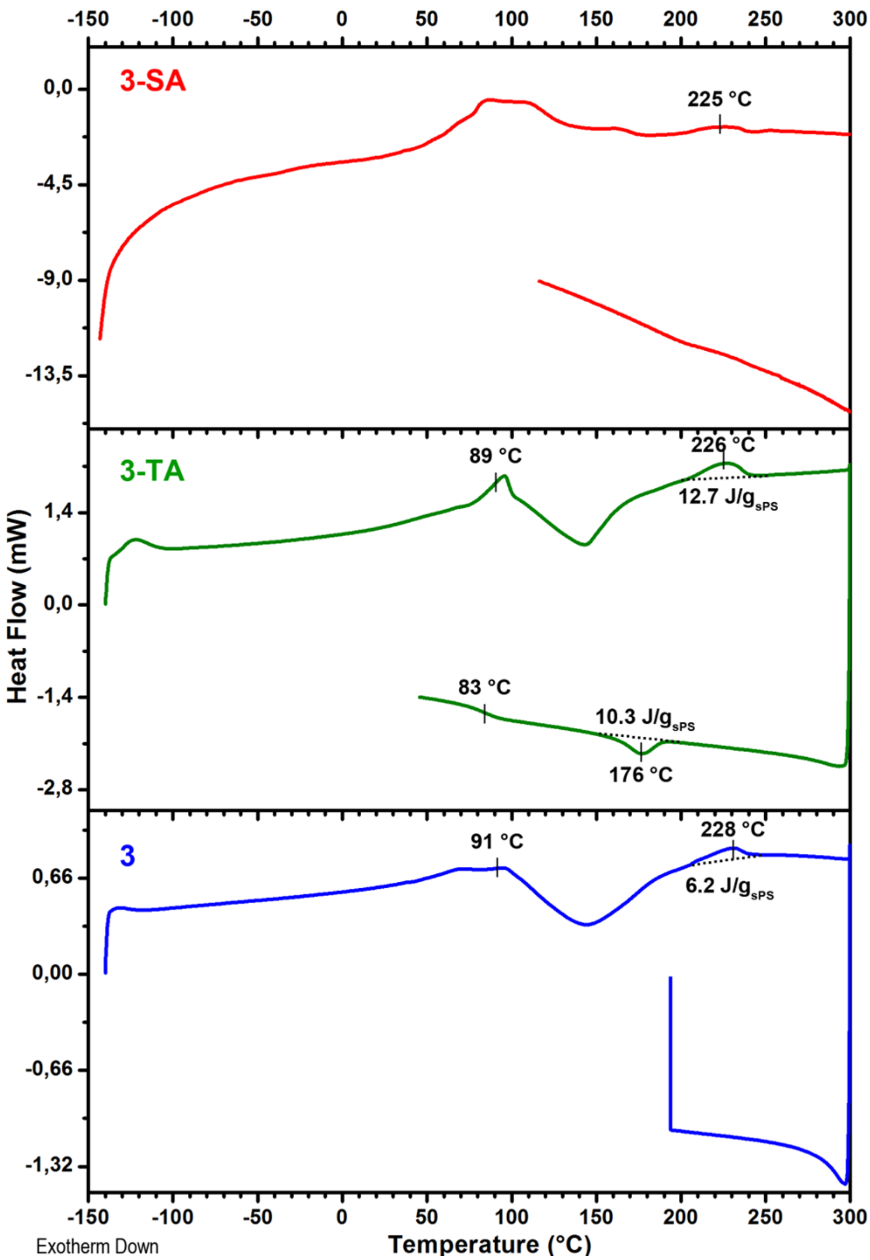


Fig. S8. DSC thermograms of the samples **3**, **3−*TA*** and **3−*SA***.

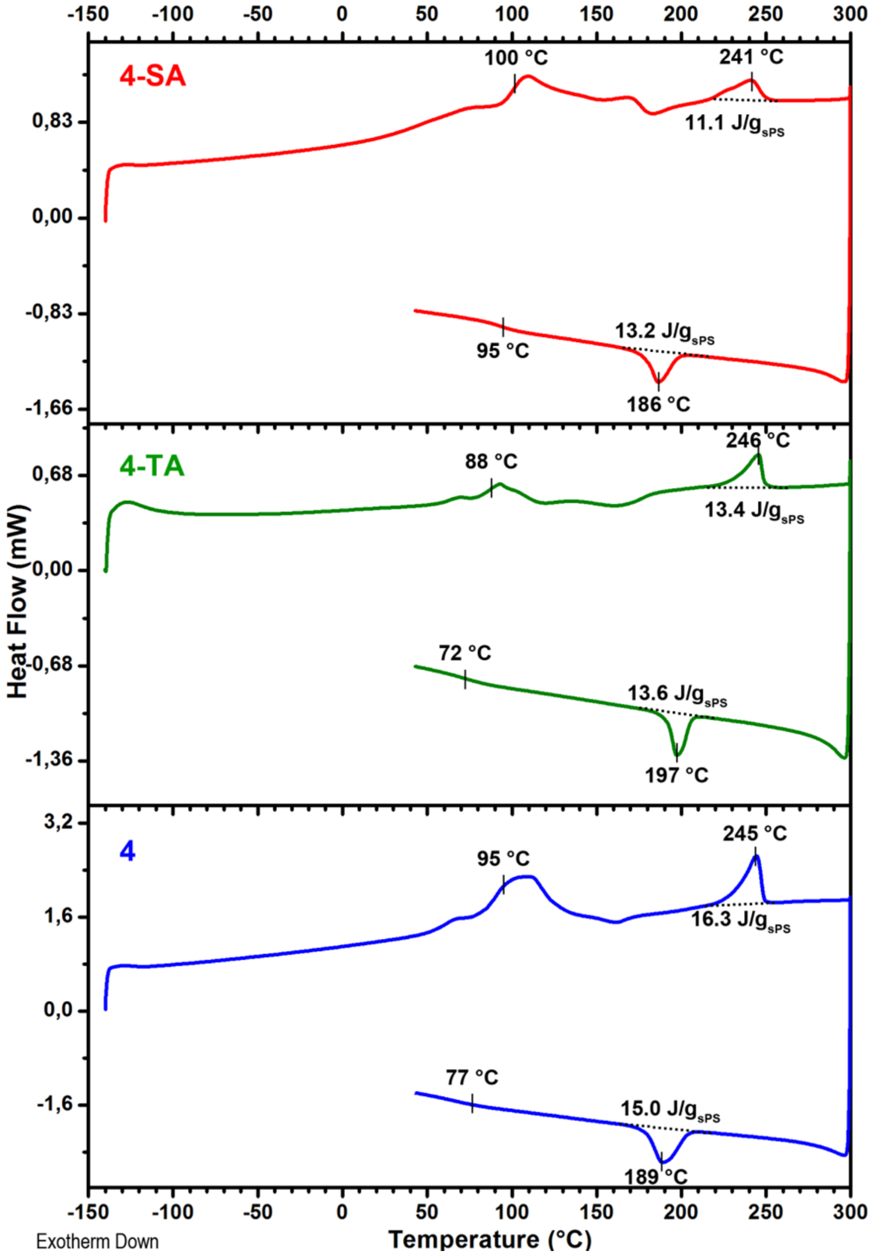


Fig. S9. DSC thermograms of the samples **4**, **4−*TA*** and **4−*SA***.

