Electronic Supplementary Information (ESI)

Towards New Proton Exchange Membrane Materials with Enhanced Performance via RAFT Polymerization

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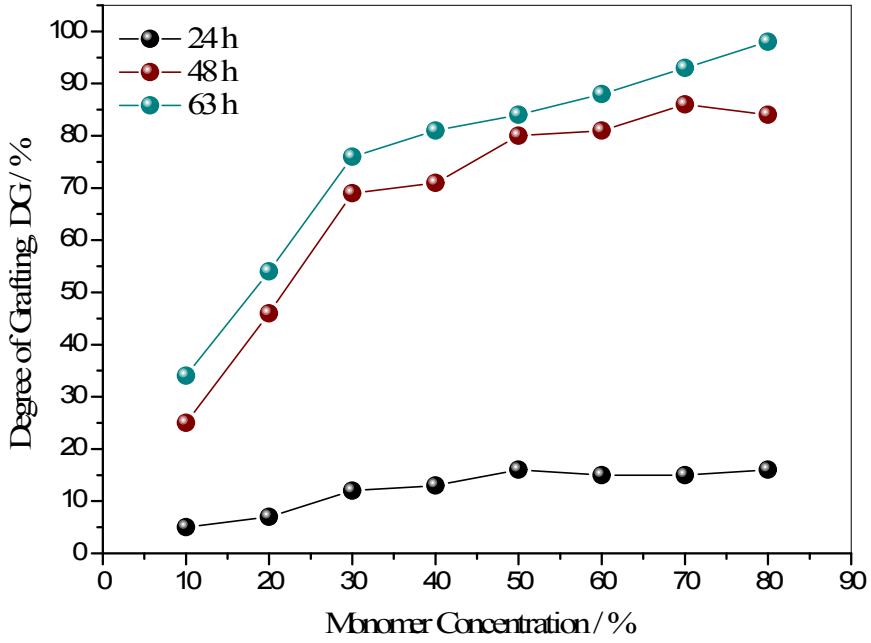

Fig. S1 Change in degree of grafting (DG) versus monomer concentration (%, v/v) attained at various reaction times during γ-initiated graft polymerization of styrene (St) from ETFE mediated via the RAFT agent cumyl phenyldithioacetate (CPDA); [St]:[CPDA]=700:1, ETFE (ca. 0.02 g), dose rate=0.032 $kGyh^{-1}$, in toluene, at room temperature.

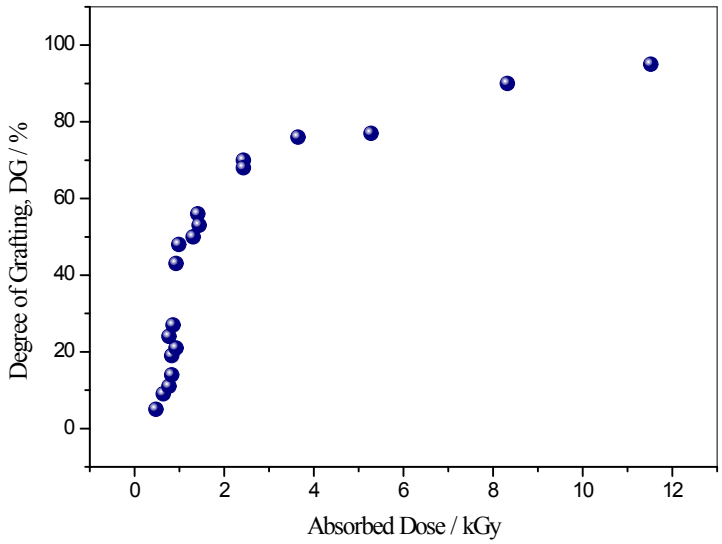

Fig. S2 Change in degree of grafting (DG) versus absorbed dose during γ-initiated graft polymerization of styrene (St) from ETFE mediated via the RAFT agent cumyl phenyldithioacetate (CPDA); [St]:[CPDA]=700:1, [St]=2.62 mol·L^{-1} (30 % St, v/v), ETFE (ca, 0.02 g), dose rate=0.032 kGy·h^{-1}, in toluene, at room temperature.

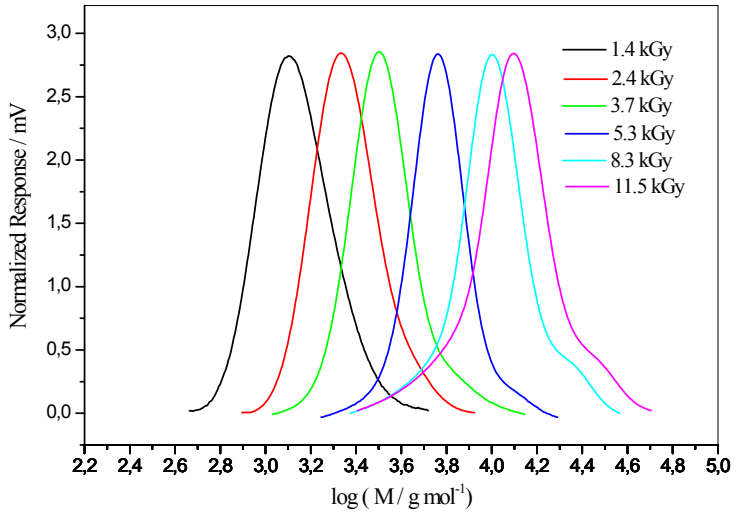

Fig. S3 Evolution of molecular weight distribution versus absorbed radiation dose for free polystyrene formed during γ-initiated graft polymerization of styrene (St) from ETFE mediated via the RAFT agent cumyl phenyldithioacetate (CPDA); [St]:[CPDA]=700:1, [St]=2.62 molL^{-1} (30 % St, v/v), ETFE (ca. 0.02 g), dose rate=0.032 kGyh^{-1}, in toluene, at room temperature

