

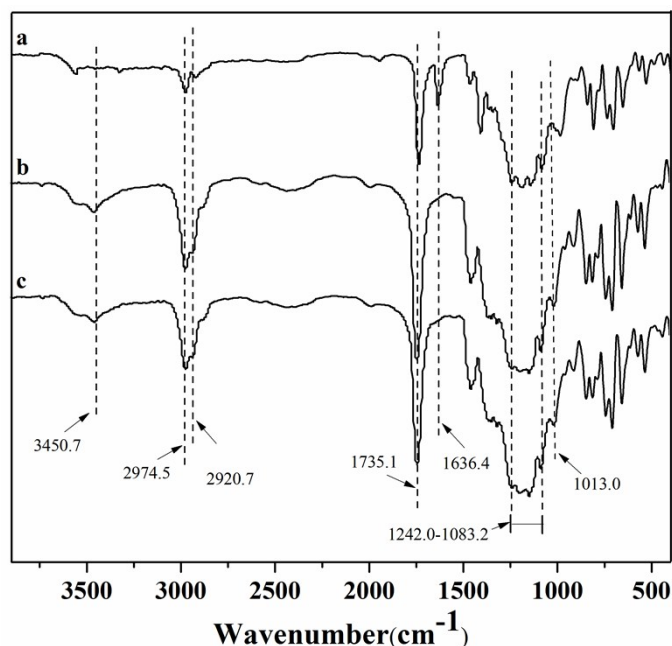
# Preparation of fluorinated PCL porous microspheres and super-hydrophobic coating on fabric via electrospraying

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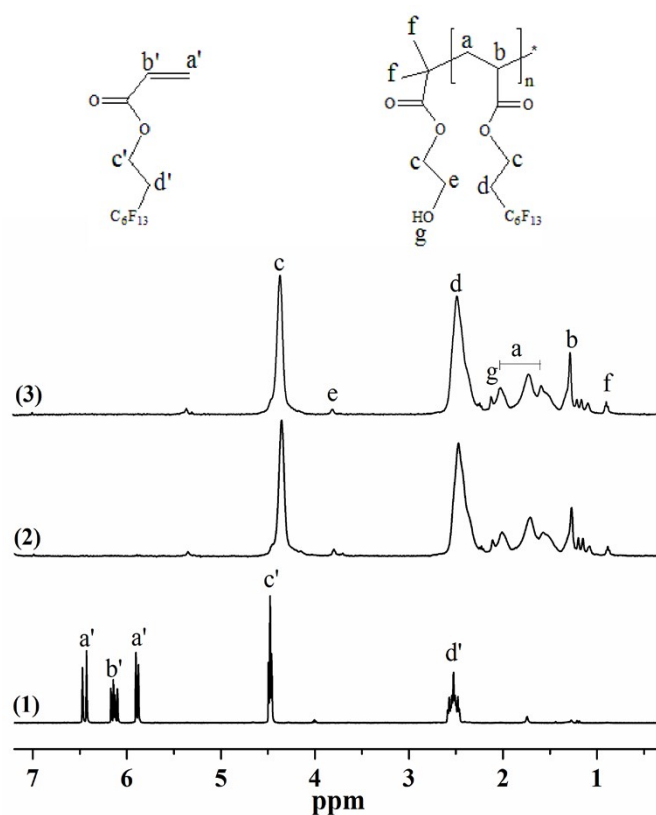
The monomer TFOA (a) and fluoropolymer PTFOA(2h)(b),PTFOA(6h) (c) were characterized by FT-IR as shown in S.1 It can be seen that monomer TFOA and polymer PTFOA exhibit the characteristic absorption peak of C=O stretching vibration at 1735.1  $\text{cm}^{-1}$ , asymmetrical stretching vibration and symmetrical stretching vibration of C-H ( $-\text{CH}_2$ ) at 2974.5  $\text{cm}^{-1}$  and 2920.7  $\text{cm}^{-1}$  respectively. Furthermore, the FTIR spectra of monomer and polymer both show the asymmetric stretching vibration band of  $-\text{CF}_3$  at 1242.0  $\text{cm}^{-1}$ , the antisymmetric stretching vibration band of  $-\text{CF}_2-$  at 1185.6  $\text{cm}^{-1}$  and the symmetric stretching vibration at 1083.2 and 1142.0  $\text{cm}^{-1}$ . When comparing curve a with curves b and c, the characteristic peak of C=C at 1636.4  $\text{cm}^{-1}$  in curve a unambiguously disappear in curves b and c after polymerization, and a new absorption peak at 1013.0  $\text{cm}^{-1}$ , which ascribes to C-Br, was observed. This indicates the completion of the polymerization and the successful preparation of the fluoropolymer. The characteristic stretching vibration of -OH from HEBiB initiator at 3450.7  $\text{cm}^{-1}$  can be clearly seen in curves b and c except a. This results further confirmed that PTFOA polymers with terminal hydroxyl groups are successfully fabricated via ATRP by using the functionalized initiator(HEBiB).