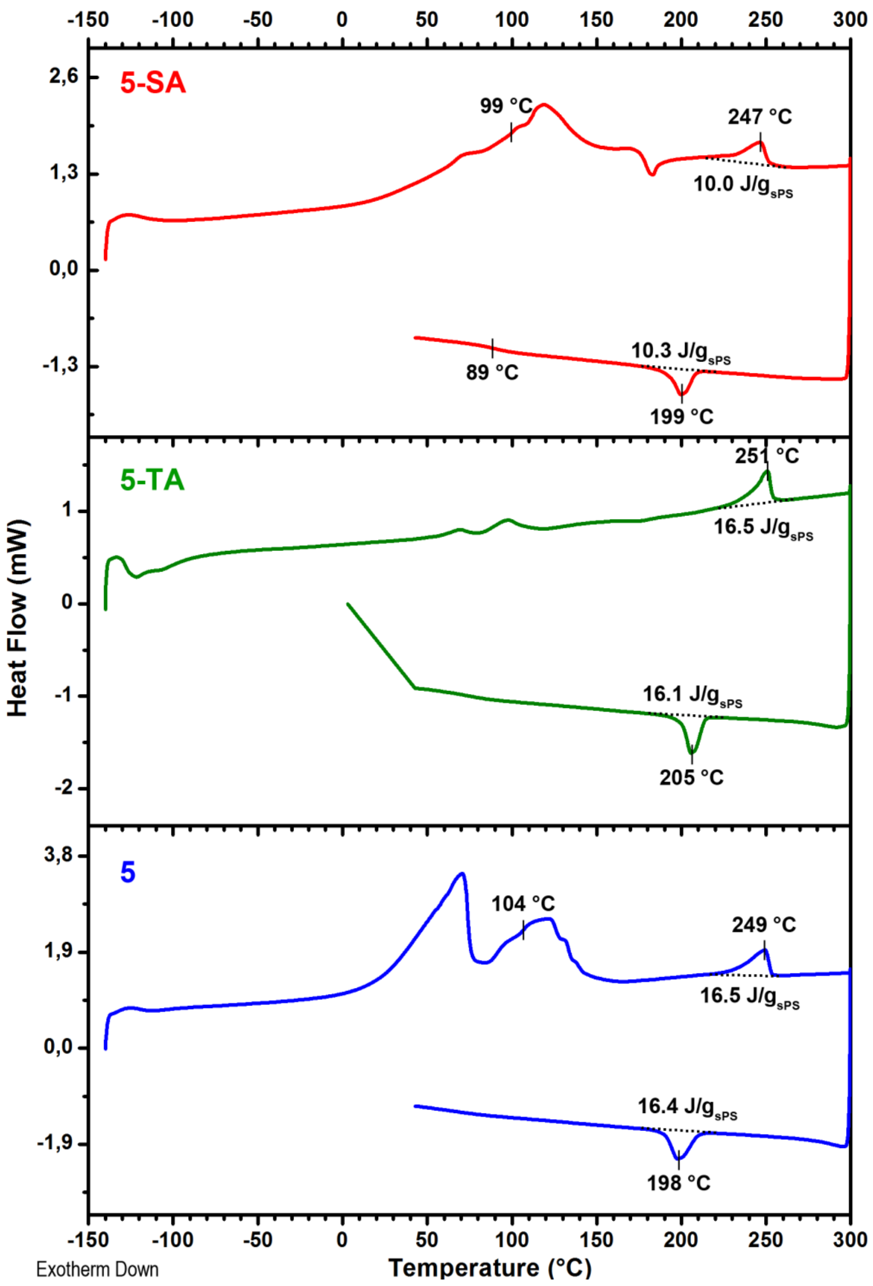


Fig. S10. DSC thermograms of the samples **5**, **5−*TA*** and **5−*SA***.

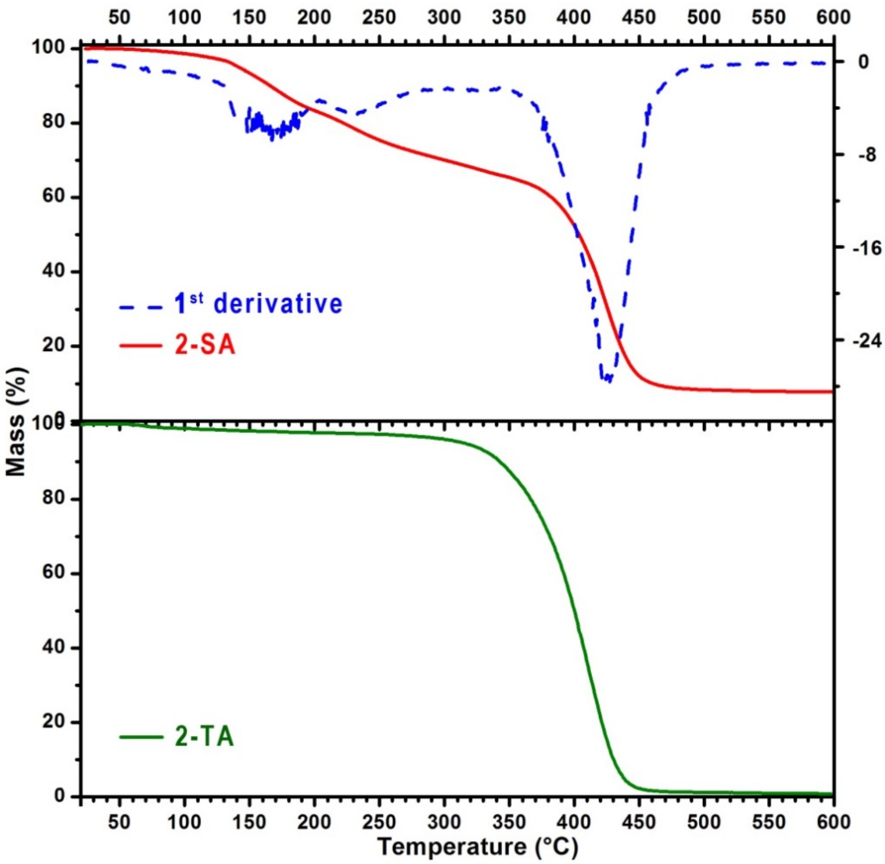


Fig. S11. TGA traces of the samples **2−*TA*** and **2−*SA***.

