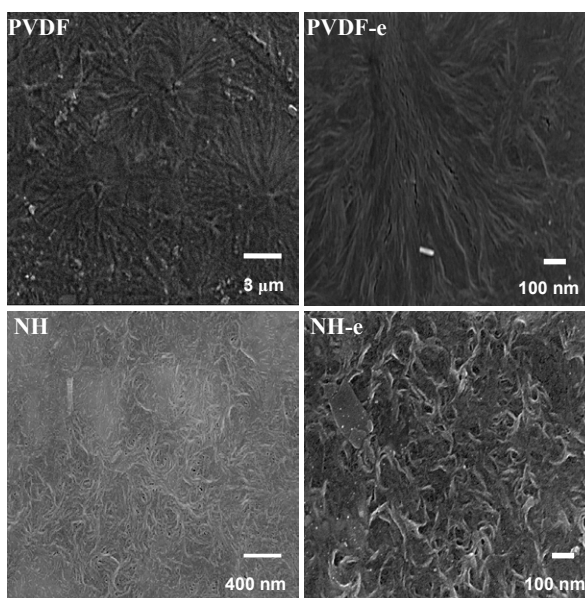


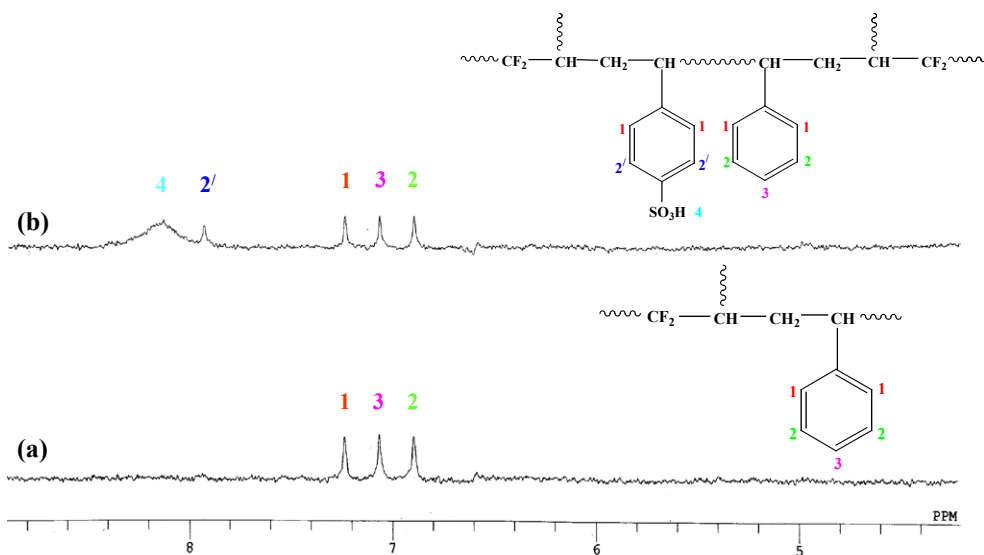
## Supplementary Data

### Conducting Nano-channels in Induced Piezoelectric Polymeric Matrix Using Swift Heavy Ions and Subsequent Functionalization

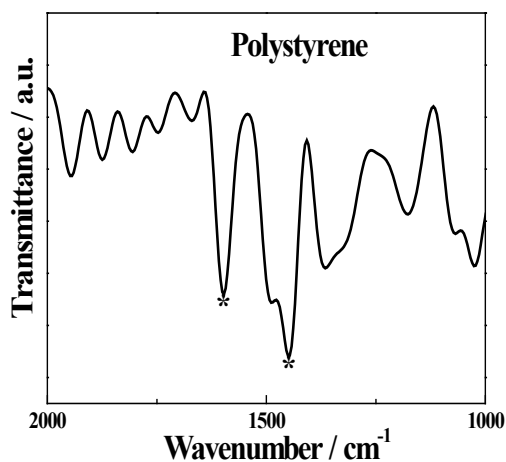
Karun Kumar Jana<sup>1</sup>, Biswajit Ray<sup>2</sup>, Devesh K. Avasthi<sup>3</sup> and Pralay Maiti<sup>\*,1</sup>



