

Supplemental Information

Continuous flow SET-LRP in the presence of P(VDF-co-CTFE) as macroinitiator in copper tubular reactor

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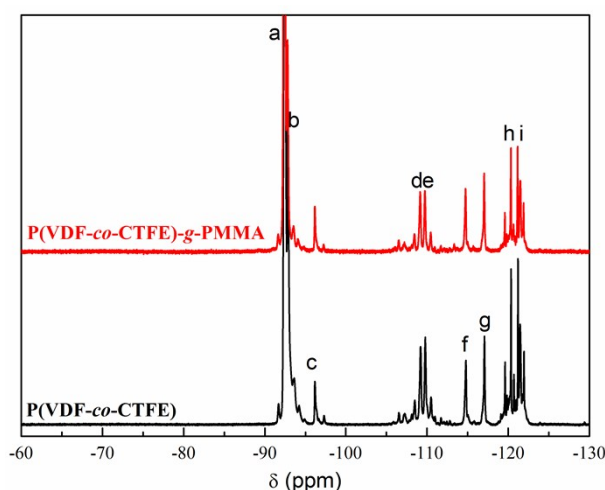


Fig. S1 ¹⁹F NMR of pristine P(VDF-co-CTFE) and P(VDF-co-CTFE)-g-PMMA (Acetone-*d*₆) prepared in copper tubular reactor ([Cl]:[L]:[M]=1:0.125:30, 10 min, 40 °C).

A ¹⁹F NMR spectrum was employed to further demonstrate the structure of graft copolymers as shown in Fig. S1. By taking P(VDF-co-CTFE)-g-PMMA as example, the microstructure of the P(VDF-co-CTFE) copolymer is dominated by the presence of VDF-VDF head-to-tail (-CH₂CF₂CH₂CF₂-) sequence appearing around -92.4 ppm, which is assigned as peak *a* in Fig. S1. VDF-CTFE in tail-to-tail (-CH₂CF₂CClFCF₂-) connection appearing around -93.4, -109.2, -119.9, and -121.3 ppm is respectively marked as peak *b*, *d*, *h*, *i* in ¹⁹F NMR spectrum. Peak *c* should be attributed to VDF-VDF-VDF in tail-to-tail-to-head connection. VDF-VDF in tail-to-tail connection is signed as peak *f* and *g*. The height reducing of -

C-Cl- on CTFE units at -121.2 ppm should be assigned to the MMA units inserting into the C-Cl bond, where the C-C bond take place of the C-Cl bond.

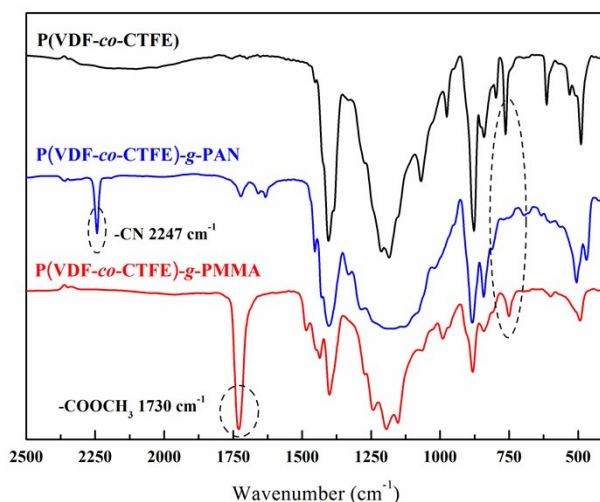


Fig. S2 FT-IR of pristine P(VDF-co-CTFE), P(VDF-co-CTFE)-g-PMMA and P(VDF-co-CTFE)-g-PAN prepared in copper tubular reactor ([Cl]:[L]:[M]=1:0.125:30, 10 min, 40 °C).

Compared with the pristine polymer, P(VDF-co-CTFE)-g-PMMA copolymer display a strong absorption band at 1730 cm⁻¹ corresponding to the carbonyl group of MMA clearly confirming the presence of PMMA segments. The absorption band at 2247 cm⁻¹ is assigned to be the cyano group of AN, which indicate the presence of PAN segments. The decrease in the intensity of the absorption band at 840 cm⁻¹ corresponding to the Cl on CTFE units demonstrates the replacement of a portion of C-Cl bonds by C-C bonds owing to the insertion of functional monomer.

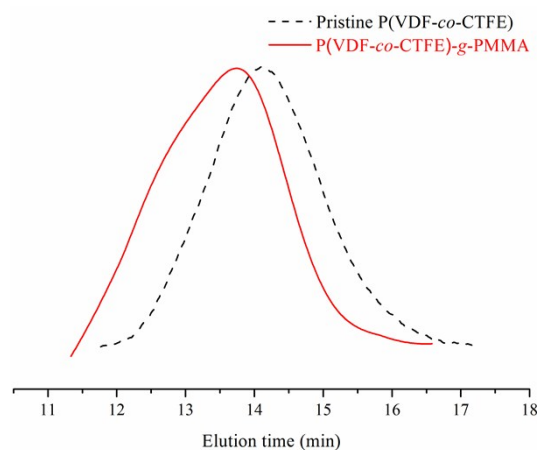


Fig. S3 SEC traces of pristine P(VDF-co-CTFE) and P(VDF-co-CTFE)-*g*-PMMA (graft length=7.61).