

Supporting Information

Direct fluorination as a one-step ATRP initiator immobilization for convenient surface grafting of phenyl ring-containing substrates

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This supplemental document contains 2 descriptions and 8 Figures.

1. Experimental

1.1. Molecule simulation experiments

First, PQP and PE were fluorinated using the same process as PET fabrics. For the preparation of P(TFEMA) brushes from FPQP and FPE, TFEMA (3ml, 10% v/v), CuBr (47.1 mg, 0.33 mmol), and bpy (51.8 mg, 0.33 mmol) were added to 27 mL of tetrahydrofuran. The mixture was stirred and purged with argon for 30 min. The FPQP/FPE was then introduced into the solution. The reaction flask was sealed and kept in a 60 °C oil bath for a predetermined period. For the preparation of P(HEMA) blocks from the FPQP-g-P(TFEMA), HEMA (3ml, 10% v/v), CuBr (47.1 mg, 0.33 mmol), and bpy (51.8 mg, 0.33 mmol) were added to 27 mL of tetrahydrofuran. The mixture was stirred and purged with argon for 30 min. The FPQP-g-P(TFEMA) was then introduced into the solution. The reaction flask was sealed and kept in a 60 °C oil bath for a predetermined period.

1.2. Characterization

The surface of the PET fabric and other fibers were observed by scanning electron microscopy (SEM) FEI Inspect F (FEI Company, EU / USA). X-ray photo-electron spectroscopy (XPS) was performed on an Escalab250Xi spectrometer (Thermo scientific). ¹HNMR spectroscopy was performed using Bruker AV II-400 MHz. Water contact angle (CA) and water shedding angle (SA) were carried out using the conventional Owens-Wendt method on the Germany Krüss 100 type surface tension meter with deionized water at room temperature.¹ Fourier-transform infrared (FTIR) spectra of all samples were operated on the Nicolet 560 infrared spectrometer employing transmission mode. Electron paramagnetic resonance (EPR) measurements were carried out on

Bruker EPR EMX Plus (Bruker Beijing Science and Technology Ltd, USA) at a frequency of approximately 9.8 GHz using a standard microwave power of 1 mW.²

The washing durability was tested by a standard procedure according to AATCC Test Method 61-2003 Test No. 1A. The washed fabrics were rinsed with abundant water to remove the residual detergent and dried at 80 °C. The abrasion tests were performed according to a modified procedure based on the AATCCA Test Method 8-2001. The number of sandpaper is 300 meshes, and the fabrics are rubbed by 10 cm on the sandpaper under a pressure of 10g weight for one cycle.³ Uv resistance of PET fabrics was tested by exposing to Uv radiation in a Uv irradiation chamber, the sample was placed at a distance of 35 cm below the lamp, the radiation chamber was ventilated and the temperature was maintained at 60 °C. The Uv irradiation was initiated by focusing a mercury vapor discharge lamp ($\lambda = 365 \text{ nm}$, 2.66 W cm^{-2}) on the sample. The irradiation times were controlled at different times.⁴

Single modified and unmodified amid fibers were straightened and pasted on a metal frame. To perform single fiber pull-out testing, epoxy resin (E-51) and polyether resin as curing agent were mixed as the ratio of 3:1. Drops of the mixed resin were stuck to the filaments. The single fiber/resin microdrop composites were cured at 80 °C for 4 h. To calculate interfacial shear strength of the composites, following formula was applied:

$$IFSS = F/\pi dl$$

where F is the maximum force loaded on the resin drop, d is the diameter of fiber, l is the length that fiber embedded in the resin.⁵