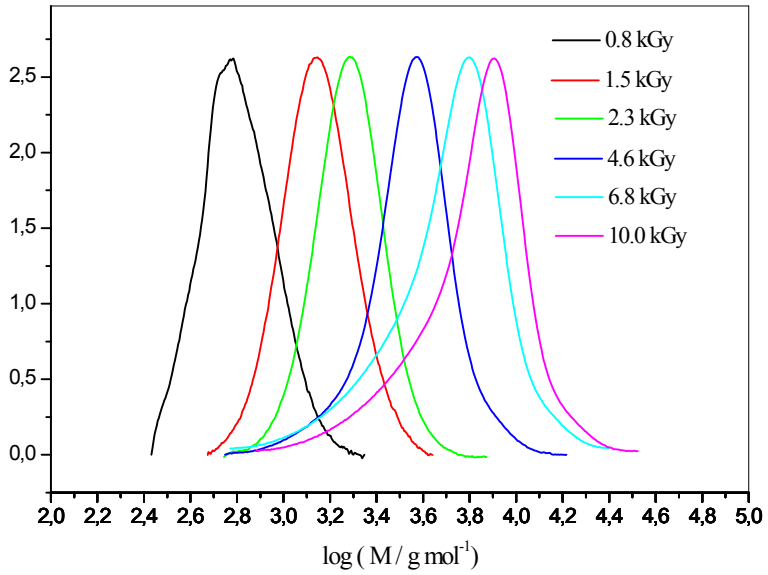

Fig. S4 Evolution of molecular weight distribution versus absorbed radiation dose for free polystyrene formed during γ-initiated graft polymerization of styrene (St) from ETFE mediated via the RAFT agent cumyl phenyldithioacetate (CPDA); [St]:[CPDA]=700:1, [St]=0.87 molL^{-1} (10% St, v/v), ETFE (ca. 0.02 g), dose rate=0.032 kGyh^{-1}, in toluene, at room temperature.

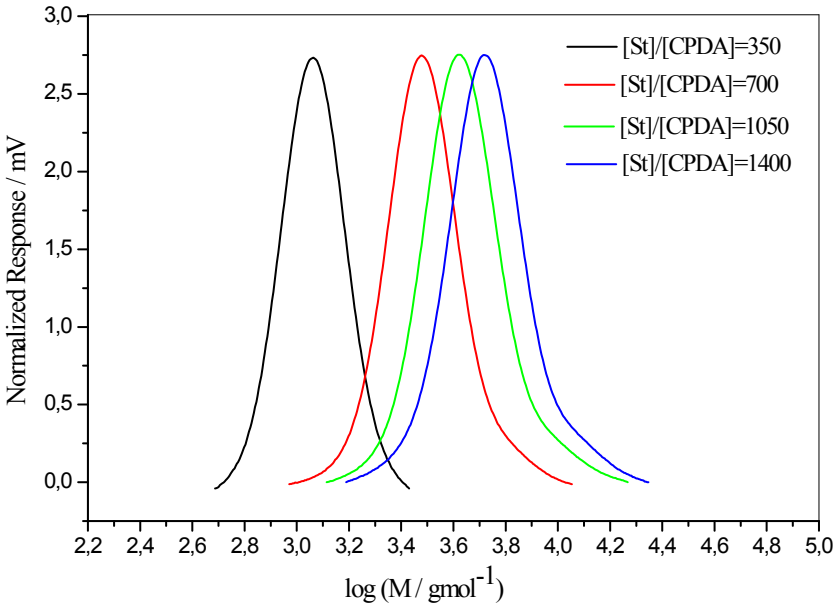

Fig. S5 Evolution of molecular weight distribution versus the RAFT agent concentration for free polystyrene formed during γ-initiated graft polymerization of styrene (St) from ETFE mediated via the RAFT agent cumyl phenyldithioacetate (CPDA): polymerization time = 97 h (absorbed radiation dose = 3.1 kGy), [St]=2.62 molL^{-1} (30 % St, v/v), ETFE (ca. 0.02 g), dose rate=0.032 kGy·h^{-1}, in toluene, at room temperature.

