

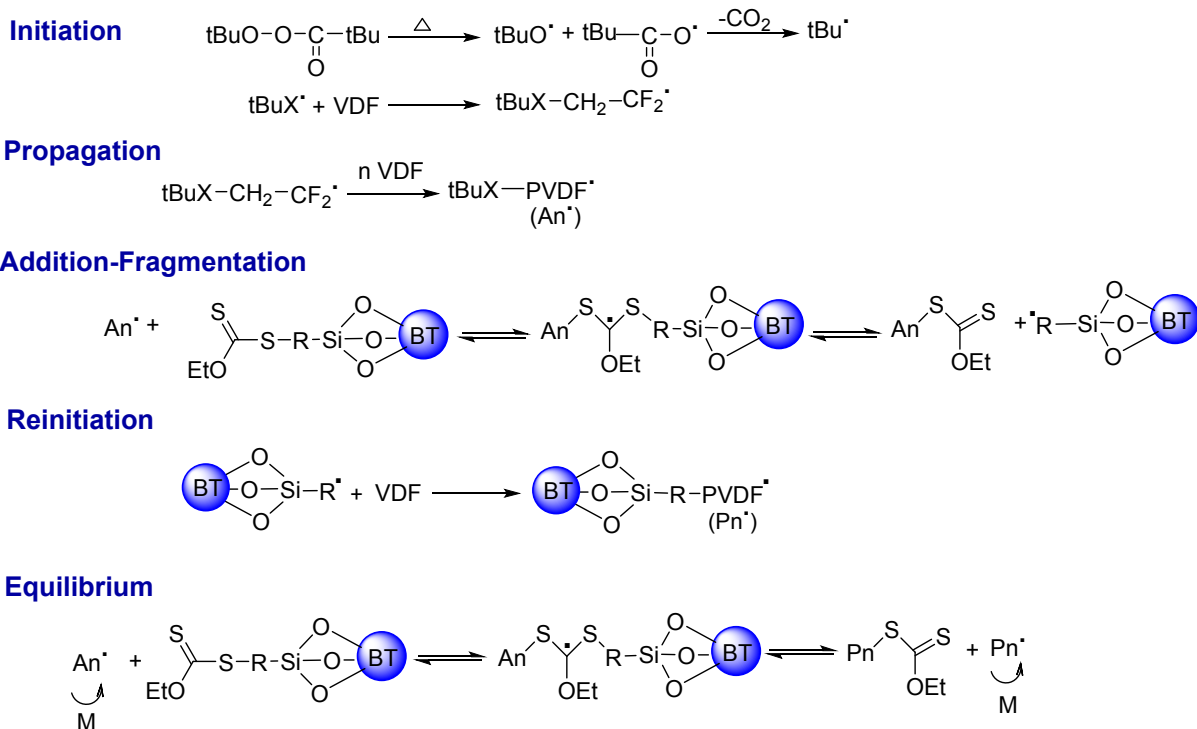
Supporting information

Core shell structured Poly(Vinylidene Fluoride) *-grafted-* BaTiO₃ nanocomposites prepared via Reversible Addition-fragmentation chain transfer (RAFT) polymerization of VDF for high energy storage capacitors

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Scheme S1. Mechanism of Reversible Addition-Fragmentation Chain-Transfer Polymerization (RAFT) of VDF.