2. Figures

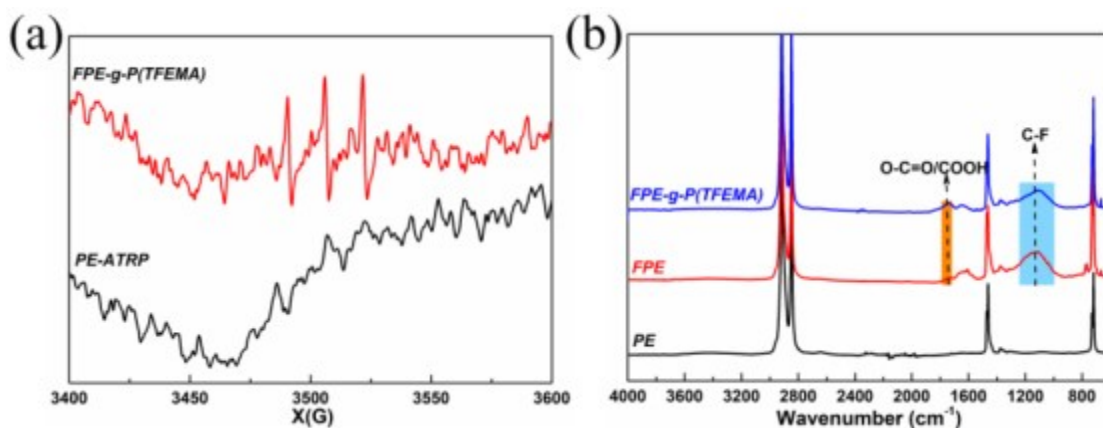


Figure S1. (c) EPR spectra recorded during PE and FPE initiated ATRP polymerizations; (d) FTIR spectra of PE, FPPE and FPE-g-P(TFEMA).

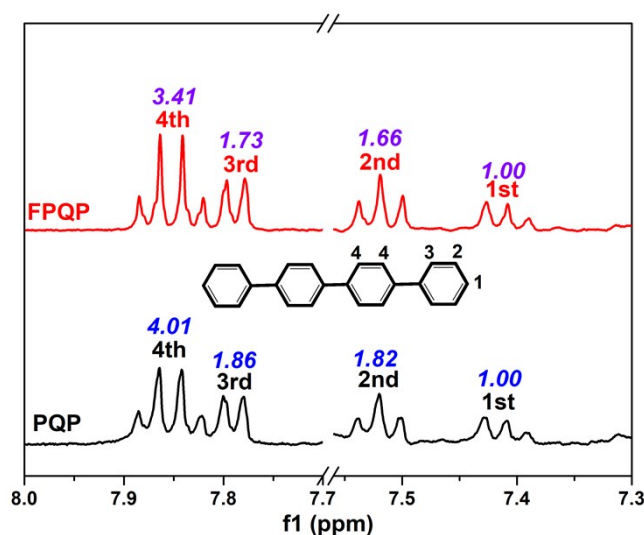


Figure S2. ^1H NMR spectrum of PQP and FPQP.

Here, ^1H NMR was investigated for the analysis of the chemical structure change during fluorination. ^1H NMR spectra of PQP before and after fluorination are exhibited in Fig. S2. As can be seen from the structure, there are four kinds of H atoms in virgin PQP. Those four kinds of H atoms are respectively corresponding to their chemical shifts shown in Fig. R1. Using the H atom (1st) as internal standard, the peak integral results are in good conformity with H atomic numeric

ratio in chemical structure with nearly 1:2:2:4 from 1st to 4th. While compared with original PQP, H atom integrals in 2nd to 4th spot reveal a significant decrease from 1.82, 1.86 and 4.01 to 1.66, 1.73 and 3.41 after fluorination, which illustrates that part of the hydrogen atoms on phenyl rings were replaced by fluorine atoms, but most of the hydrogen atoms were remained.