S.1. FT-IR spectra of monomer TFOA (a), PTFOA(2h) (b), PTFOA(6h) (c).

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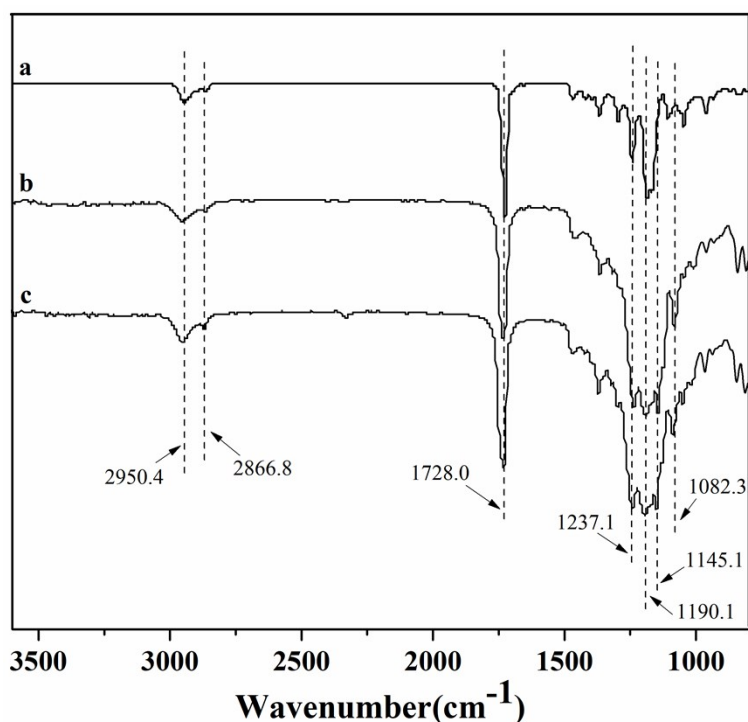
The  $^1\text{H}$  NMR spectra of monomer TFOA and fluoropolymer PTFOA(2h), PTFOA(6h) are shown as curves (1), (2) and (3), respectively, in S.2. In curve (1), the peaks at 6.45 ppm and 5.89 ppm are assigned as two protons of  $-\text{CHCH}_2(\text{a}')$ , while the peak at 6.13 ppm is corresponding to  $-\text{CHCH}_2(\text{b}')$ . Two additional peaks at 4.48 ppm and 2.52 ppm in Figure 2.(1) are attributed to the methylene protons of  $-\text{OCH}_2\text{CH}_2\text{CF}_2(\text{c}')$  and  $-\text{OCH}_2\text{CH}_2\text{CF}_2(\text{d}')$  respectively. In curves (2) and (3), the peaks at 4.36 ppm and 2.47 ppm are assignable to methylene protons of  $-\text{OCH}_2\text{CH}_2\text{CF}_2(\text{c})$  and  $-\text{OCH}_2\text{CH}_2\text{CF}_2(\text{d})$  on PTFOA side chain respectively, while the signal of resonance at 1.27-2.01 ppm is attributed to  $-\text{CH}_2(\text{a})$  and  $-\text{CH}(\text{b})$  protons of structural unit on PTFOA main chain. It is shown that peaks signal of the double bond protons disappear compared to curves (2) and (3) with curve (1). This indicates that the polymerization was completed successfully. The number of the repeating units is calculated by the ration of integration of  $-\text{OCH}_2\text{CH}_2\text{CF}_2(\text{c})$  (4.36 ppm) for PTFOA and  $\text{HOCH}_2(\text{e})$  (3.82 ppm) for HEBiB initiator. The ratios for PTFOA(2h) and PTFOA (6h) are 28.9:1, 49.2:1, respectively. This demonstrates that the chain propagation of the PTFOA can be controlled by regulating the reaction time during the ATRP. On the one hand, the peak of  $-\text{CH}_3(\text{f})$  at 0.90 ppm, the peak of  $-\text{OH}(\text{g})$  at 2.11 ppm and the small peak of  $\text{HOCH}_2(\text{e})$  at 3.82 ppm from HEBiB initiator can be observed in the spectra of PTFOA products as well. As a result, it can be concluded that PTFOA polymers with different molecular weight were successfully synthesized via ATRP.