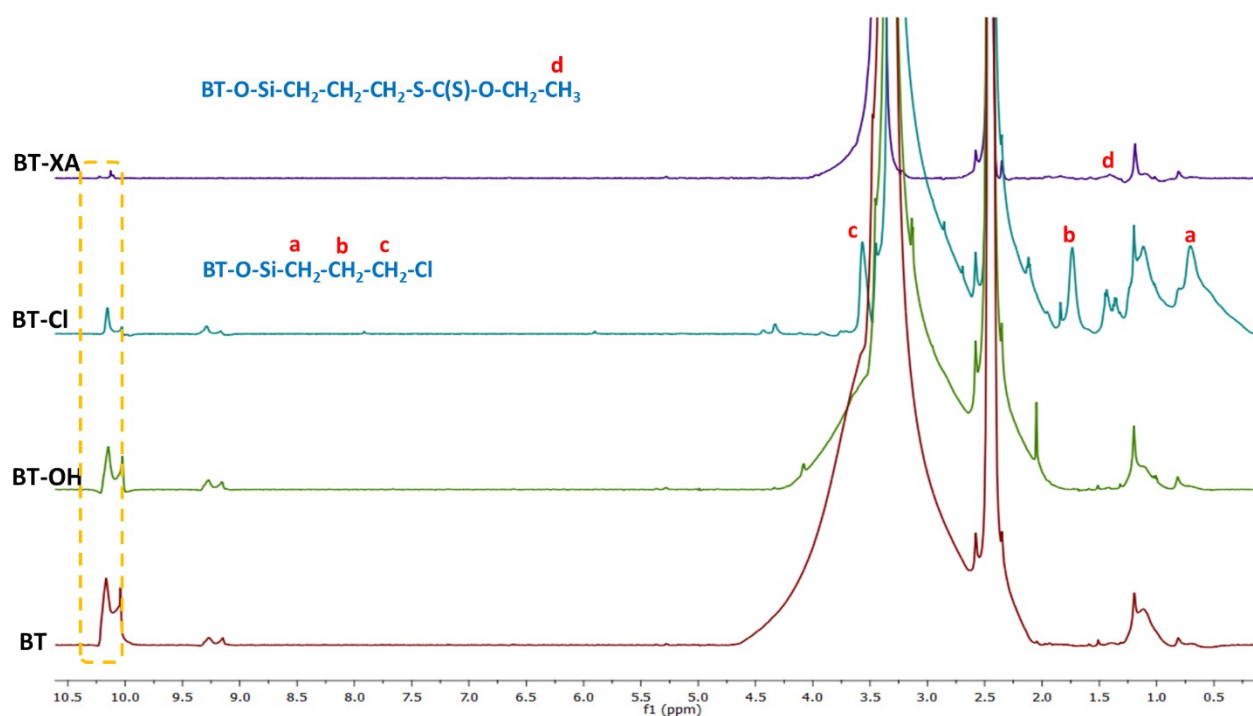


Figure S1. Expansion of the 0.5 to 10.5 ppm region of the ¹H HRMAS spectrum in DMSO of pristine BaTiO₃ (BT), modified with hydrogen peroxide (BT-OH), with silane agent (BT-Cl) and with chain transfer agent (BT-XA).