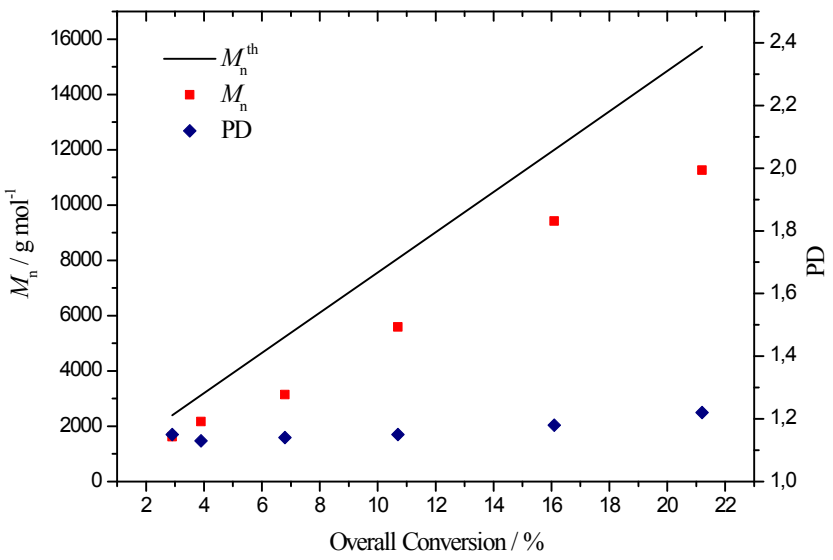

Fig. S6 Evolution of number-average molecular weight (M_n) and polydispersity (PD) as a function of monomer conversion for free polystyrene formed during γ-initiated graft polymerization of styrene (St) from ETFE mediated via the RAFT agent cumyl phenyldithioacetate (CPDA); [St]:[CPDA]=700:1, [St]=2.62 molL^{-1} (30% St, v/v), ETFE (ca. 0.02 g), dose rate=0.032 kGyh^{-1}, in toluene, at room temperature.

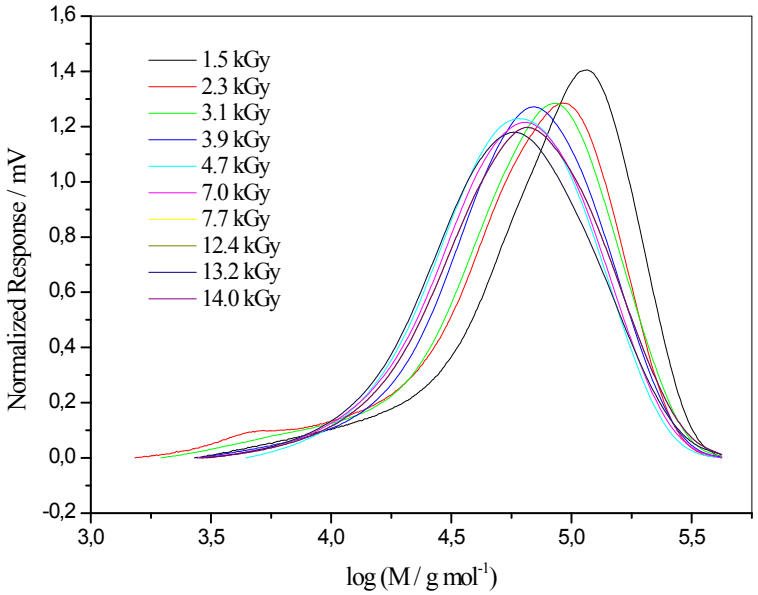

Fig. S7 Evolution of molecular weight distribution versus absorbed radiation dose for free polystyrene formed during conventional γ-initiated graft polymerization of styrene (St) from ETFE: [St]=2.62 molL^{-1} (30% St, v/v), ETFE (ca. 0.02 g), dose rate=0.032 kGyh^{-1}, in toluene, at room temperature.

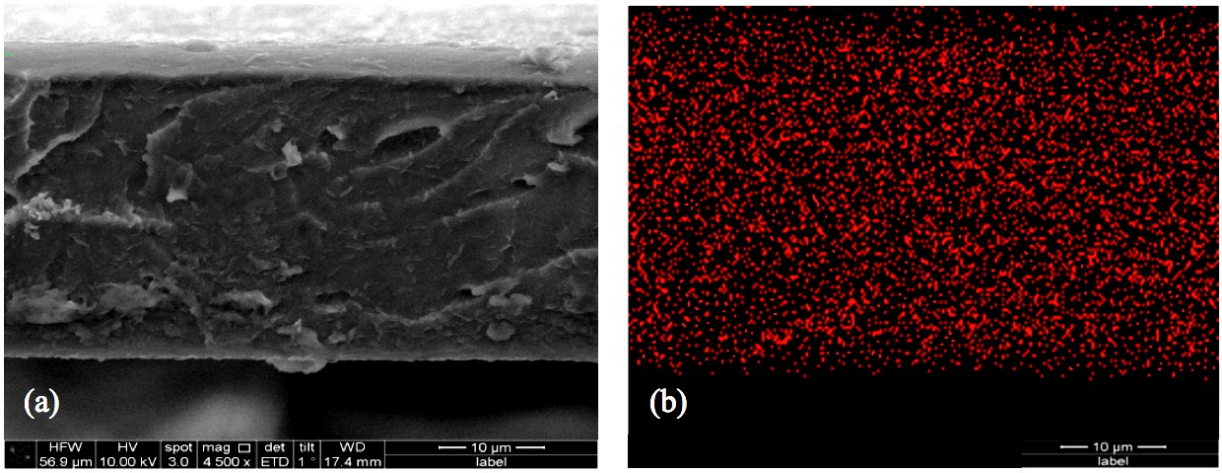

Fig. S8 (a) SEM and (b) corresponding SEM-EDX dot mapping illustrating the distribution of sulfur atoms across the cross-section of ETFE-*g*-PSSA, DG: 26%.