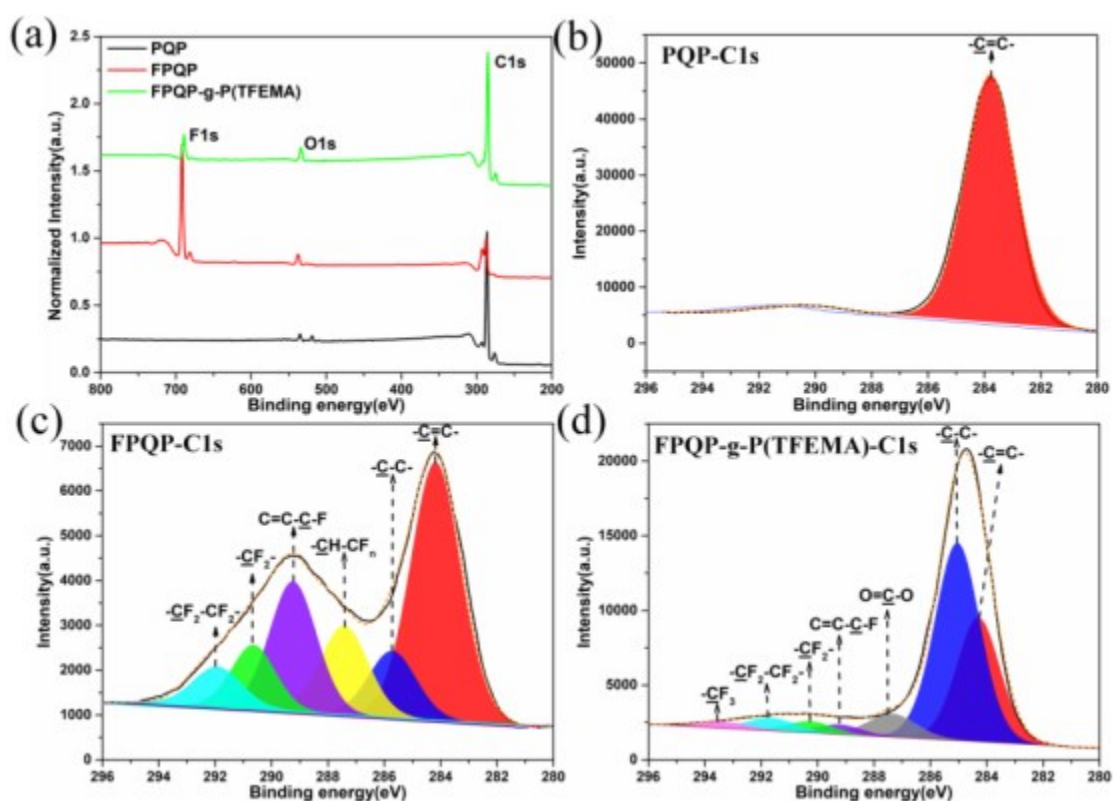


Figure S3. (a) XPS spectra of the pristine PQP, FPQP, and FPQP-g-P(TFEMA); C1s XPS spectra with fitting curves of the (b) pristine PQP, (c) FPQP, and (d) FPQP-g-P(TFEMA).

There is only one component for the C1s peak of the pristine PQP: C=C (284.1 eV). After fluorination, new absorption peaks corresponding to -C-C-, -CH-CF_n, C=C-C-F, -CF₂- and -CF₂-CF₂- were formed at 285.8 eV, 287.4 eV, 289.3 eV, 290.7 eV and 292.0 eV, respectively, indicating that F atoms were added to the phenyl ring and replaced part of the hydrogen, which was consistent with our previous research. After initiating ATRP of TFEMA with FPQP as an initiator, the O=C-O at 287.5 eV and -CF₃ at 293.5 eV were detected in the C1s spectrum of the obtained product FPQP-g-P(TFEMA), which implies that FPQP successfully initiated ATRP.

Besides, the content changes of different C-F before and after grafting were compared as shown in Table R2. The ratios of $-CF_2-/-CF_2-CF_2-$ and $C=C-C-F/-CF_2-CF_2-$ changed from 1.51 and 3.25 to 0.83 and 0.69, respectively, indicating that $C=C-C-F$ might be the main initiating site of ATRP, which was consistent with our prediction.