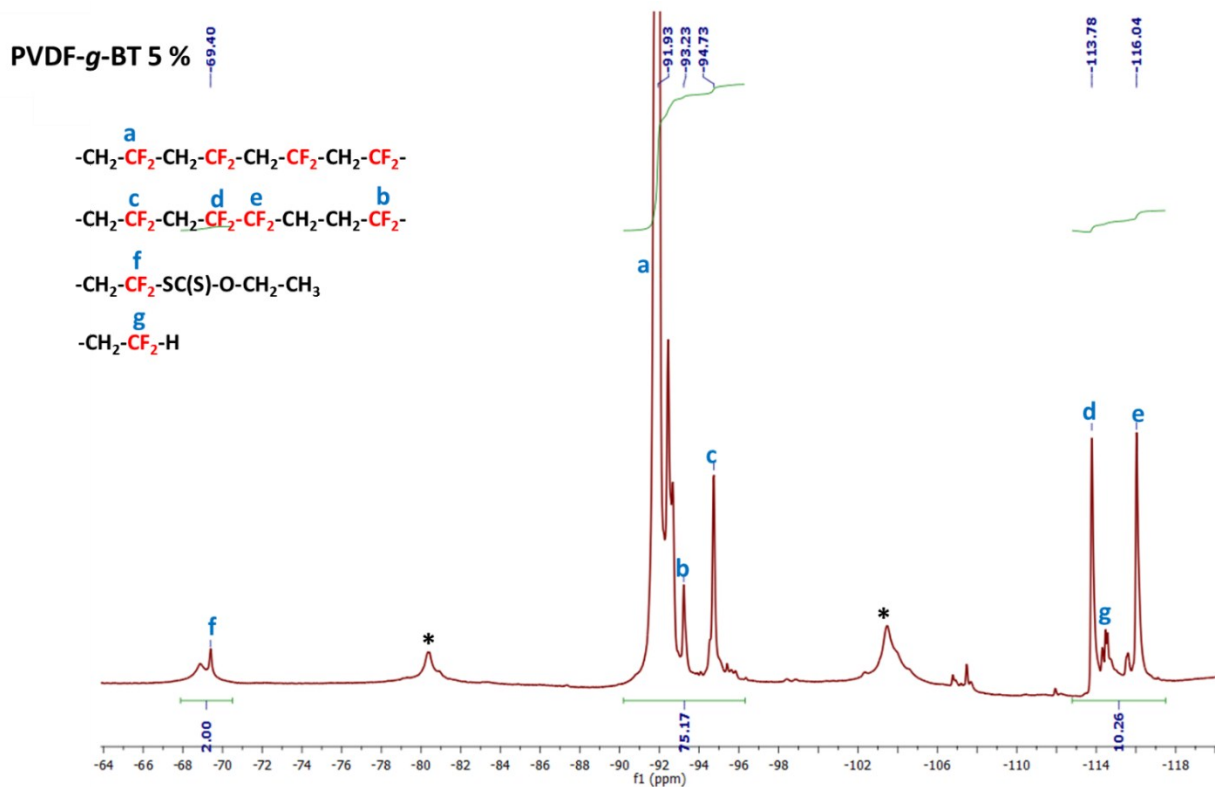


Figure S2. Expansion of the -64 to -120 ppm region of the ^{19}F HRMAS spectrum recorded in $\text{d}_6\text{-DMSO}$ of PVDF-*g*-BaTiO₃ nanocomposite filled with 5 wt % of BaTiO₃ (* stands for the spinning bands).

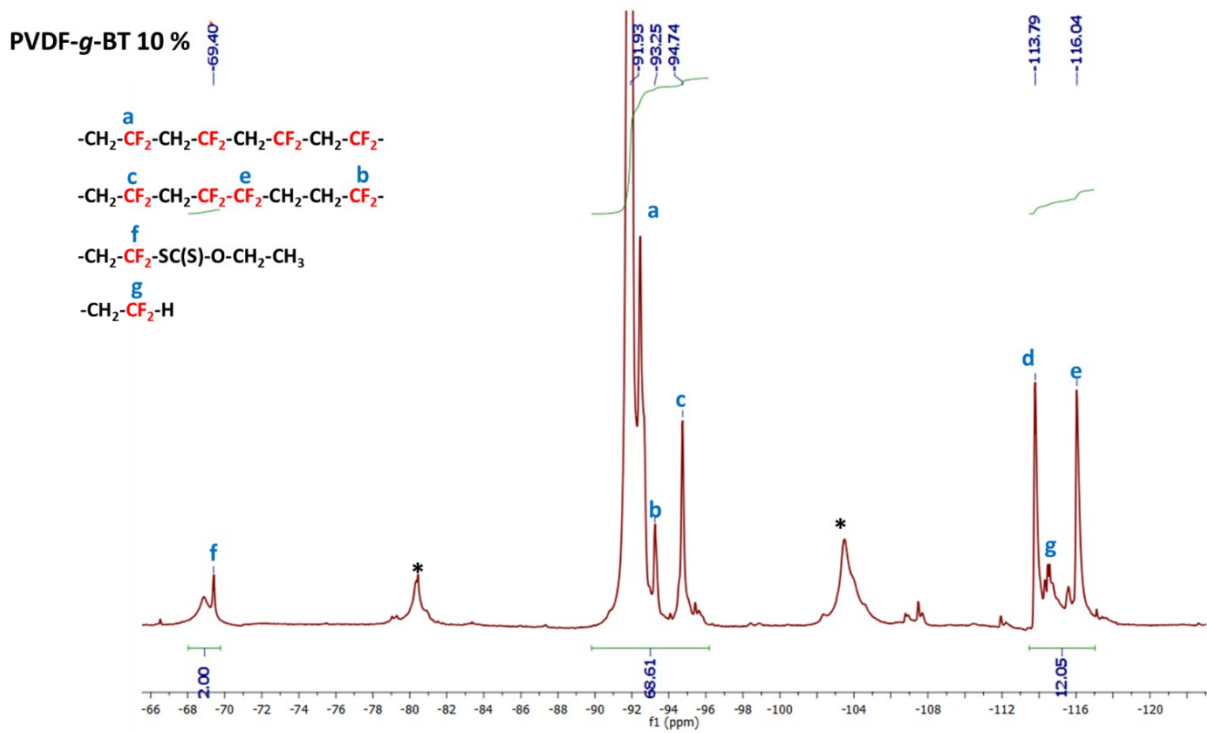


Figure S3. Expansion of the -64 to -120 ppm region of the ^{19}F HRMAS spectrum recorded in d_6 -DMSO of PVDF-g-BaTiO₃ nanocomposite filled with 10 wt % of BaTiO₃ (* stands for the spinning bands).