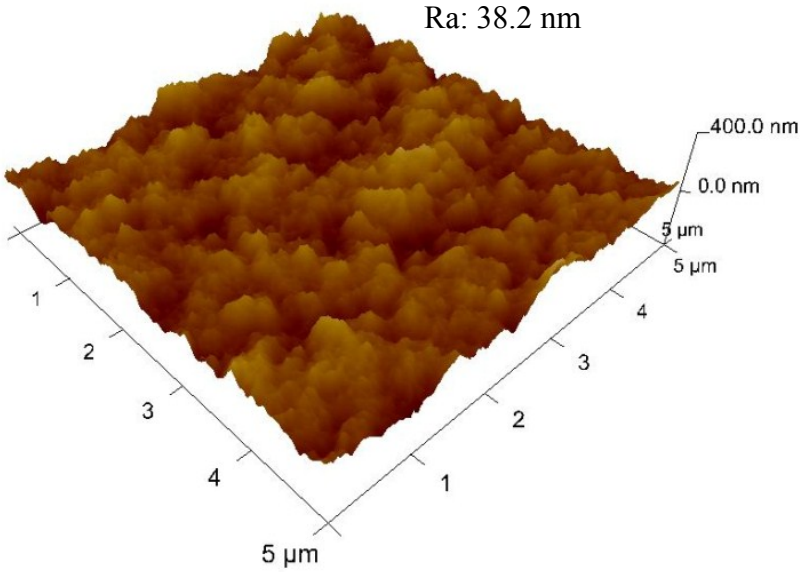

Fig. S9 AFM image and roughness (Ra) of pristine (non-pressed) ETFE film

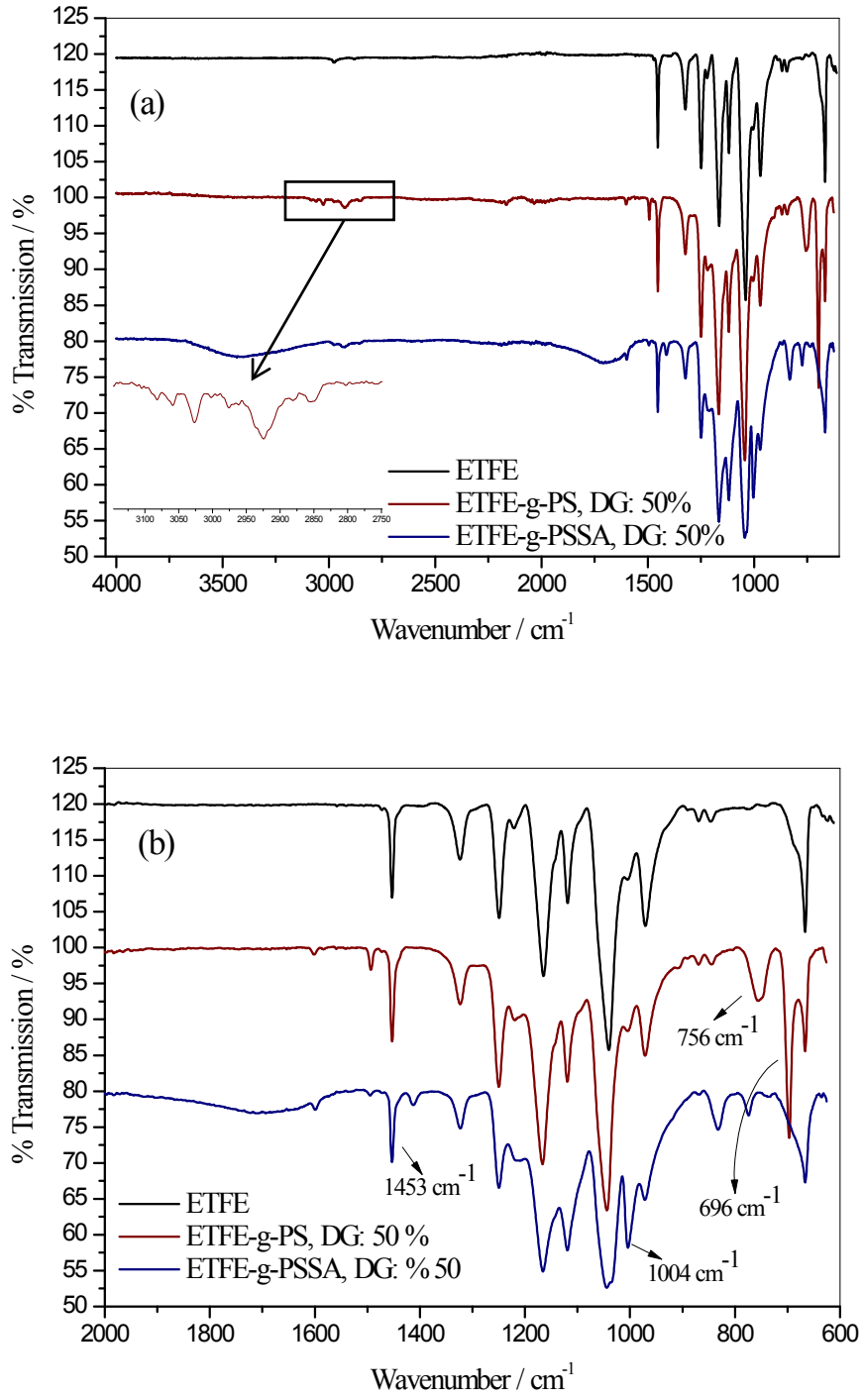

Fig. S10 ATR-FTIR spectra of pristine ETFE, ETFE-*g*-PS film with 50% degree of grafting. (a) 600–4000 cm^{-1} region, (b) 600–2000 cm^{-1} region. The inset in Figure S10a are the magnified characteristic peaks of PS at 3002, 3027, 3059, 3082, 3104, 2855 and 2925 cm^{-1}