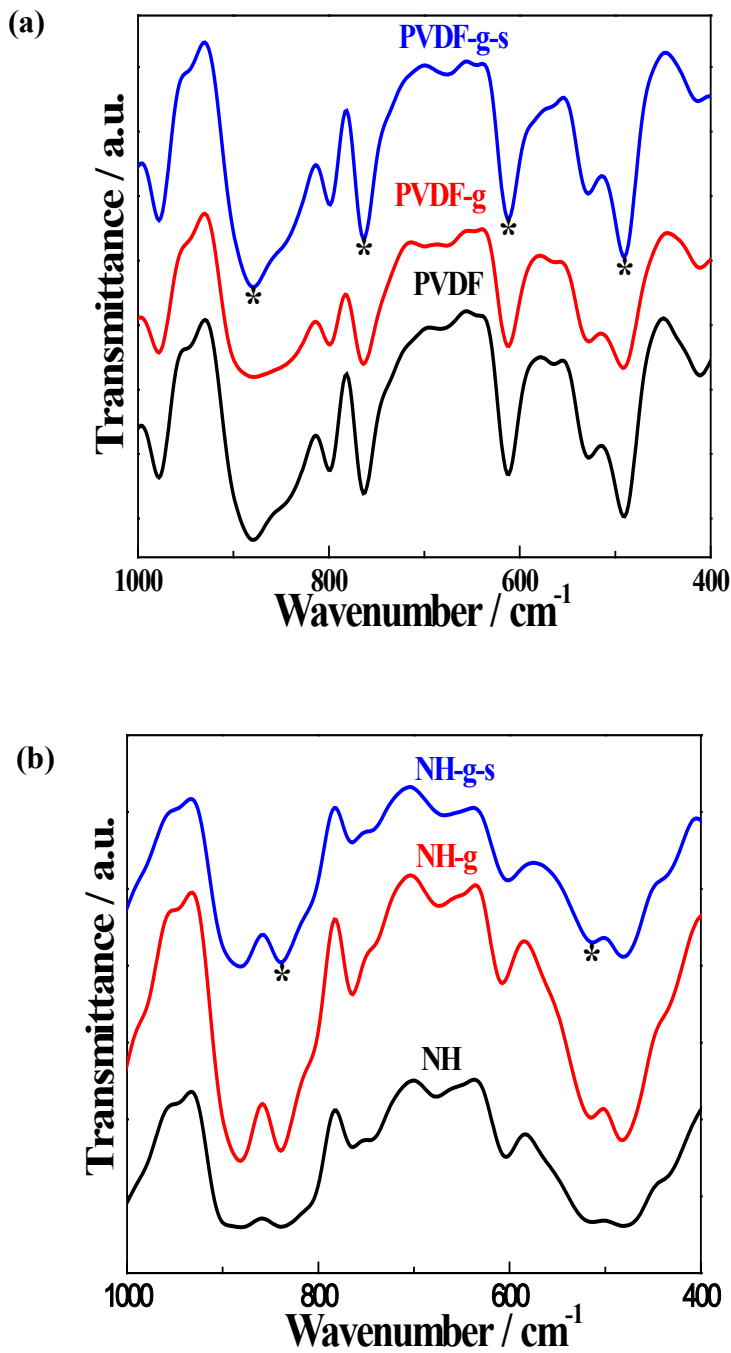
**Figure S1:** SEM images of pure *PVDF*, *PVDF* after etching (*PVDF-e*), pure *NH*, *NH* after etching (*NH-e*). It is obvious that unirradiated specimens do not exhibit any channels or holes alternatively confirm that irradiation is a precondition to create channel in polymeric matrix/membrane. Spherulitic morphology is evident for pure *PVDF* while mesh-like morphology is prominent in nanohybrid and their respective morphologies do not change after etching.



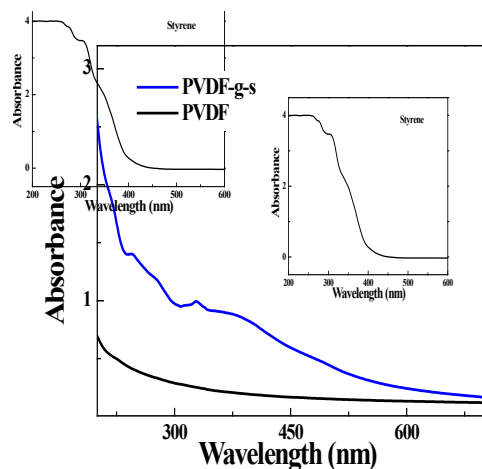
**Figure S2:** NMR spectrum showing a) grafting of polystyrene in PVDF chain and b) subsequent sulphonation on grafted specimens. The peak no. '4' is due to sulphonated proton. This is to mention that pure PVDF does not exhibit any peak in the above scale range (4 – 9 ppm) as presented in Fig. 3 in the manuscript. Hence, the grafting of polystyrene and its sulphonation has been confirmed.