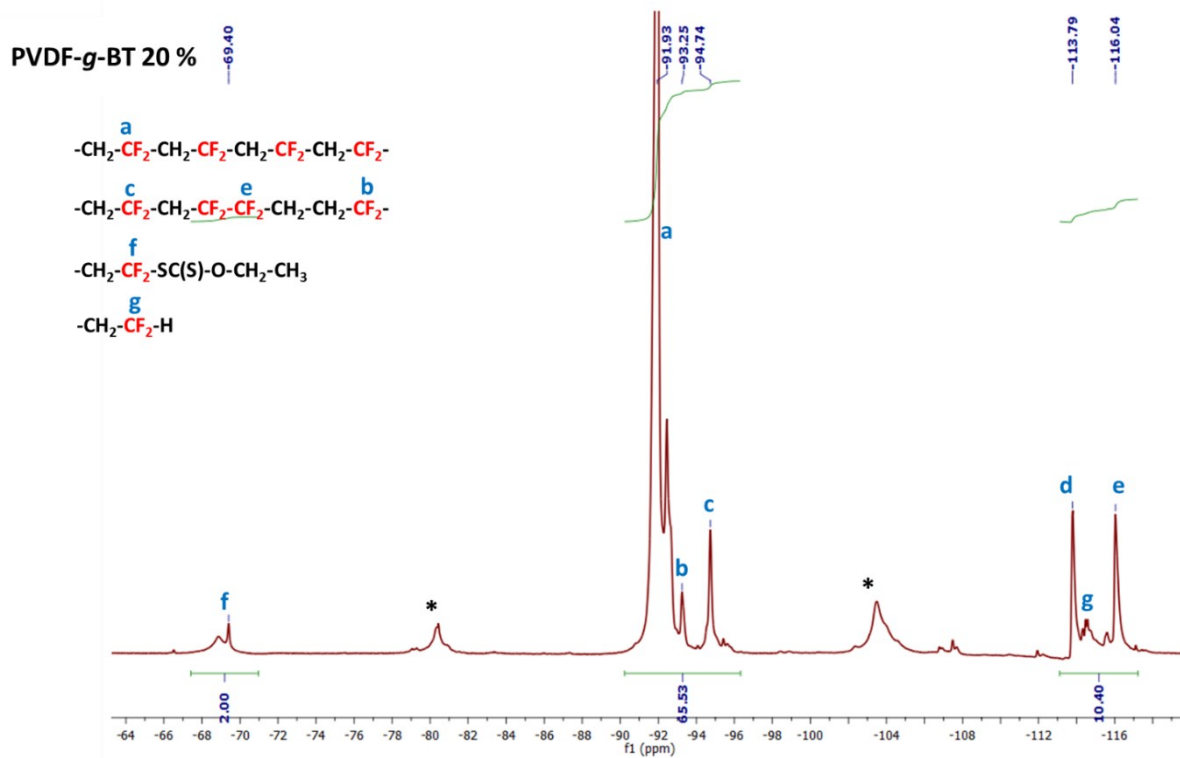


Figure S4. Expansion of the -64 to -120 ppm region of the ^{19}F HRMAS spectrum recorded in d_6 -DMSO of PVDF-g-BaTiO₃ nanocomposite filled with 20 wt % of BaTiO₃ (* stands for the spinning bands).