S. 2.  $^1\text{H}$  NMR spectra of monomer TFOA (1), polymers PTFOA(2h) (2) and PTFOA (6h) (3), in  $\text{CDCl}_3/\text{Freon-113}$ .

S.3 depicts the FT-IR spectra of PCL(a), the corresponding block copolymers(PCL-PTFOA(2h) (b) and PCL-PTFOA(6h) (c)). It can be seen that all the PCL derivatives exhibit the characteristic absorption peak

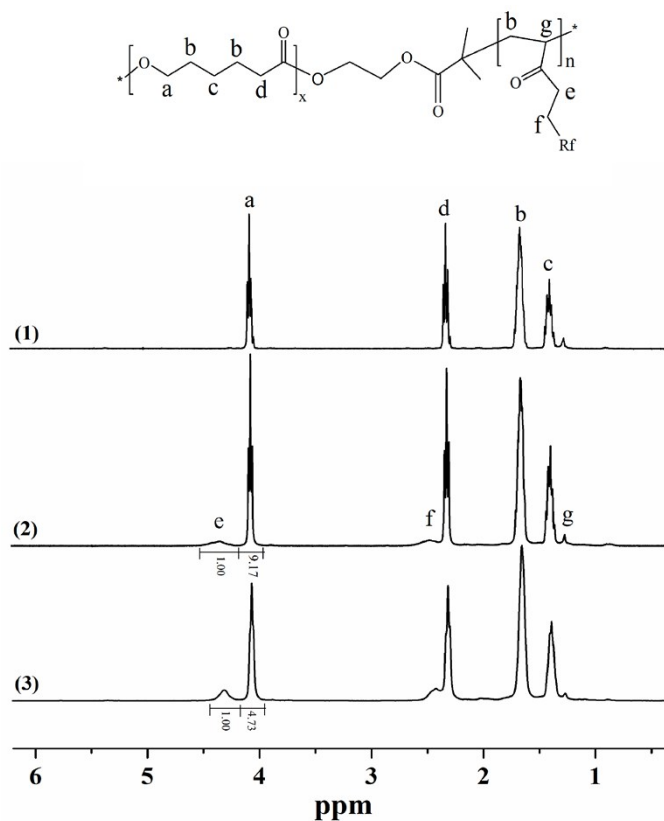
of C=O stretching vibration at  $1728.0\text{ cm}^{-1}$ , asymmetrical stretching vibration and symmetrical stretching vibration of C-H ( $-\text{CH}_2$ ) at  $2950.4\text{ cm}^{-1}$  and  $2866.8\text{ cm}^{-1}$ . In comparison with the FT-IR spectrum of PCL (curve a), the curve of PCL-PTFOA copolymers exhibit both the asymmetric vibration band of  $-\text{CF}_3$  at  $1237.1\text{ cm}^{-1}$ , the antisymmetric stretching vibration band of  $-\text{CF}_2-$  at  $1190.1\text{ cm}^{-1}$  and the symmetric stretching vibration at  $1082.3$  and  $1145.1\text{ cm}^{-1}$ . Besides, the peaks of the asymmetrical deformation vibration of C(O)-O (at  $1241.5\text{ cm}^{-1}$ ) and the asymmetrical deformation vibration of O-C(C) ( $1178.2\text{ cm}^{-1}$ ) in PCL chain overlap with the characteristic absorption peaks of C-F bond. The above results indicate that the PTFOA chain was bonded into the PCL chains successfully by the esterification reaction.