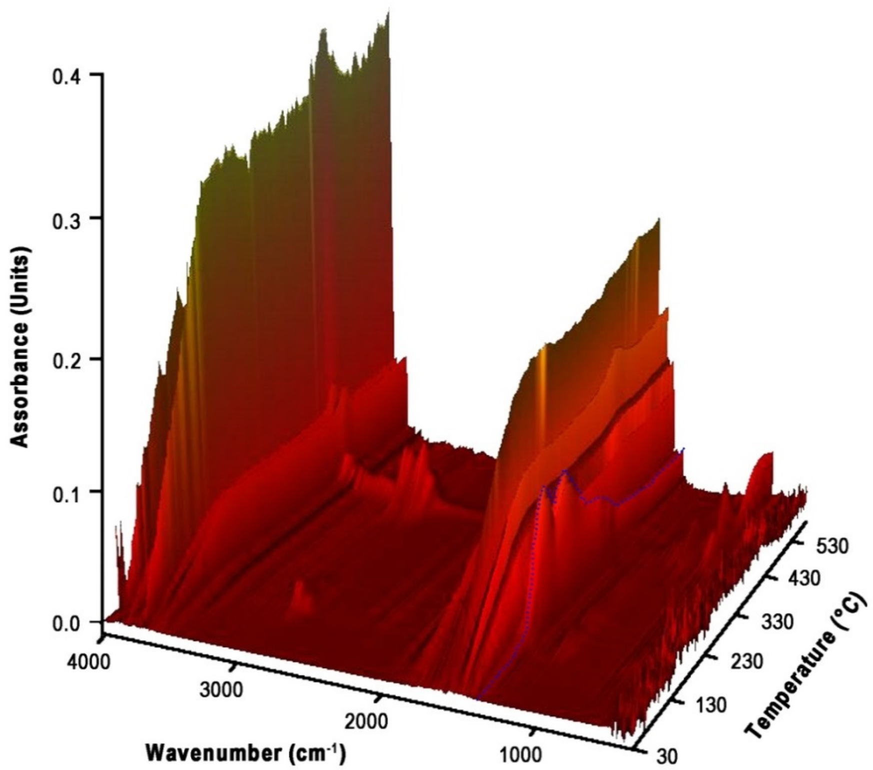


Fig. S12. FTIR spectra of the gas evolved during the thermal decomposition of sample **2−*SA*** by TGA−IR analysis. The dotted curve highlights the SO_2 evolution.

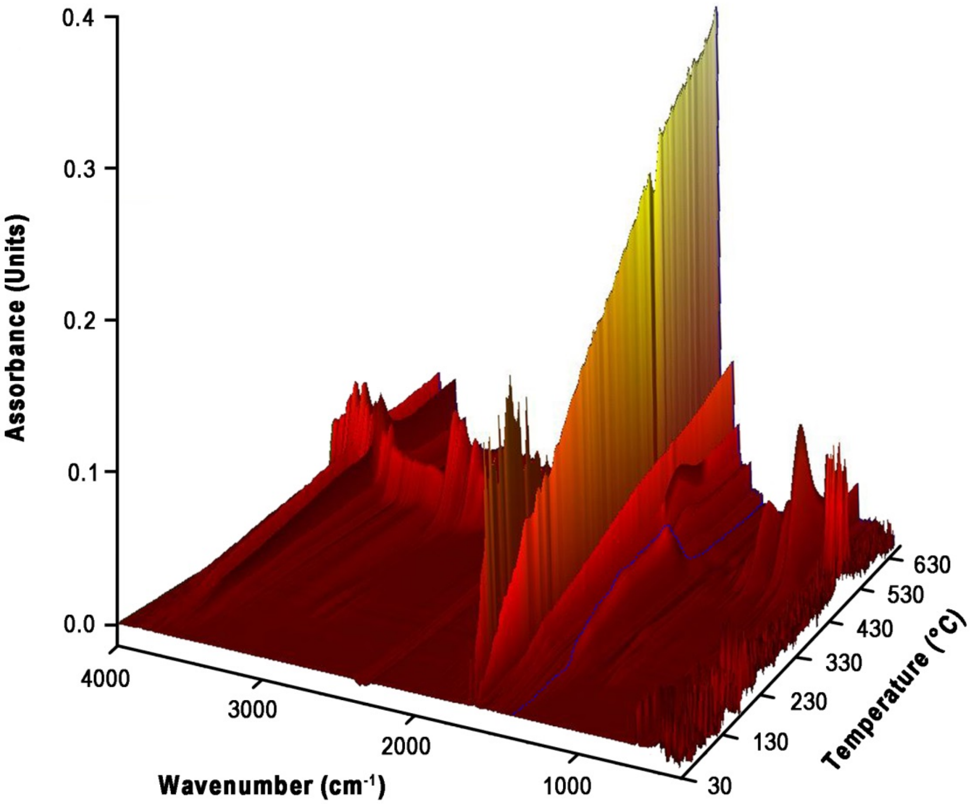


Fig. S13. FTIR spectra of the gas evolved during the thermal decomposition of sample **3−*SA*** by TGA−IR analysis. The dotted curve highlights the SO_2 evolution.

