Supporting information

Core shell structured Poly(Vinylidene Fluoride) -grafted- BaTiO$_3$ nanocomposites prepared via Reversible Addition-fragmentation chain transfer (RAFT) polymerization of VDF for high energy storage capacitors

Fatima Ezzahra BOUHARRAS, a,b Mustapha RAIHANE, a* Gilles SILLY,b Cedric TOTEE,b Bruno AMEDURI b*

a Laboratory of Organometallic and Macromolecular Chemistry-Composite Materials (LCO2MC). Faculty of Sciences and Techniques, Cadi-Ayyad University, Av. Abdelkrim Khattabi, BP 549, 40000 Marrakesh, Morocco

b Ingénierie et Architectures Macromoléculaires Team, Institut Charles Gerhardt, UMR 5253 CNRS, UM, ENSCM, Place Eugène Bataillon, 34095 Cedex 5 Montpellier, France
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 $^1$H HRMAS spectrum in DMSO of pristine BaTiO$_3$ (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 d$_6$-DMSO of PVDF-g-BaTiO$_3$ nanocomposite filled with 5 wt % of BaTiO$_3$ (* 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-BaTiO$_3$ nanocomposite filled with 10 wt % of BaTiO$_3$ (* 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-BaTiO$_3$ nanocomposite filled with 20 wt % of BaTiO$_3$ (* stands for the spinning bands).
Figure S5. Expansion of the 0.2 to 6.4 ppm region of the \(^1\)H HRMAS NMR spectrum in DMSO PVDF-g-BT nanocomposites filled with 5 wt % of BaTiO\(_3\)
Figure S6. Expansion of the 0.2 to 6.4 ppm region of the $^1$H HRMAS NMR spectrum in DMSO PVDF-g-BT nanocomposites filled with 10 wt % of BaTiO$_3$
Figure S7. Expansion of the 0.2 to 6.4 ppm region of the $^1$H 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.

<table>
<thead>
<tr>
<th>Exp N°</th>
<th>wt$_{\text{PVDF-g-BT}}$ (% of BT) (mg)</th>
<th>wt (Aliquat) (mg)</th>
<th>V$_{\text{DMF}}$ (ml)</th>
<th>V$_{\text{acid}}$ (ml)</th>
<th>time (T, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 (10%)</td>
<td>5</td>
<td>3</td>
<td>0.5 (HF)</td>
<td>16 hr (25)</td>
</tr>
<tr>
<td>2</td>
<td>50 (10%)</td>
<td>5</td>
<td>3</td>
<td>0.5 (HF)</td>
<td>3 days (25)</td>
</tr>
<tr>
<td>3</td>
<td>30 (5%)</td>
<td>5</td>
<td>3</td>
<td>0.5 (HF)</td>
<td>5 days (25)</td>
</tr>
<tr>
<td>4</td>
<td>50 20%</td>
<td>0</td>
<td>5</td>
<td>0.5 (HCl)</td>
<td>16 hr (80)</td>
</tr>
<tr>
<td>5</td>
<td>40 (3%)</td>
<td>0</td>
<td>4</td>
<td>0.4 (HCl)</td>
<td>16 hr (80)</td>
</tr>
</tbody>
</table>

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. Since, whatever the experimental conditions reported above, the cleavage did not work, the Mn of the nanocomposites were determined using the $^1$H and $^{19}$F 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 BaTiO$_3$ 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-BaTiO$_3$ nanocomposites with different BT fractions: (a) heating process, (b) cooling process.