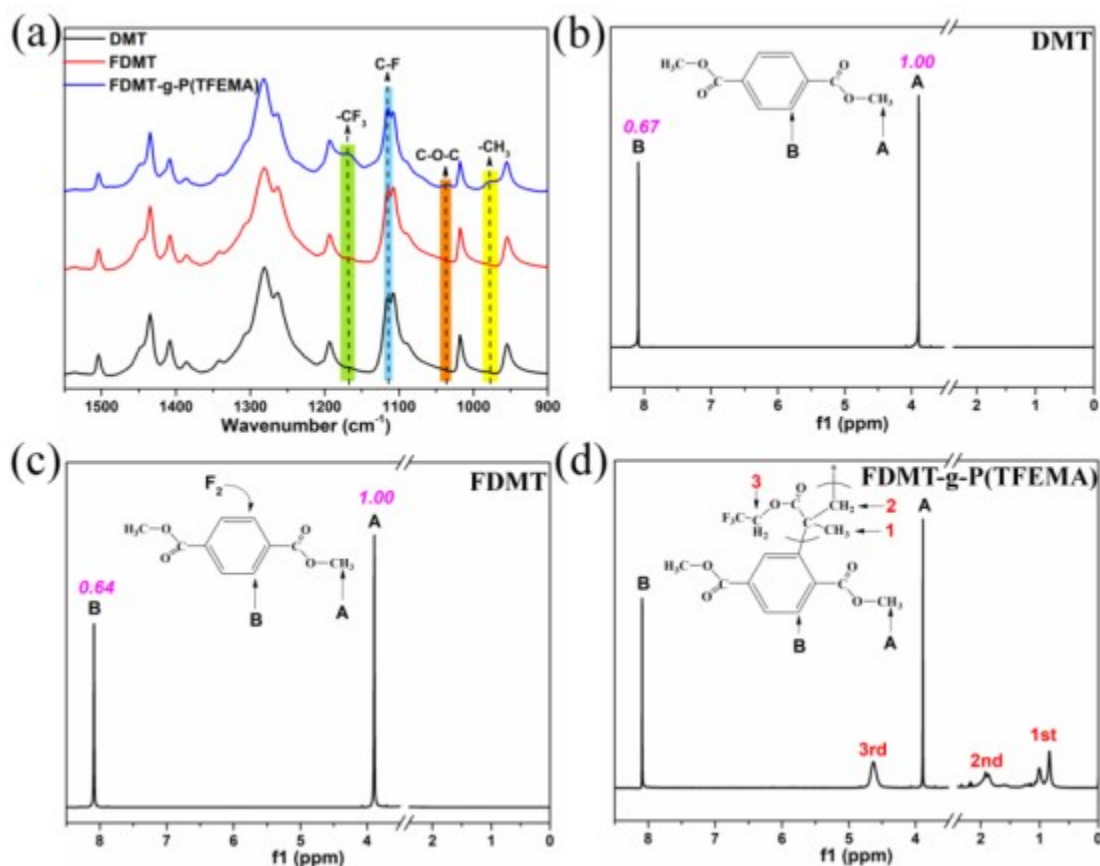


Figure S4. (a) FTIR spectra of the pristine DMT, FDMT, and FDMT -g-P(TFEMA); 1H NMR spectrum of the (b) pristine DMT, (c) FDMT, and (d) FDMT-g-P(TFEMA).

As shown in Fig. S4, FTIR spectra confirmed that F atoms were successfully introduced into DMT through direct fluorination and FMIT can be used as an initiator to successfully initiate ATRP. In addition, 1H NMR was investigated for the analysis of the chemical structure change during fluorination. As can be seen from the structure, there are two kinds of H atoms in virgin DMT. Those two kinds of H atoms are respectively corresponding to their chemical shifts shown in Fig. R4. Using the H atom (A) as internal standard, the peak integral results are in good conformity with H atomic numeric ratio in chemical structure with nearly 3:2. While compared with original DMT, H atom integrals in B spot reveal a significant decrease from 0.67 to 0.64 after

fluorination, indicating that the hydrogen on the phenyl ring reacts more than the hydrogen on the methyl group, which is consistent with our previous research results. Moreover, characteristic peaks belonging to P(TFEMA) was detected in the product of FDMT-initiated ATRP, which illustrates that C-F on FDMT can indeed initiated ATRP.