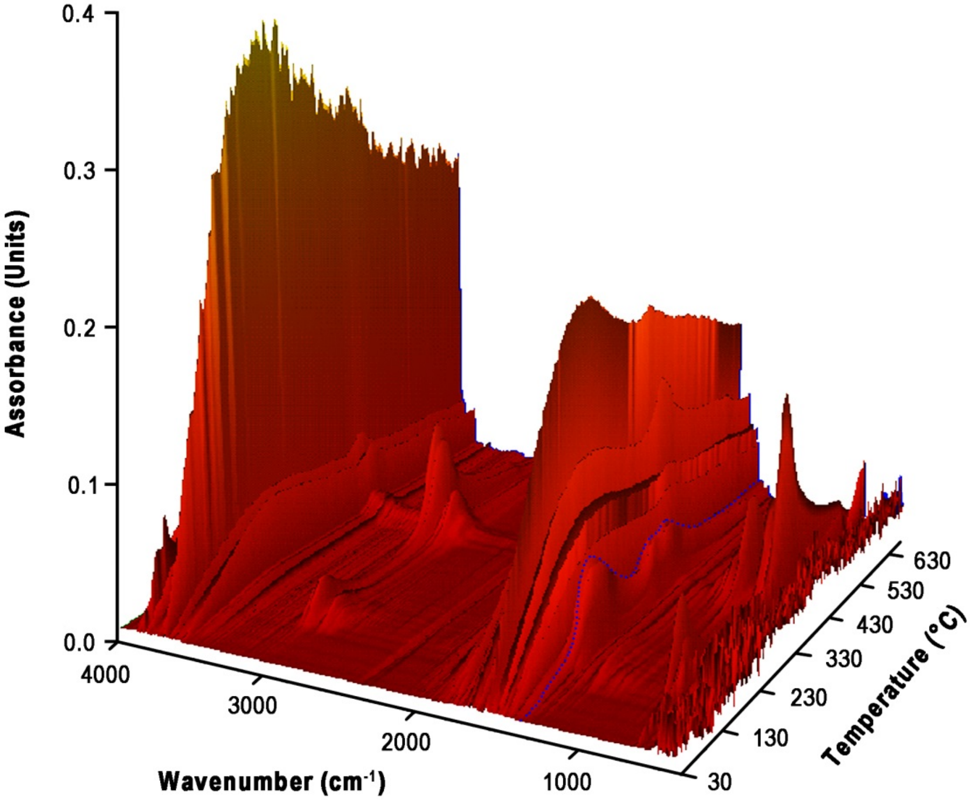


Fig. S14. FTIR spectra of the gas evolved during the thermal decomposition of sample **5−*SA*** by TGA−IR analysis. The dotted curve highlights the SO_2 evolution.

5. Powder Wide Angle x-Ray Diffraction Analysis.

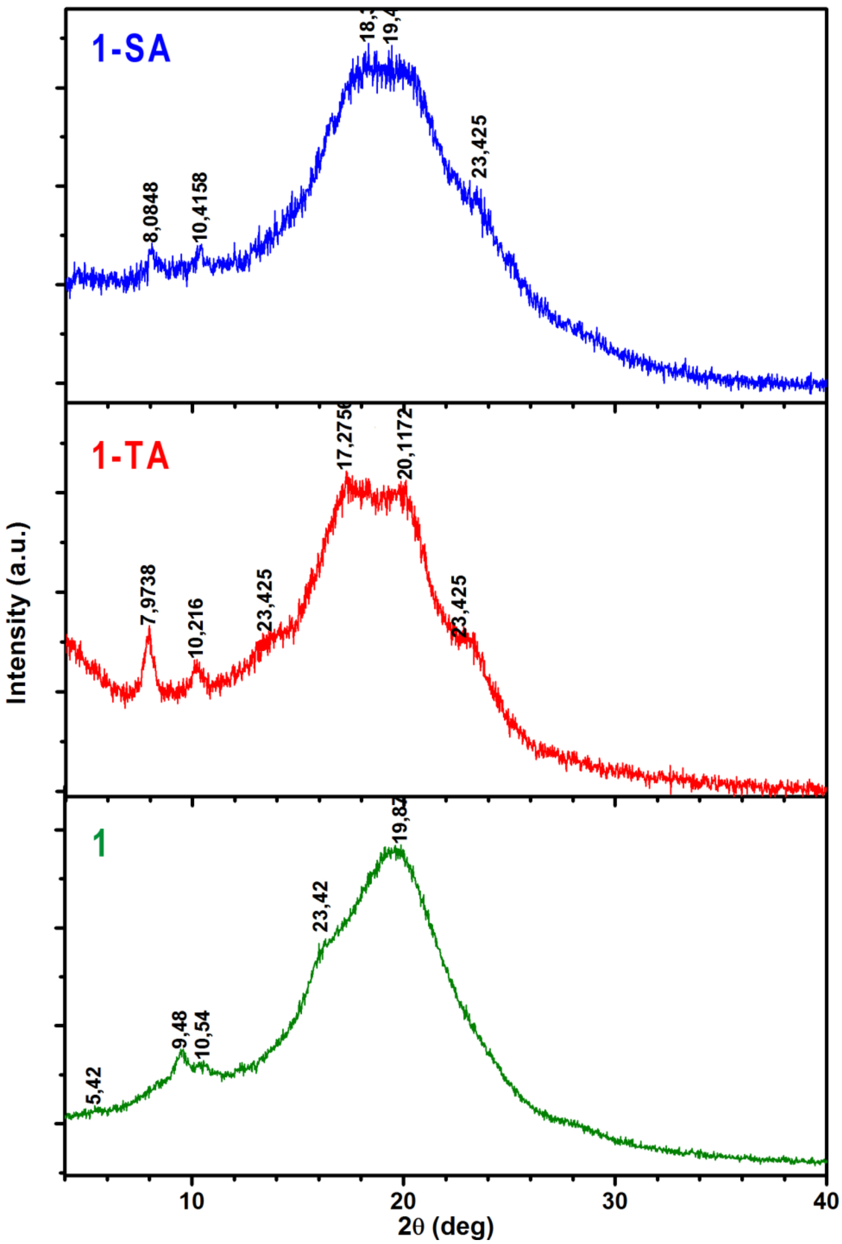


Fig. S15. WAXD patterns of the samples **1**, **1−*TA*** and **1−*SA***.