PVDF-g-BT 5 %

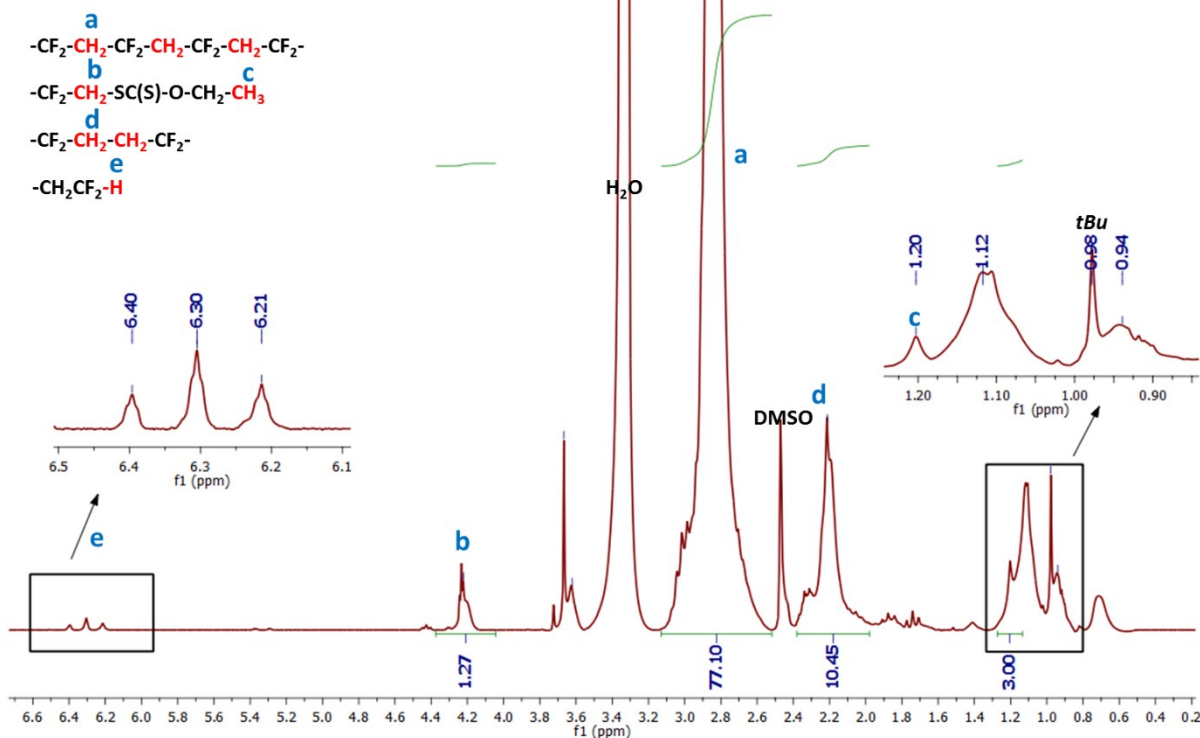


Figure S5. Expansion of the 0.2 to 6.4 ppm region of the ¹H HRMAS NMR spectrum in DMSO PVDF-g-BT nanocomposites filled with 5 wt % of BaTiO₃