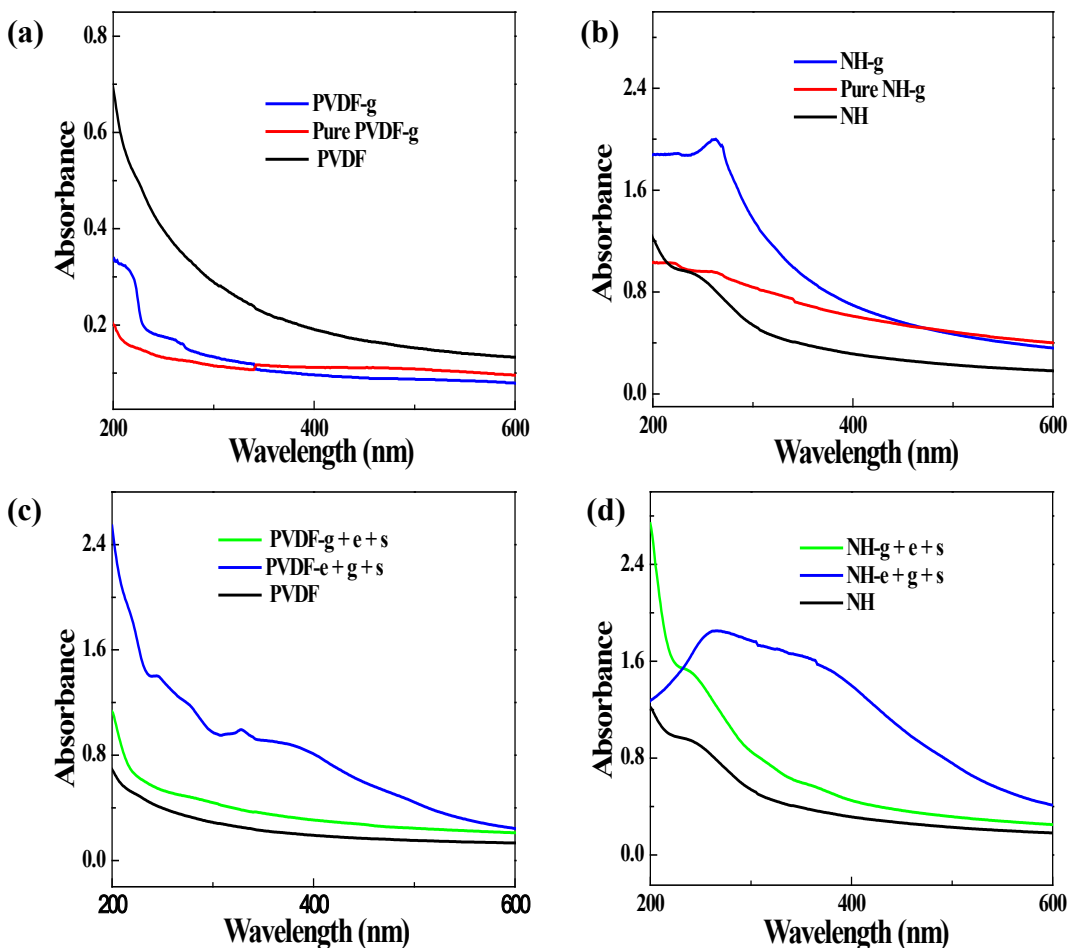
**Figure S3:** FTIR spectra of the pure polystyrene showing two strong and characteristic peaks which are present in the grafted specimen indicating PS grafting on to PVDF as shown in Fig. 4 of the manuscript.



**Figure S4:** FTIR spectra of a) *PVDF*, and b) NanoHybrid comparing pure, grafted (*PVDF-g* and *NH-g*) and sulphonated specimens (*PVDF-g-s* and *NH-g-s*). For pure *PVDF* the  $\alpha$ -phase and for nanoHybrid  $\beta$ -phase have been shown by (\*) marks. The  $\beta$ -peaks are getting sharper after grafting and sulphonation