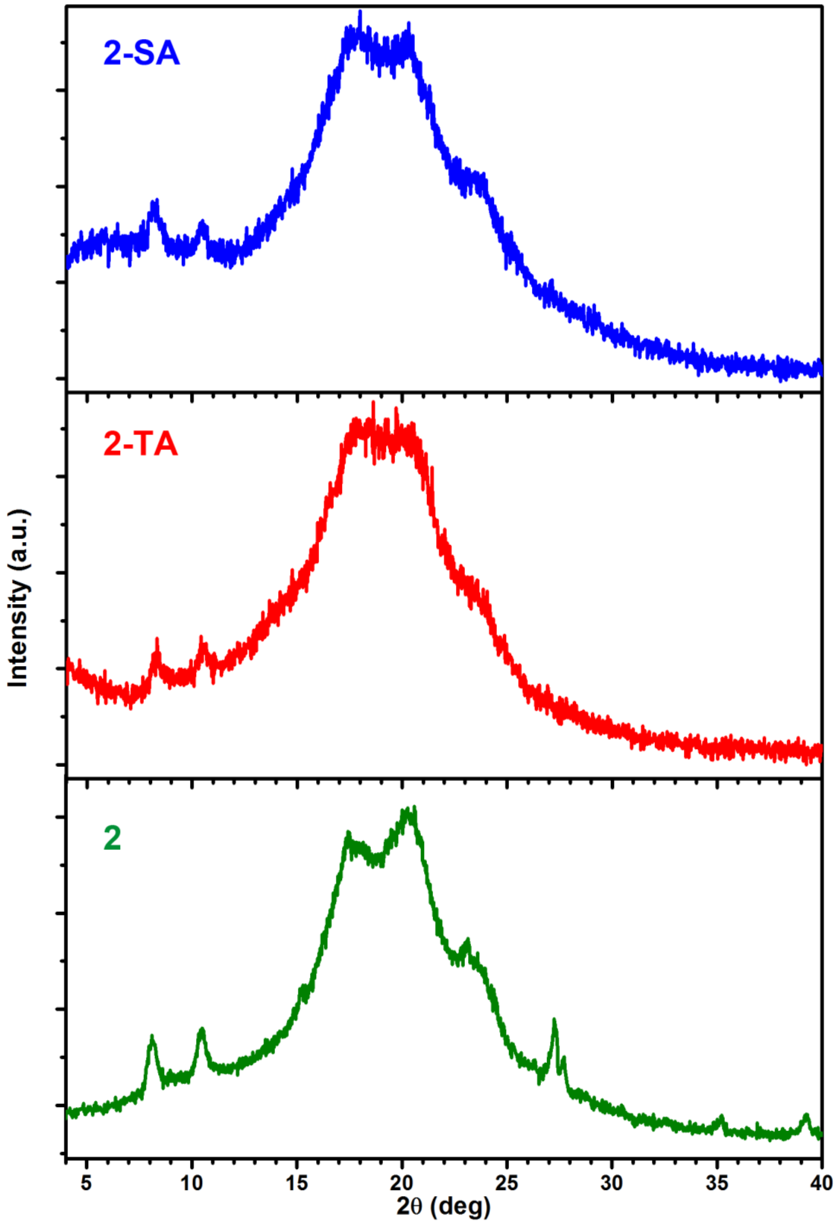


Fig. S16. WAXD patterns of the samples **2**, **2−*TA*** and **2−*SA***.

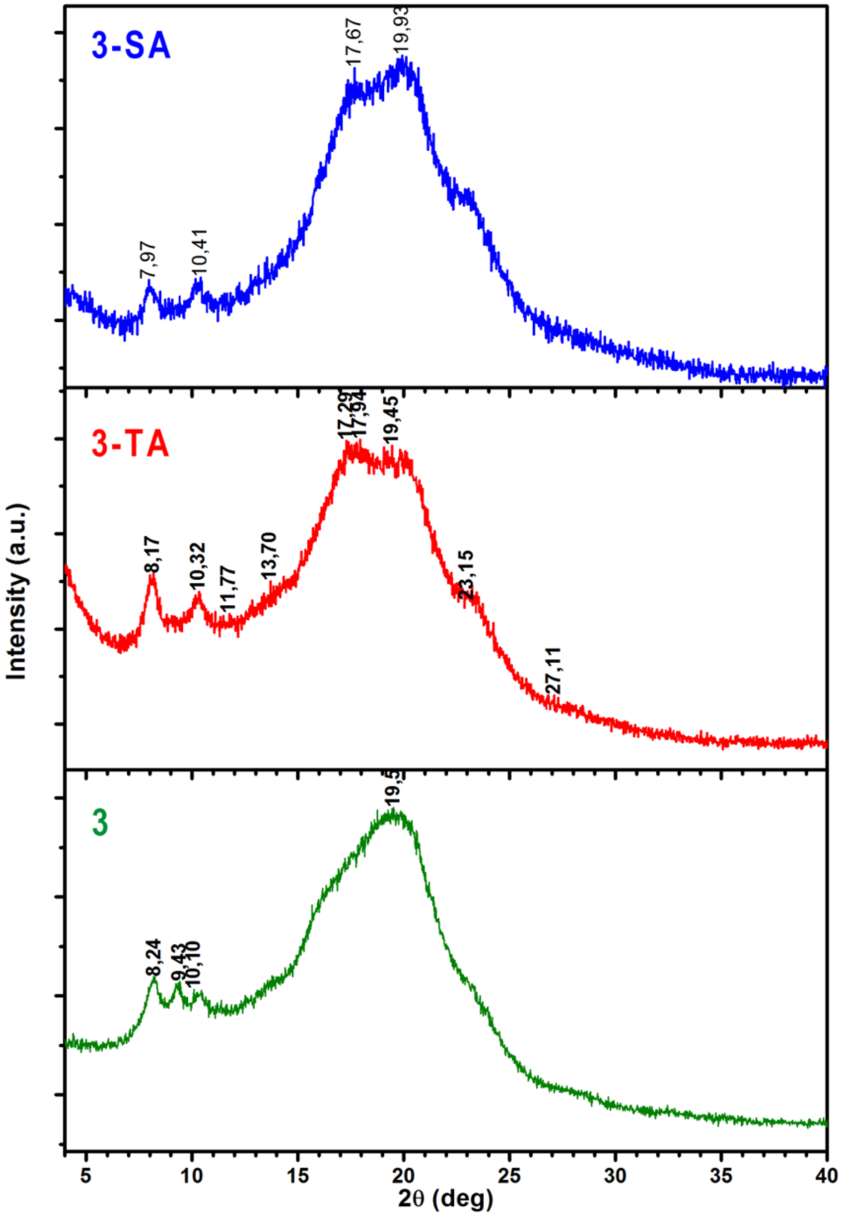


Fig. S17. WAXD patterns of the samples **3**, **3−*TA*** and **3−*SA***.