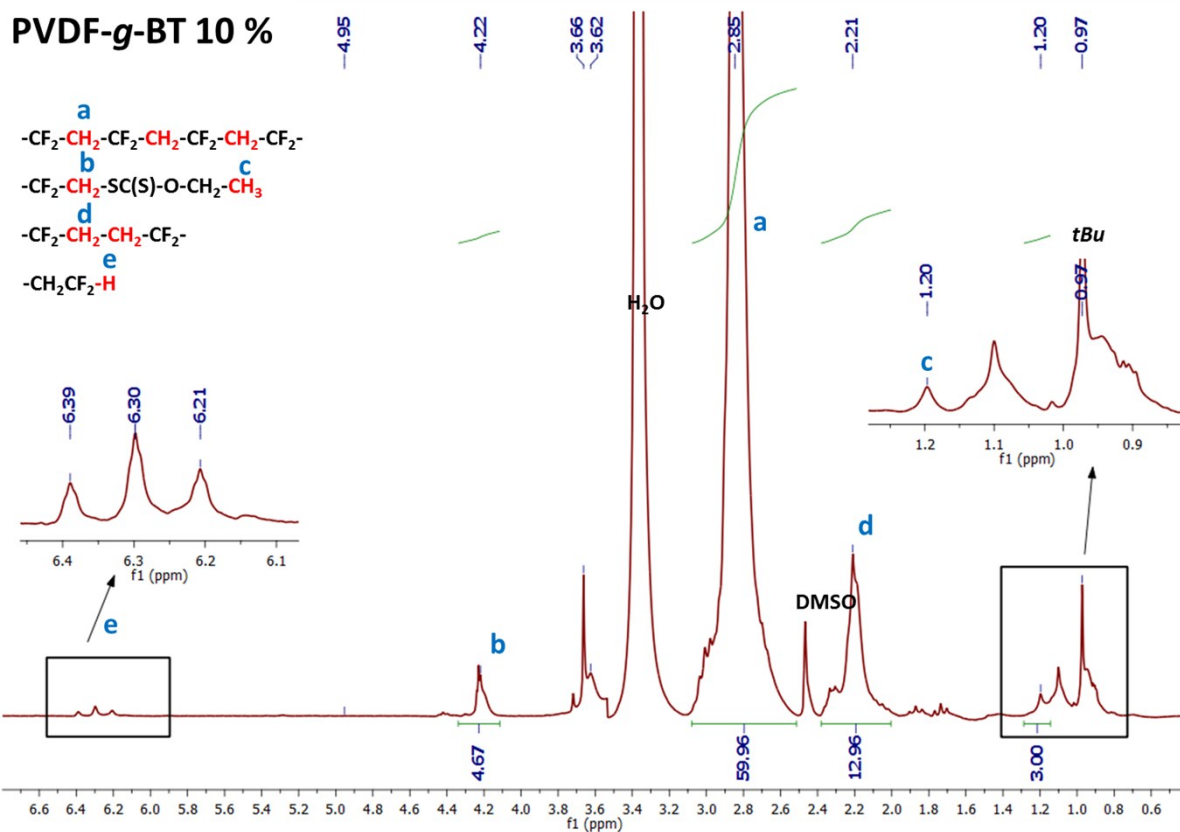


Figure S6. Expansion of the 0.2 to 6.4 ppm region of the ¹H HRMAS NMR spectrum in DMSO PVDF-g-BT nanocomposites filled with 10 wt % of BaTiO₃