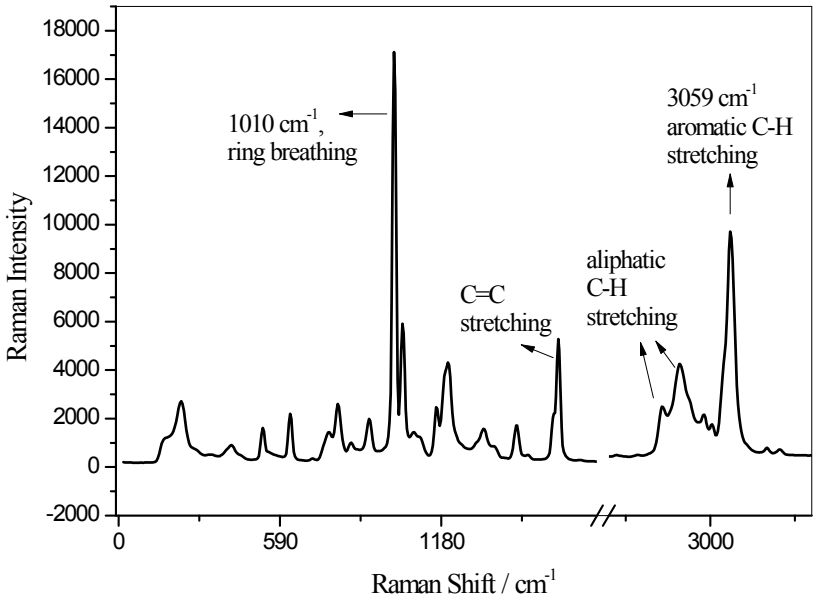

Fig. S11 Raman spectrum of pure polystyrene (PS)

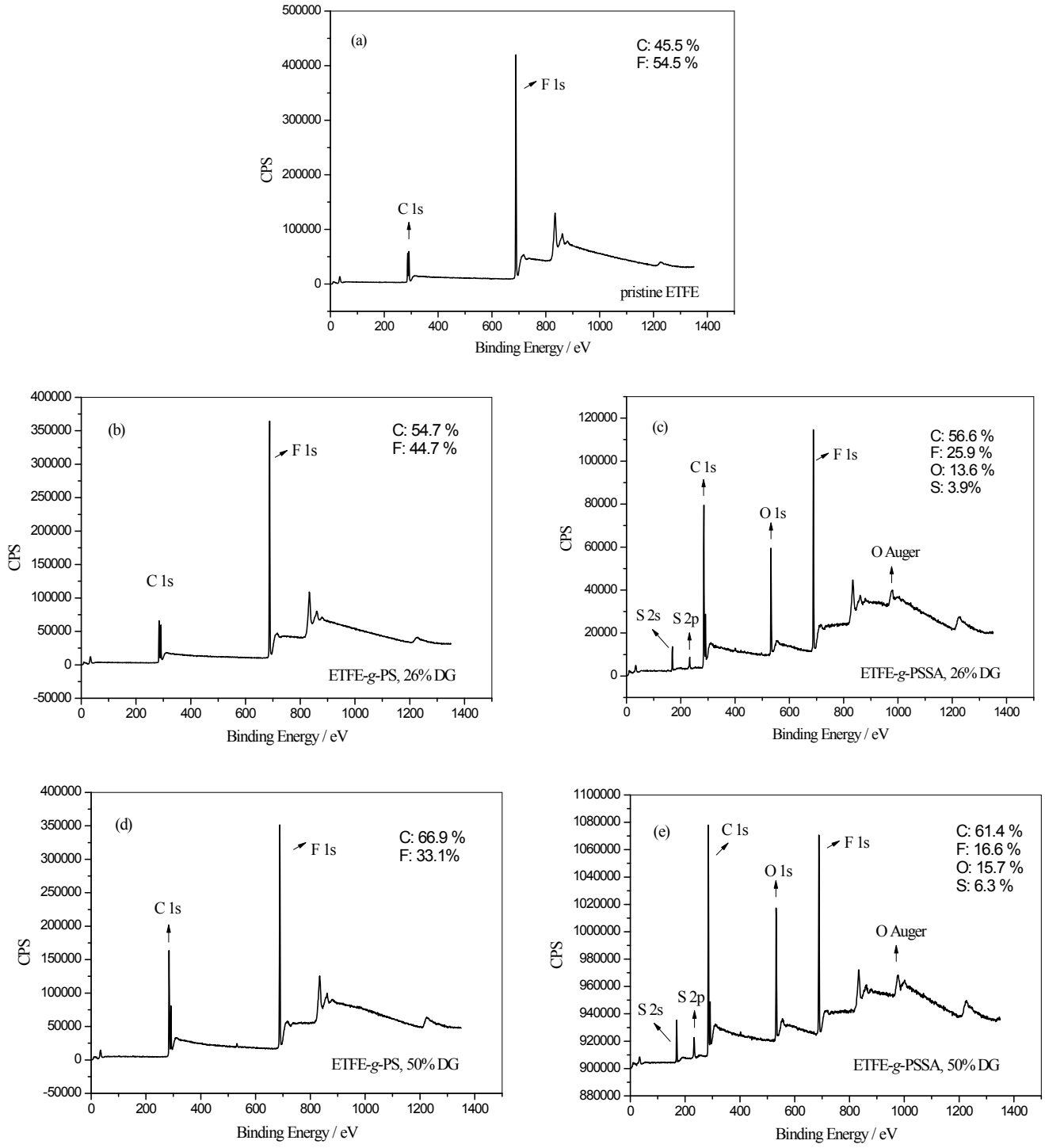

Fig. S12 XPS wide-scan survey spectra of (a) pristine ETFE, (b) ETFE-*g*-PS film with 26% degree of grafting (DG) and (c) its sulfonated membrane, (d) ETFE-*g*-PS film with 50% degree of grafting (DG) and (e) its sulfonated membrane.