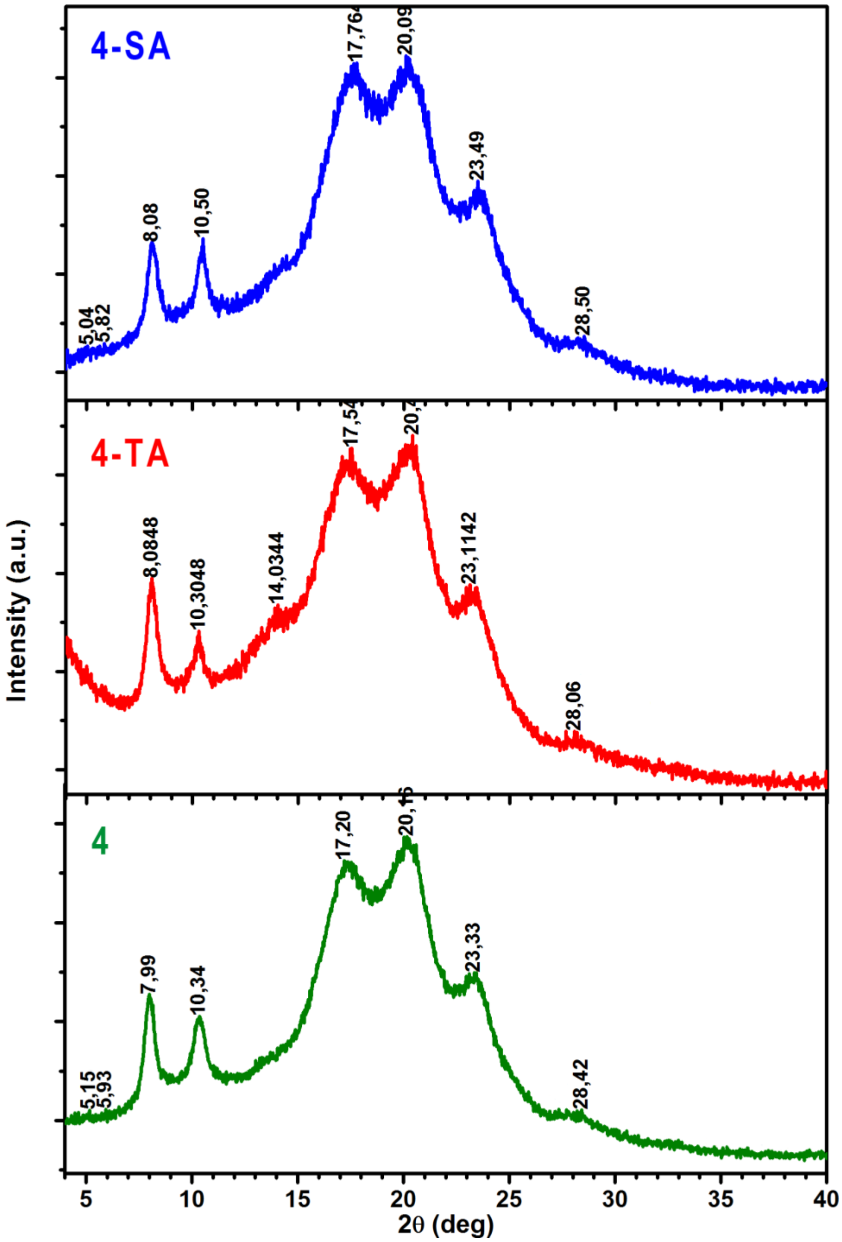


Fig. S18. WAXD profiles of the samples **4**, **4−*TA*** and **4−*SA***.

6. Scanning Probe Microscopy.

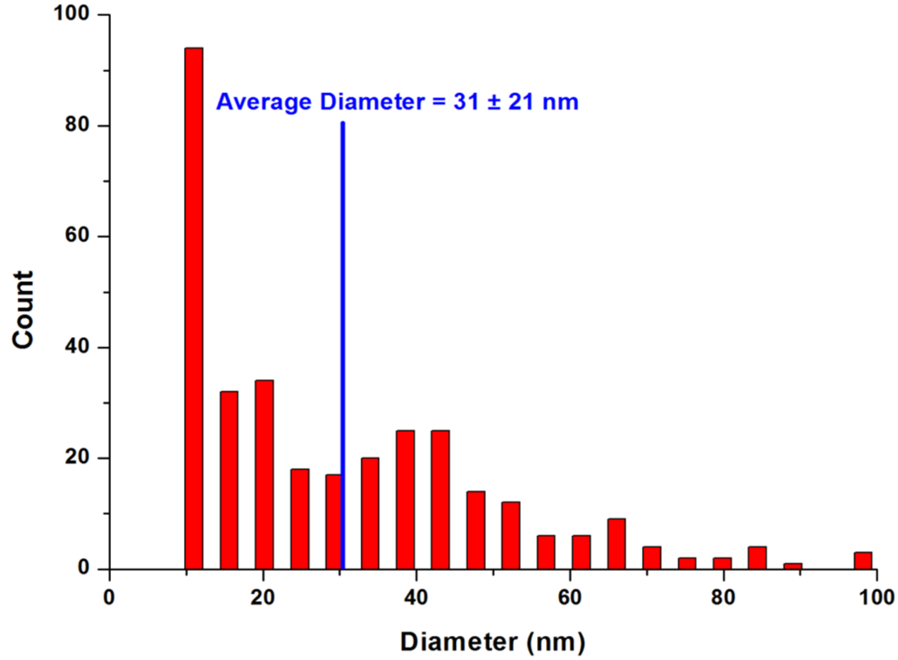


Fig. S19. Diameter distribution of PB domains in thin film of sample **5** by TM-AFM.

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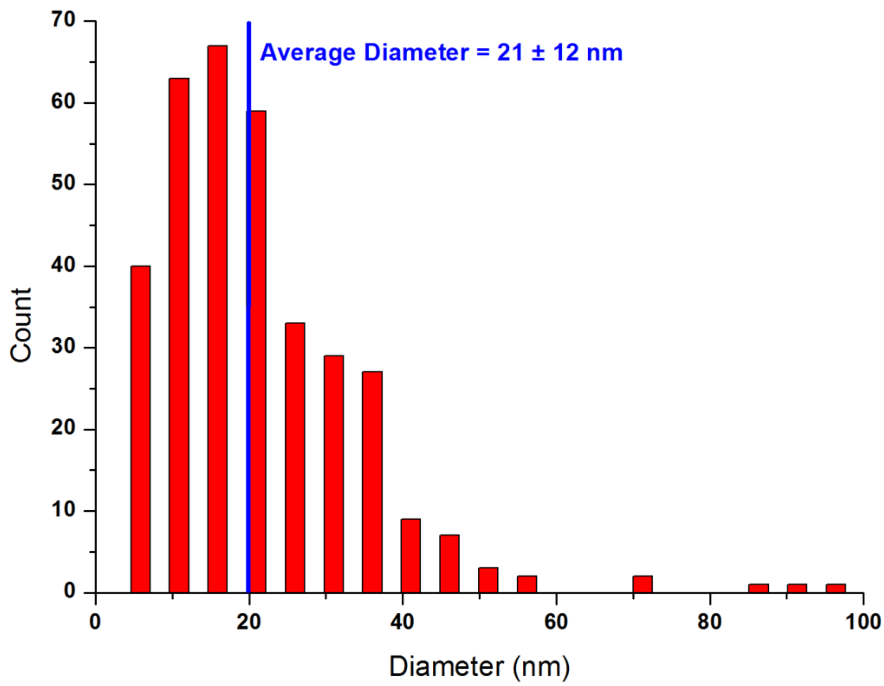

Fig. S20. Diameter distribution of sulfonated PB domains in thin film of sample **5−*SA*** by TM-AFM.