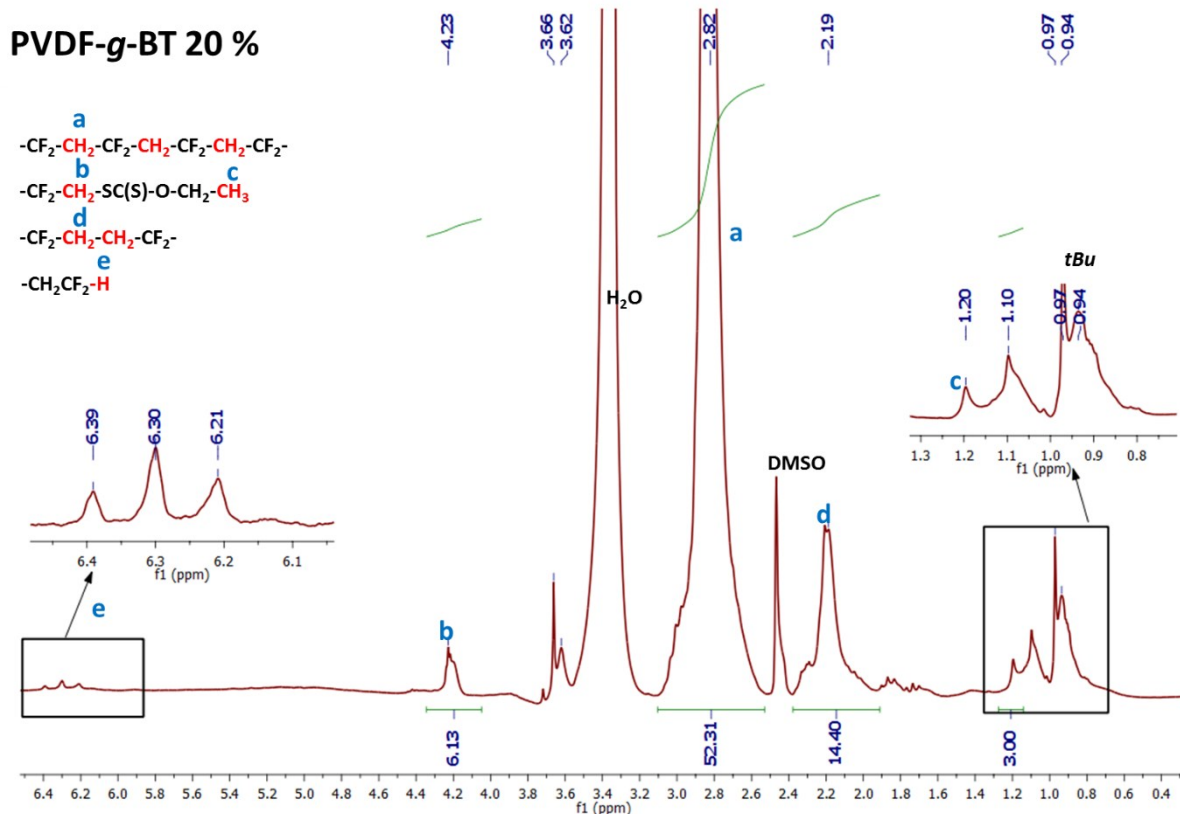


Figure S7. Expansion of the 0.2 to 6.4 ppm region of the ^1H HRMAS NMR spectrum in DMSO PVDF-g-BT nanocomposites filled with 20 wt % of BaTiO_3

Determination of Molar Mass of grafted PVDF

To cleave the attached PVDF from the functionalized BaTiO_3 nanoparticles, an amount of PVDF-g-BT was dispersed in a mixture of DMF or DMF/Aliquat according to procedures describe in literature.^{1,2} Then Acid (HF or HCl) was added and the mixture was allowed to stir for a certain time and temperature. At the end of the reaction, the mixture was centrifuged and the supernatant was concentrated then precipitated over cold pentane or methanol.

Table S1: Experiments conducted to enable the acidic cleavage of attached PVDF from functionalized nanoparticles.

Exp N°	wt PVDF- <i>g</i> -BT (% of BT) (mg)	wt (Aliquot) (mg)	V _{DMF} (ml)	V _{acid} (ml)	time (T, °C)
1	50 (10%)	5	3	0.5 (HF)	16 hr (25)
2	50 (10%)	5	3	0.5 (HF)	3 days (25)
3	30 (5%)	5	3	0.5 (HF)	5 days (25)
4	50 20%	0	5	0.5 (HCl)	16 hr (80)
5	40 (3%)	0	4	0.4 (HCl)	16 hr (80)

In fact, the molar mass of grafted polymer can also be determined by NMR. According to previous works, the Mn obtained from SEC is almost equal to that obtained by NMR.³ Since, whatever the experimental conditions reported above, the cleavage did not work, the Mn of the nanocomposites were determined using the ¹H and ¹⁹F HRMAS NMR spectroscopies (Table 2) according to equation previously report by Guerre et al.⁴

$$M_{n,NMR} = M_{n,CTA} + DP(Z - CTA) \times M_{n,VDF}$$

where $M_{n,CTA} = 472$ g/mol and $M_{n,VDF} = 64$ g/mol

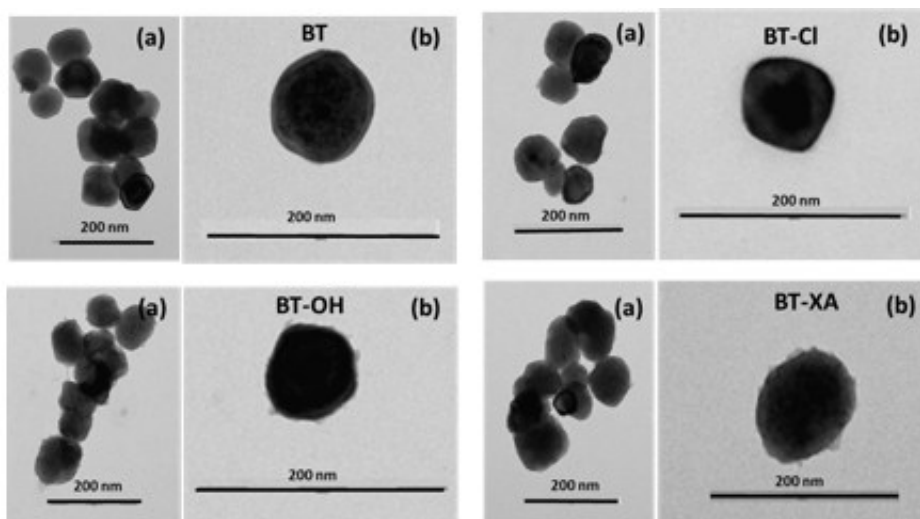


Figure S8. TEM images of the as received and functionalized BaTiO₃ particles with (a) (low magnification) and (b) (higher magnification)