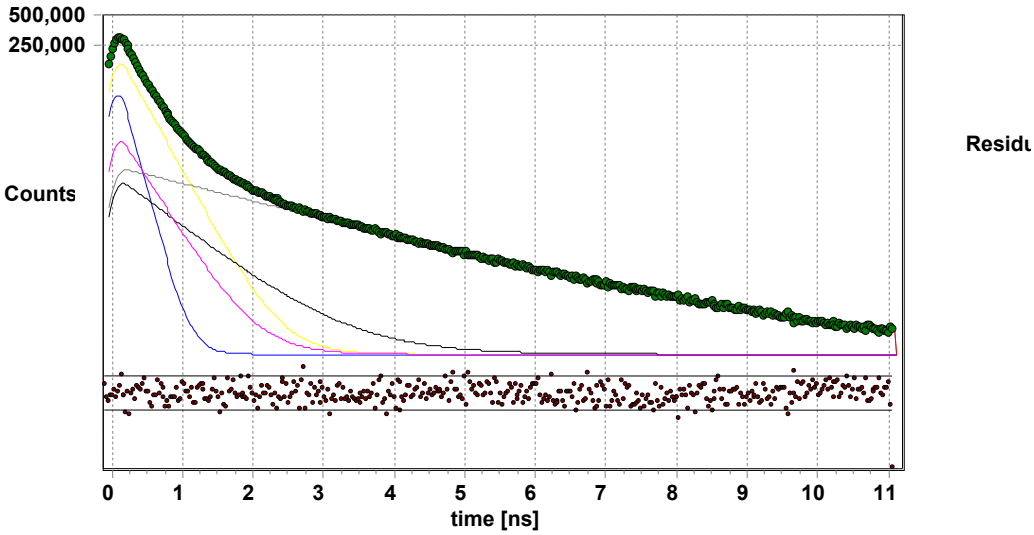

Fig. S13 A typical positron annihilation lifetime (PAL) spectrum for the ETFE-*g*-PS film with 17% degree of grafting (DG). The dark green curve (topmost) is the total lifetime spectrum. The blue curve is for τ_2. The yellow and black curves correspond to ortho-Ps annihilated in crystalline (τ_3) and amorphous (τ_4) domains, respectively.

Tao-Eldrup Equation:

$$\tau = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \quad (1)$$

Where τ is lifetime of positronium (ns), R is radius of free volume (nm) and ΔR is empirical electron layer thickness (0.1656 nm)[1,2].