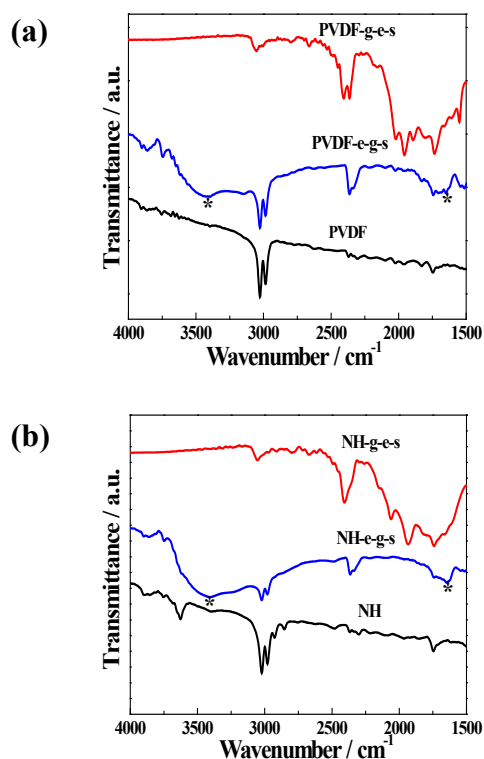
**Figure S5:** *UV-Vis.* absorption spectra of pure *PVDF* and sulphonated *PVDF* after grafting. *PVDF* does not have any absorption peak while characteristics absorption peaks of benzene and sulphonate groups are clearly visible in *PVDF-g-s* specimen suggesting grafting and sulphonation on the *PVDF* chain. The inset figure shows the *UV-Vis.* absorption spectra of pure polystyrene. The peak position of pure *PS* is slightly shifted due to constrain environment inside the nano-channel and discussed details in the manuscript.



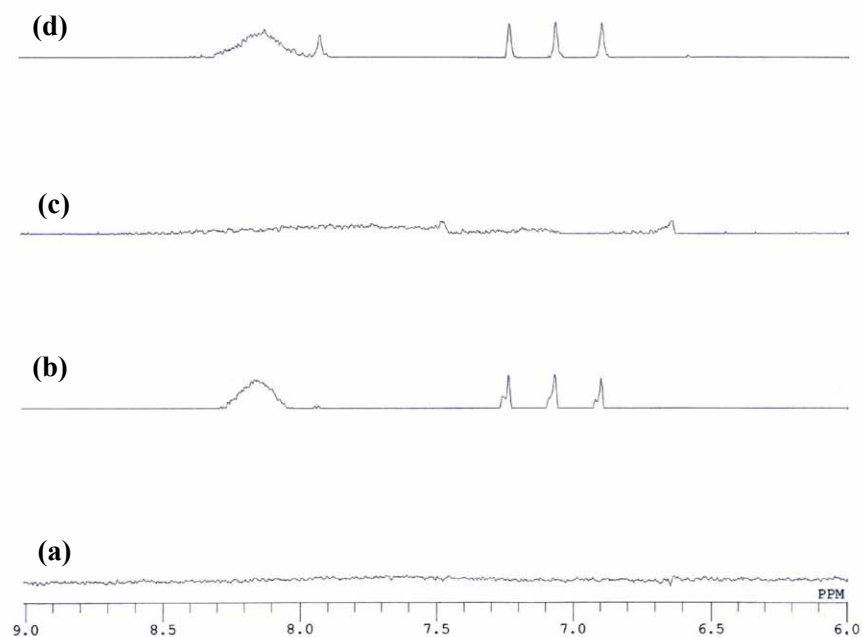
**Figure S6:** a) *UV-Vis.* absorption spectra of (a) pure *PVDF* film, irradiated and grafted *PVDF* (*PVDF-g*) and unirradiated and grafted *PVDF* (pure *PVDF-g*). Absorption peaks are observed for irradiated specimen while there is no peak for unirradiated sample indicating *SHI* irradiation is must for grafting to occur. Similar experiments on nanohybrids have been shown in (b) exhibiting distinct absorption peak for irradiated specimens (*NH-g*) against weak peak for unirradiated peak (*pure NH-g*). Hence, *SHI* irradiation is essential for grafting and enhanced grafting takes place in nanohybrids vis-à-vis pure *PVDF*.

In order to fix the sequence of reactions especially between etching and grafting all the combinations of reactions have been performed. If the grafting reaction takes place before etching followed by sulphonation (*PVDF-g-e-s*) then there is no chemical tagging