7. TEM analysis

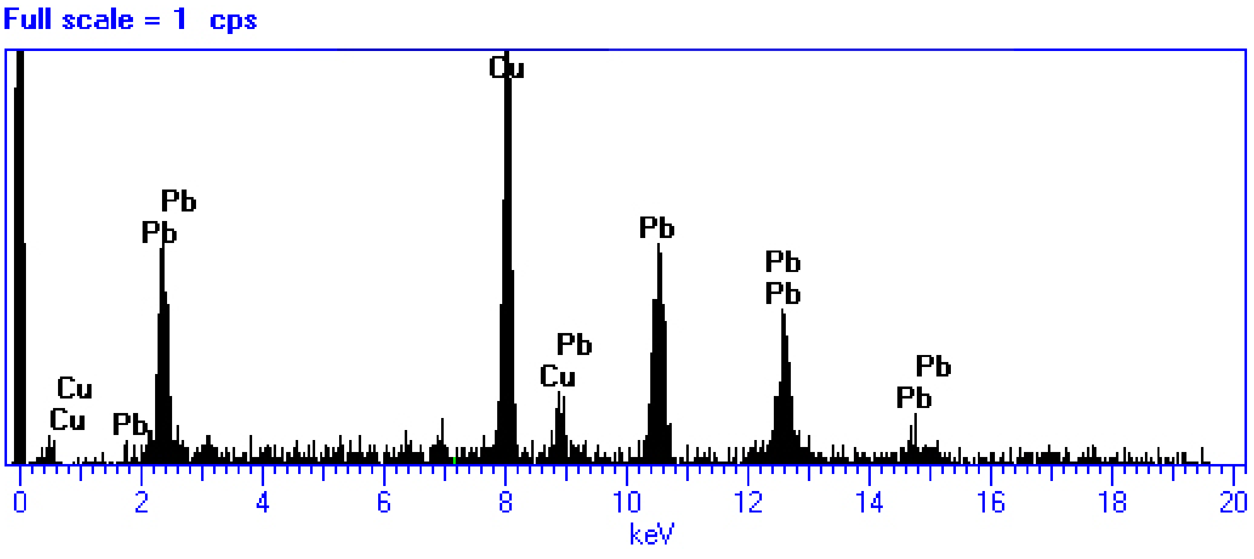

Fig. S21. Magnification of the EDX spectrum reported in Figure 5c.

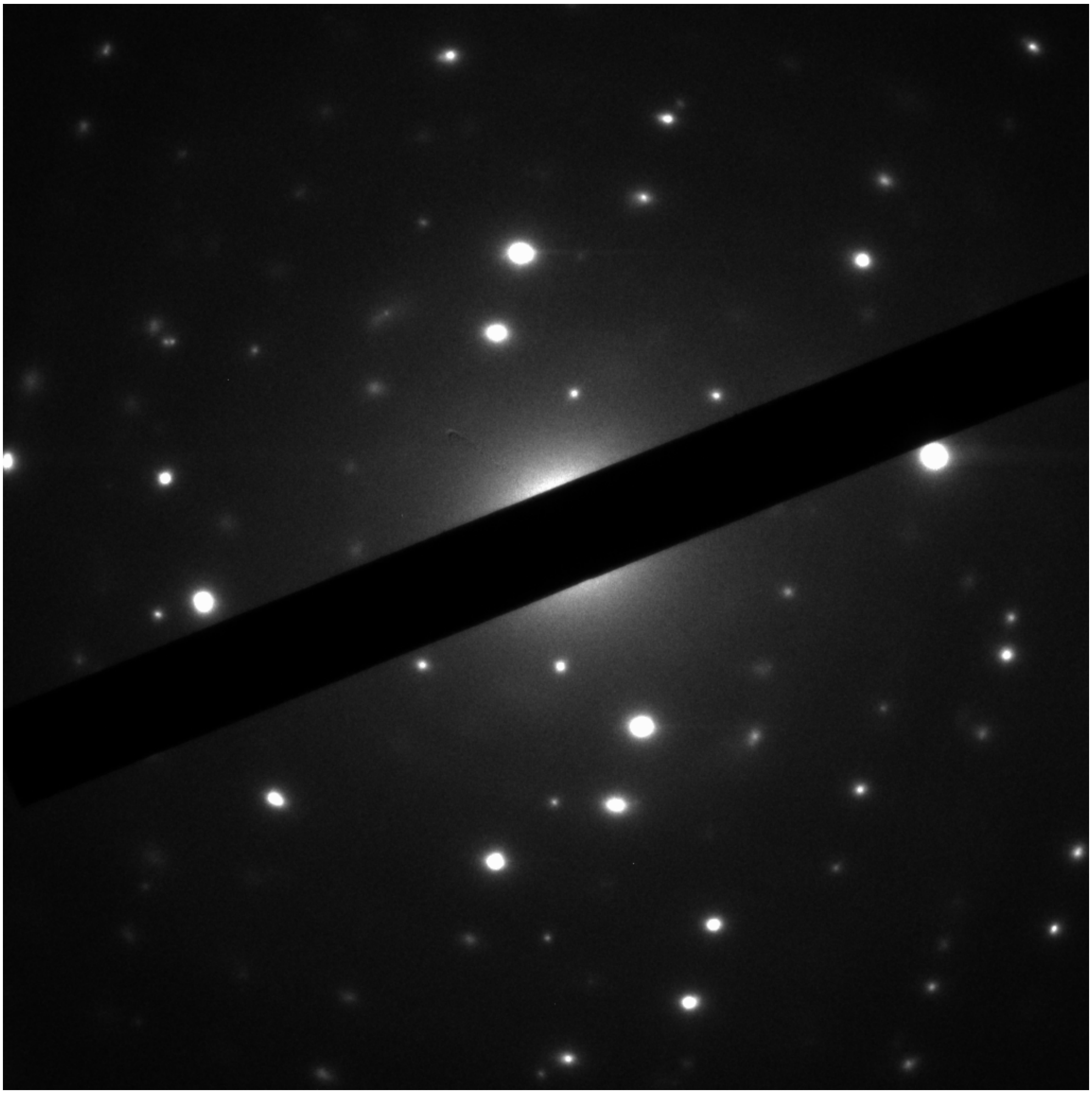

Fig. S22. Magnification of the electron diffraction pattern reported in Figure 5e of sample **5-SA**.