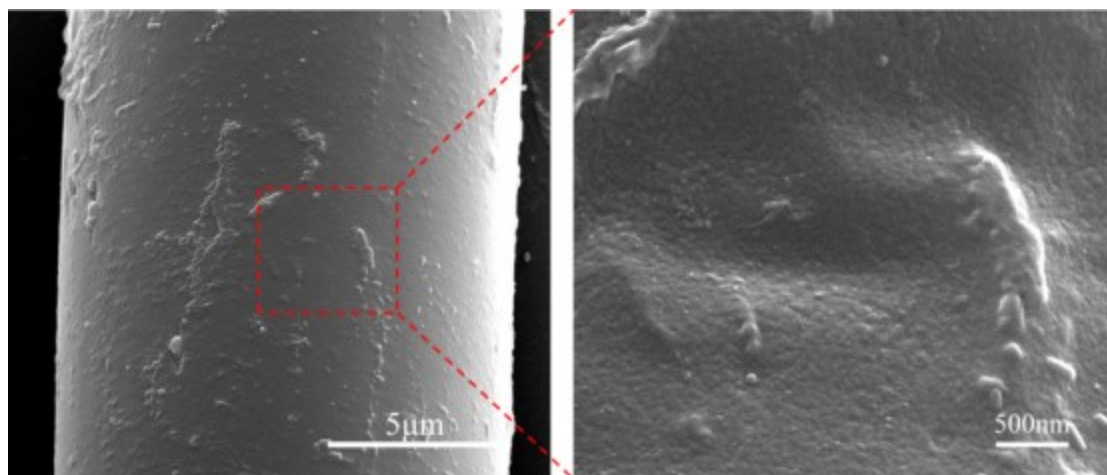


Figure S5. SEM image of the pristine PET after undergoing the same experimental processing as FPET.

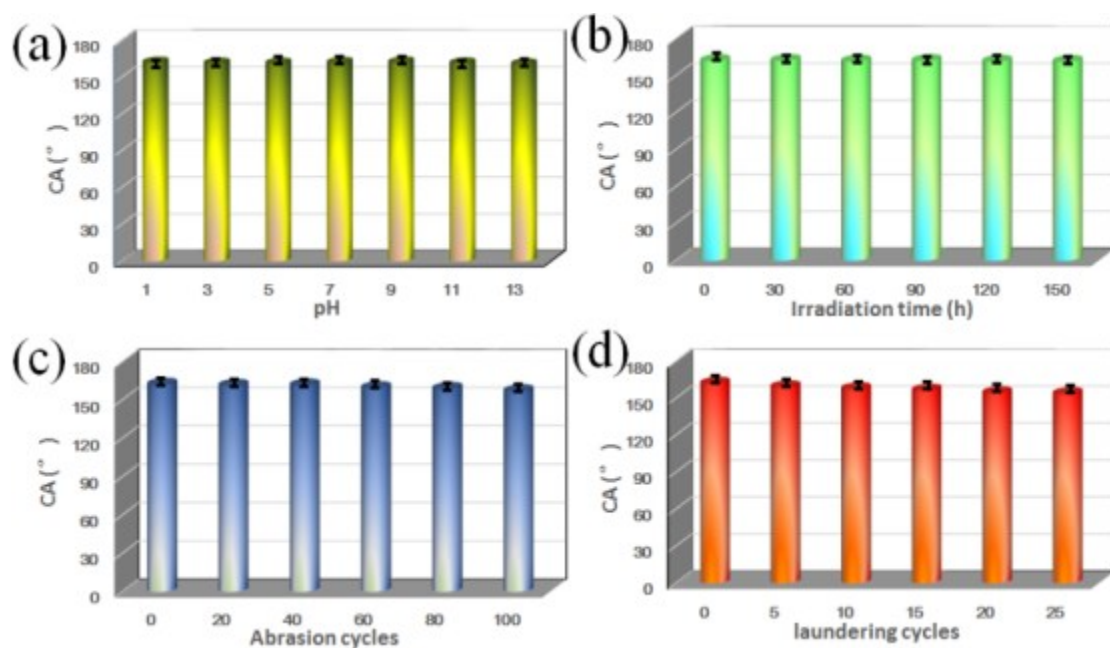


Figure S6. CA of SHPET after (a) Immersion in different pH solutions for 72 h, (b) Irradiation of

different time; (c) Abrasion of different cycles; (c) Laundering of different cycle