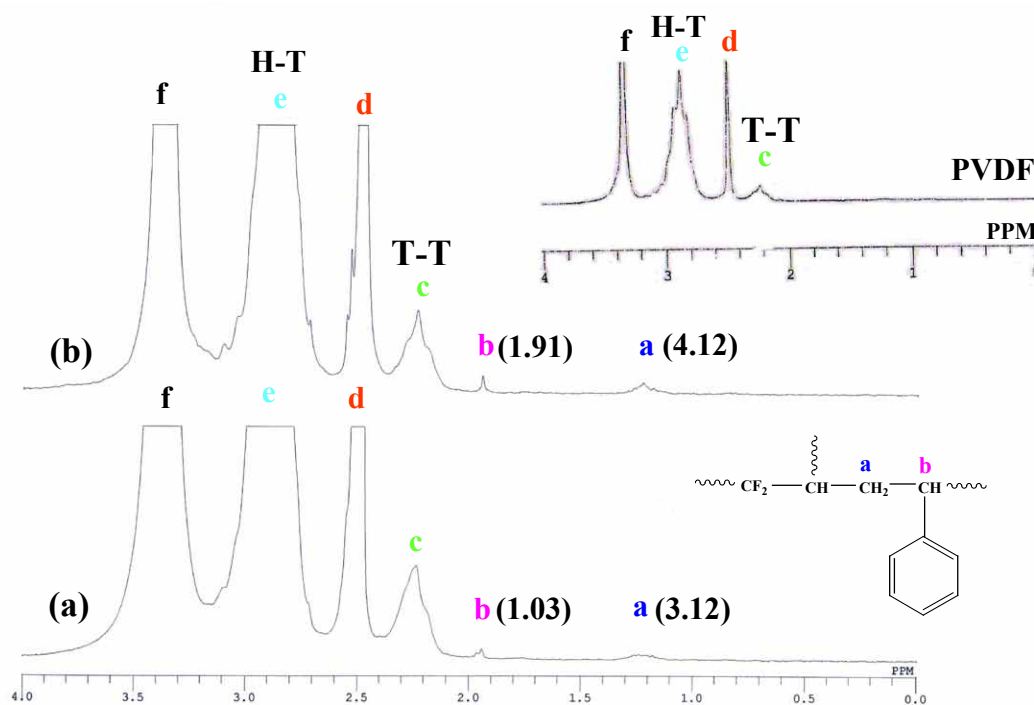
of polystyrene with *PVDF* chain (c). On the other hand, grafting after etching and subsequent sulphonation clearly shows chemical tagging of *PS* with *PVDF* chains. The similar result is also true for nanohybrids (d) showing prominent peak grafting or chemical tagging (peak at 262 nm) and sulphonation (peak at 381 nm). Etching, grafting and sulphonation should be ideal sequence of steps for obtaining good grafting and sulphonation.



**Figure S7:** FTIR evidence of etching and subsequent grafting and sulphonation is better method than grafting and subsequent etching and sulphonation. (a) *PVDF* and (b) nanohybrid and their various treatments. Transmittance peaks at 1640 and 1542 cm<sup>-1</sup> in *PVDF-e-g-s* and *NH-e-g-s* suggesting tagging of *PS* chain with *PVDF* chain while the peaks at 3411 cm<sup>-1</sup> indicate the O-H frequency from sulphonate group. The above mentioned peaks are absent if *PVDF* / *NH* are grafted first and consequently etched and sulphonated. FTIR studies confirm that etching should be performed first followed by grafting and sulphonation.



**Figure S8:** NMR spectra of (a) pure PVDF film (unirradiated and unetched) after sulphonation does not exhibit any peak suggesting no sulphonation, (b) sulphonated PVDF after irradiation and etching (*PVDF-g-s*) showing peaks for both grafting (three peaks at  $\delta = 6.9, 7.0$  and  $7.2$ ) and sulphonation (peaks at  $\delta = 7.9$  and  $8.1$ ). Sulphonation condition was kept similar for both the cases. Comparison of (a) and (b) clearly demonstrates that SHI irradiation followed by etching are essential for sulphonation to occur. (c) sulphonation of unirradiated and unetched nanohybrid showing small peak at  $\delta \sim 6.6$  and  $7.5$  suggesting little sulphonation while (d) SHI irradiated, etched and sulphonated nanohybrid (*NH-g-s*) exhibit prominent peaks for grafting as well as sulphonation. From the peak integration area it is clear that the degree of sulphonation is more in nanohybrid as compared to pure PVDF.



**Figure S9:** NMR spectra of the (a) *PVDF-g*; polystyrene grafted *PVDF* (b) polystyrene grafted nanohybrid *NH-g*. The peak marked as 'a' and 'b' are the methylene and methyne proton from polystyrene indicating grafting on *PVDF* chains. On the other hand, pure *PVDF* (inset figure) does not exhibit any peak in that region clearly suggest the chemical attachment of polystyrene with *PVDF* chain when it is irradiated, etched and grafted with polystyrene. Further, the integrated area of the above two peaks (value in bracket) are larger in nanohybrid as compared to *PVDF* suggesting greater extent of grafting in nanohybrid. It is needless to mention that other characteristics peaks of *PVDF* are present in the spectrum stating the 'head to tail (*H-T*)' and 'head to head (*H-H*)' protons in the *PVDF* chains. However, this figure confirms the grafting of polystyrene on *PVDF* chain and also indicates enhanced grafting in nanohybrid as compared to *PVDF*.