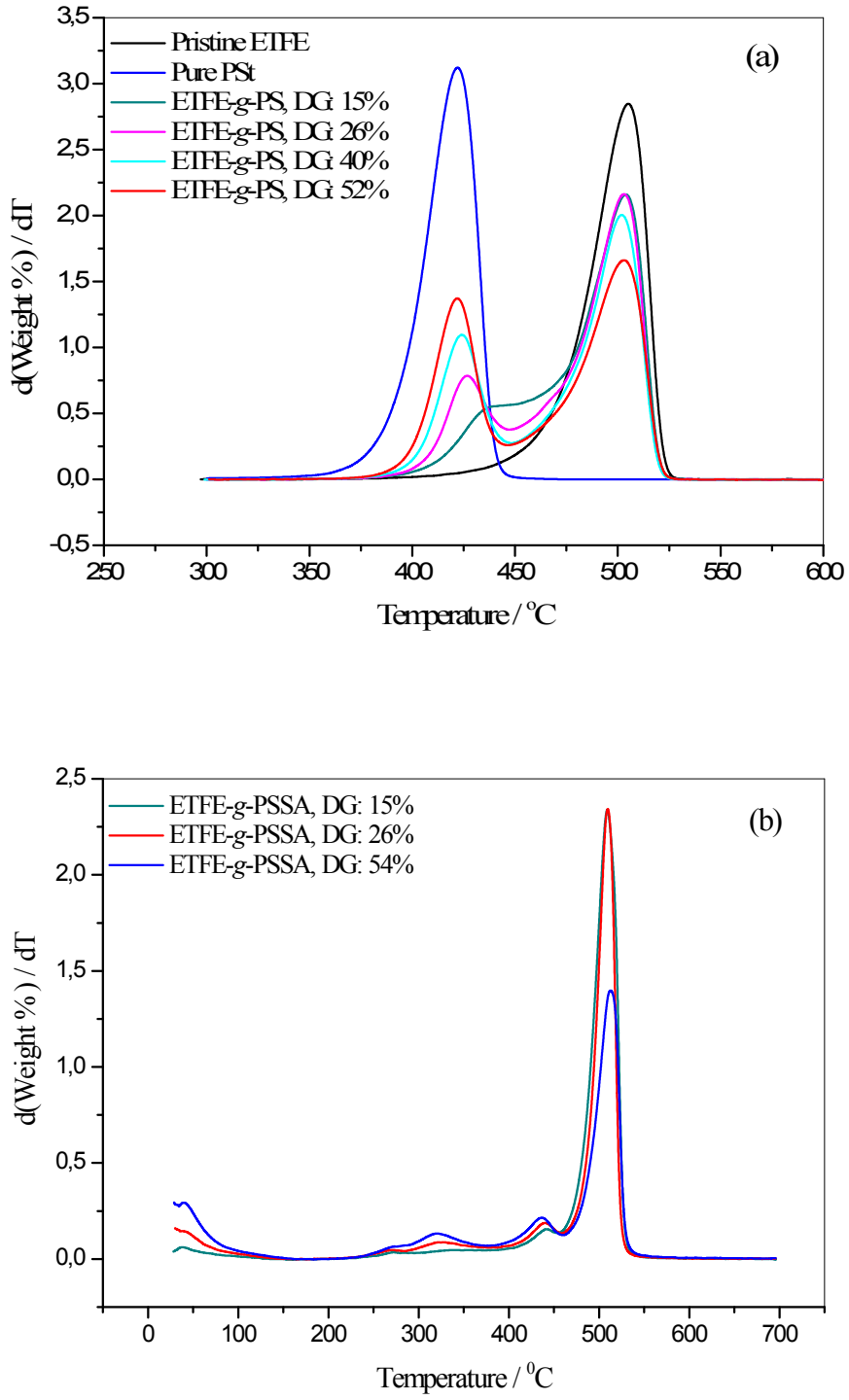

Fig. S14 Derivative thermogravimetry curves of (a) pristine ETFE, pure PS and PS-grafted films with various degree of grafting (DG) and (b) sulfonated membranes with various DGs.

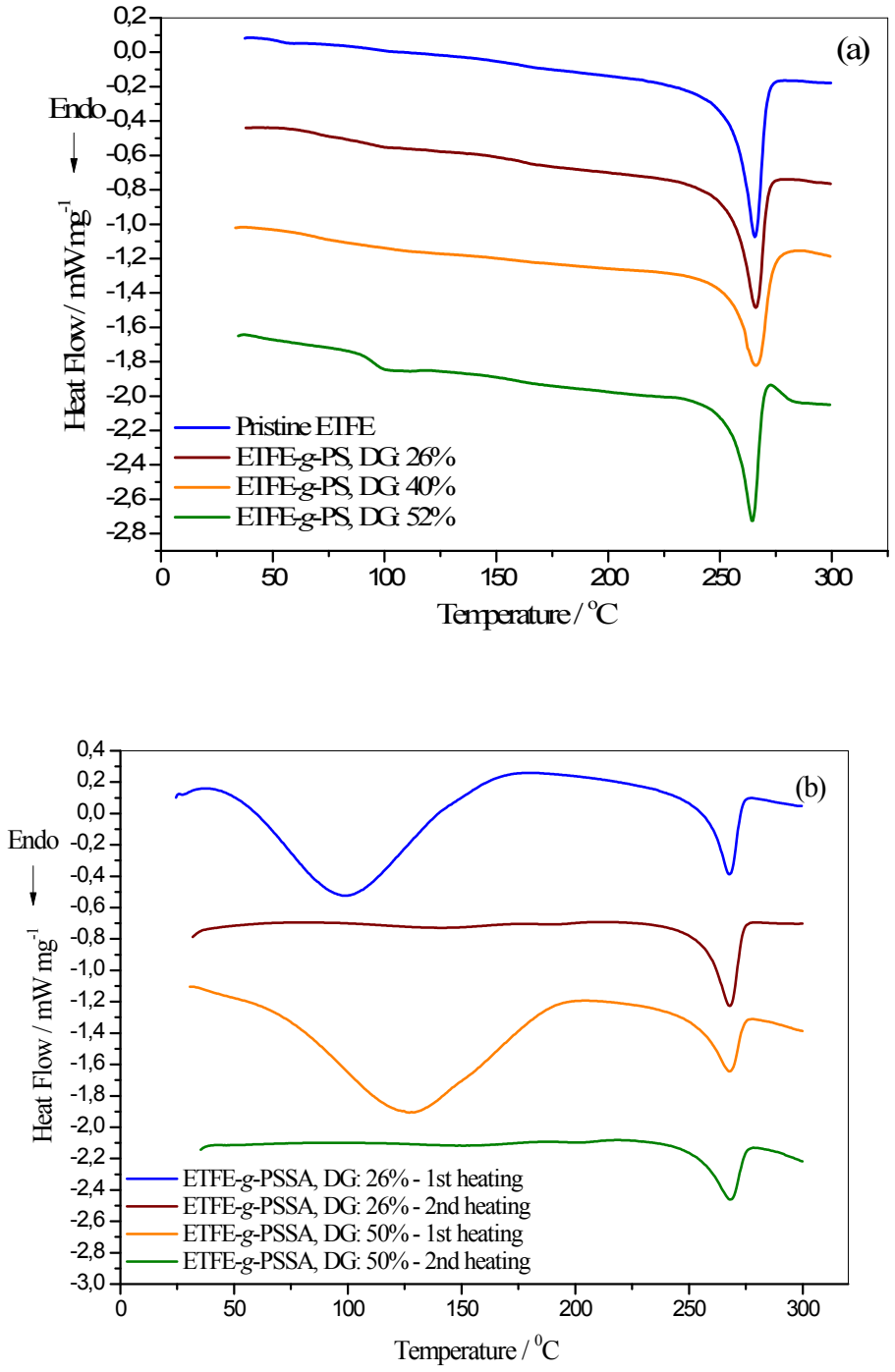

Fig. S15 DSC curves of (a) pristine ETFE and PS-grafted films with various degrees of grafting (DG) and (b) sulfonated membranes with various DGs.