8. Analysis by Cyclic Voltammetry

Equations involved for the determination of the proton conductivity from the Tafel plot[1]:

- $\eta = A\ln\left(\frac{i}{i_0}\right)$ (Tafel equation, valid for high polarization values; eq. S1)
- $\eta = \frac{RT}{nFi_0}i$ (approximate Tafel equation, valid for low polarization values; eq. S2)
- $\Delta E = Ri$ (Ohm's law; eq. S3)
- $R = \frac{RT}{nFi_0}$ (eq. S4)
- $\sigma = \frac{l}{RS} = \frac{nFi_0 l}{RTS}$ (eq. S5)

where:

- η = overpotential
- A = Tafel slope
- i = current
- R = gas constant = 8.31446 C V/mol K
- T = temperature = 298.16 K
- n = number of electrons involved in the electrolytic process
- F = Faraday constant = 96 485.3365 C/mol
- i_0 = exchange current, A/m^2
- ΔE = potential
- **R** = electrical resistance
- ρ = resistivity
- l = membrane thickness = 0.0001 m
- S = electrode section = 3.1415 10^{-6} m^2;
- σ = electrical conductivity

[1] (*a*) *Handbook of Electrochemistry*, ed. C. G. Zoski, Elsevier, Amsterdam, 2007;. (*b*) *Electrochemical methods. Fundamentals and applications*, ed. A. J. Bard, Larry R. Faulkner, John Wiley & Sons, Inc, 2001;

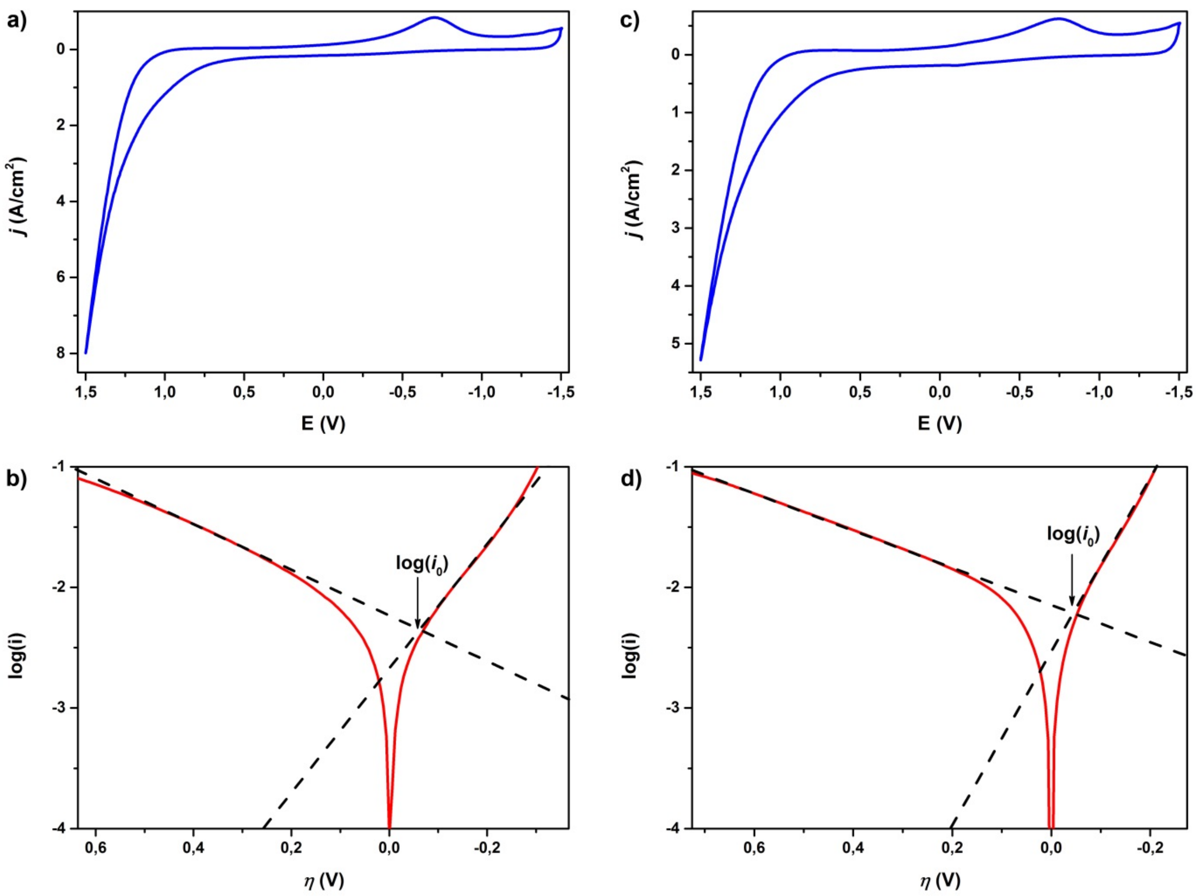

Fig. S23. Cyclic voltammograms and the corresponding Tafel plots respectively for Nafion® (a and b) and sample **5–SA** (c and d).

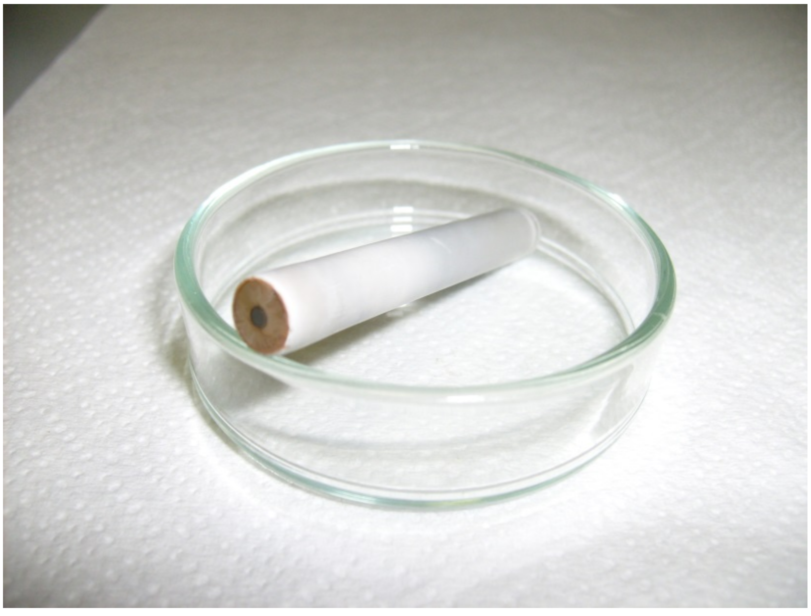

Fig. S24. Photograph of the sample ***5-SA*** casted onto glassy carbon electrode.