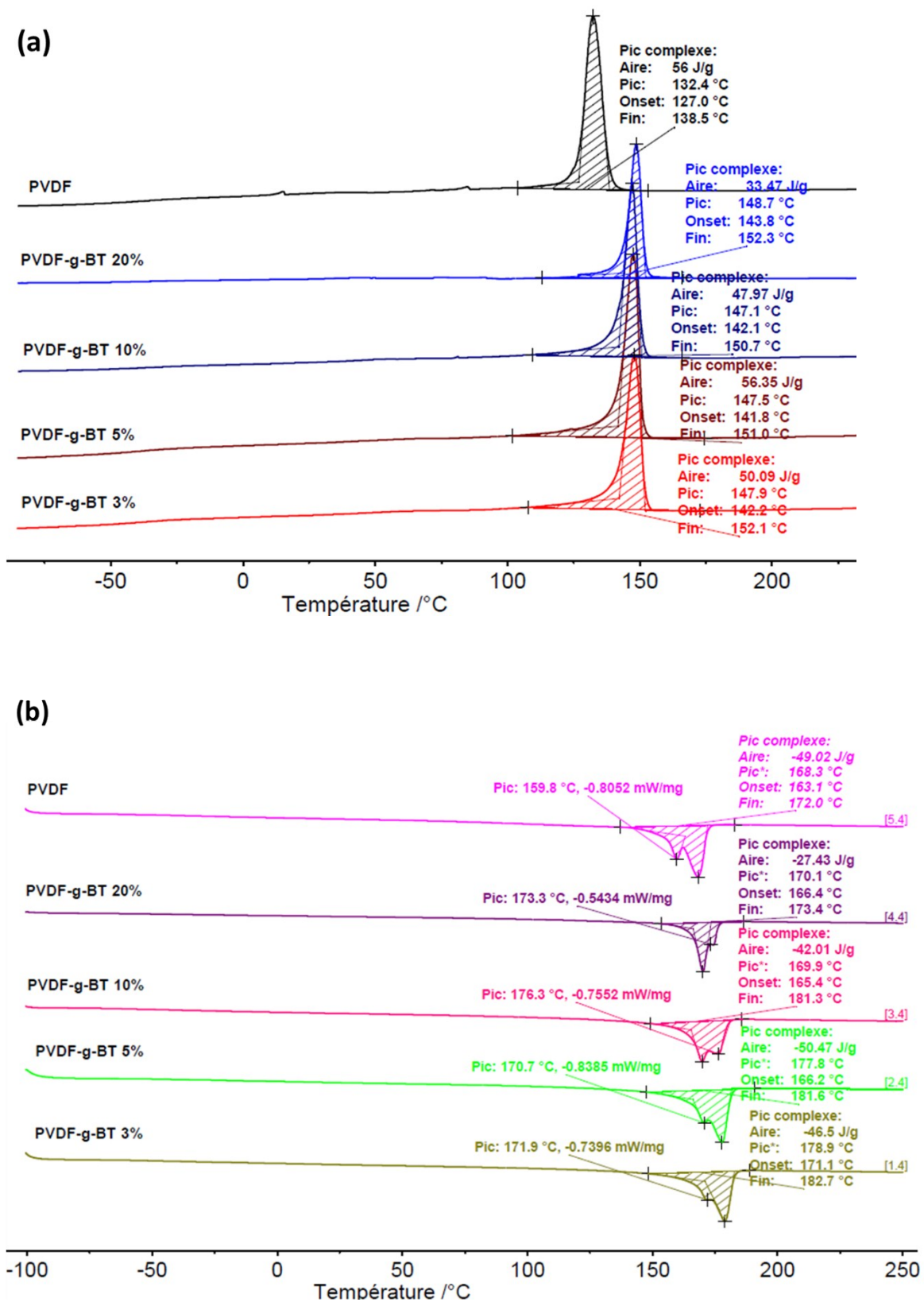


Figure S9. DSC thermograms (second heating and cooling) of PVDF from conventional radical polymerization of VDF initiated by TBPPi and PVDF-g-BaTiO₃ nanocomposites with different BT fractions: (a) heating process, (b) cooling process.

- 1 S. Jafarzadeh, V. Haddadi-Asl and H. Roghani-Mamaqani, *J. Polym. Res.*, 2015, **22**, 123.
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