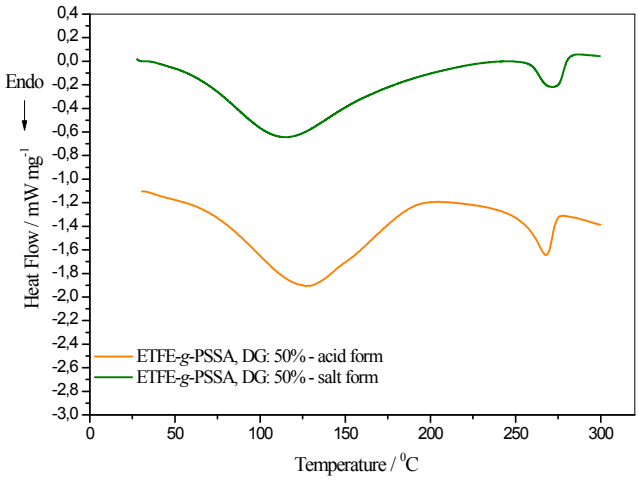

Fig. S16 DSC curves of ETFE-*g*-PSSA membrane with degree of grafting (DG) of 50% before and after converting the acid form of the membrane to the salt form according to recipe in Ref. 3.

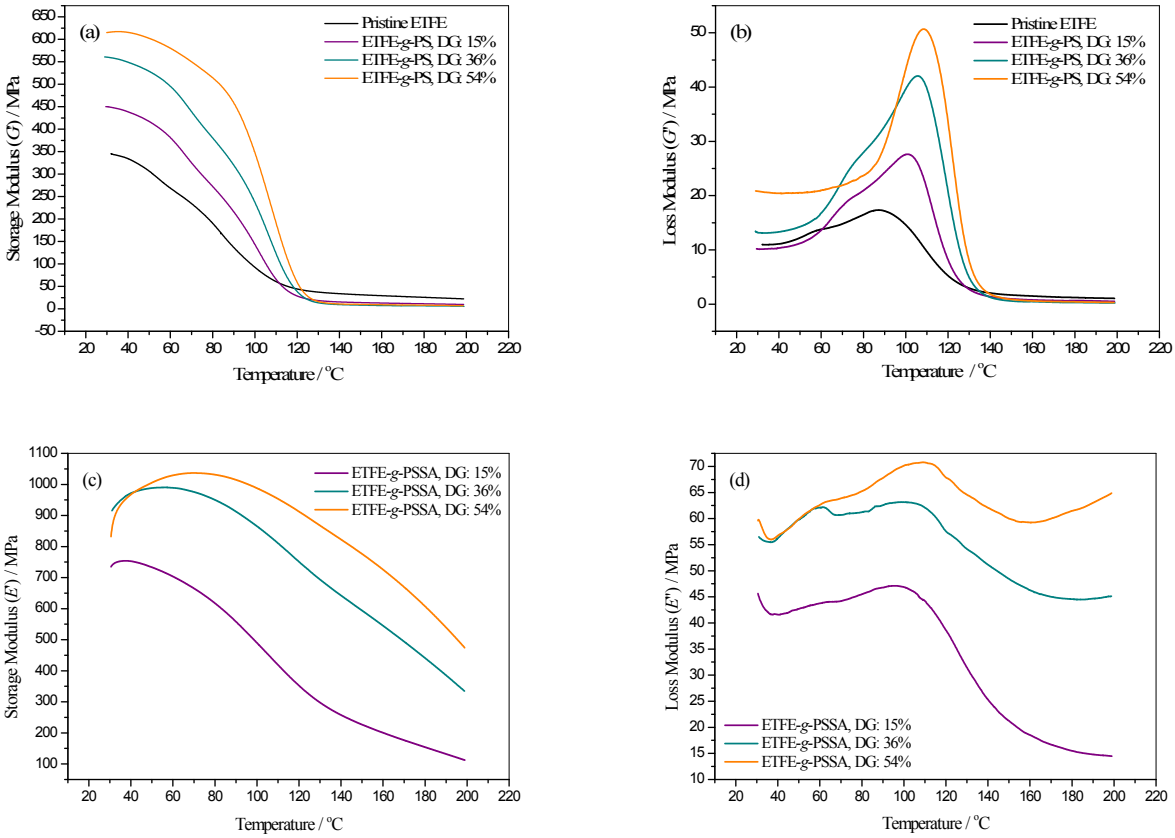

Fig. S17 Storage modulus and loss modulus curves of pristine and PS-grafted ETFE films (a and b, respectively) and sulfonated membranes (c and d, respectively).

References for the Electronic Supplementary Information (ESI)

1. S. J. Tao, *J. Chem. Phys.*, 1972, **56**, 5499 20.
2. M. Eldrup, D. Lightbody, J. N. Sherwood, *Chem. Phys.*, 1981, **63**, 51.
3. S. A. Gürsel, J. Schneider, H. B. Youcef, A. Wokaun, G. G. Scherer, *J. Appl. Polym. Sci.* 2008, **108**, 3577–3585