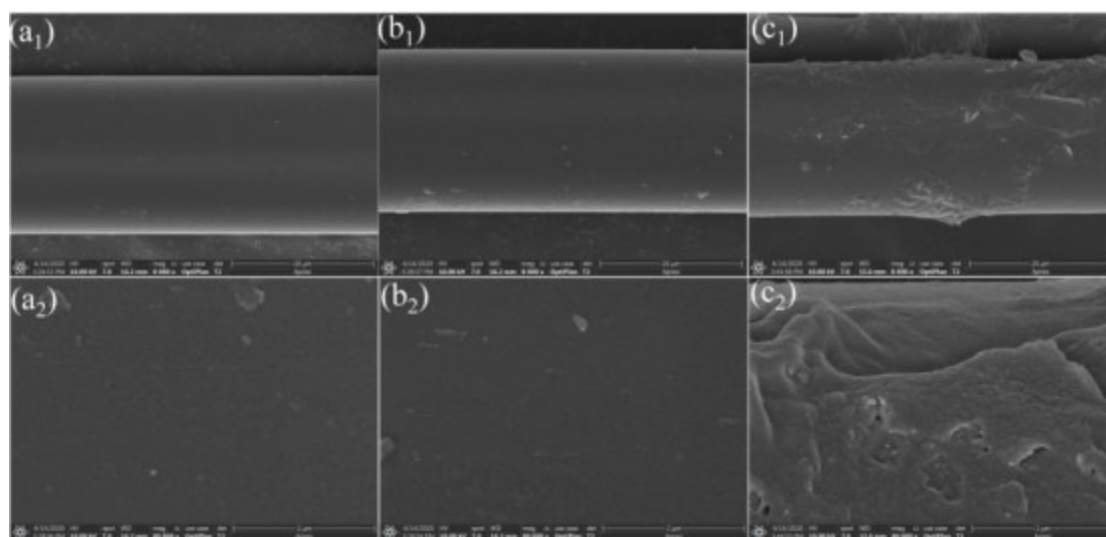


Figure S7. SEM images of (a) PI, (b) FPI and (c) FPI-g-P(HEMA).

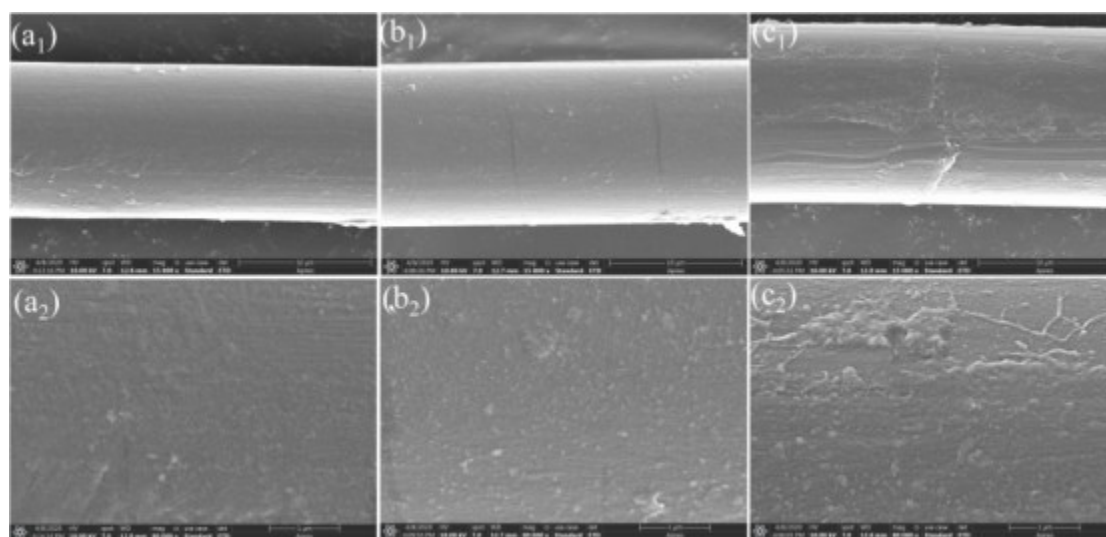


Figure S8. SEM images of (a) PBO, (b) FPBO and (c) FPBO-g-P(HEMA).

References

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