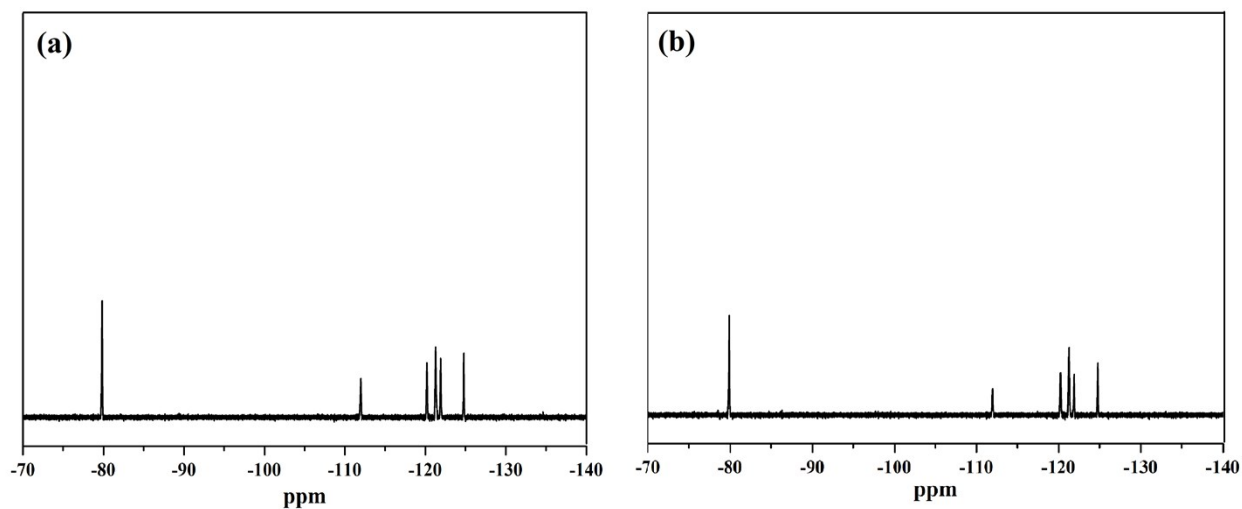
S. 3. FT-IR spectra of PCL (a), PCL-PTFOA(2h) (b) and PCL-PTFOA(6h) (c).

S.4 shows the  $^1\text{H}$  NMR spectra of PCL before and after modification with PTFOA. All the curves ((1), (2) and (3)) have four peaks with chemical shifts at 4.05, 2.30, 1.63 and 1.38 ppm, which are attributed to the methylene protons of the oxycarboxy-1 and 5-pentamethylene units on PCL main chain. In the  $^1\text{H}$  NMR spectrum of PCL-PTFOA (curve (2) and (3)), the peaks at 2.42 ppm and 4.30 ppm are assignable to methylene protons of  $-\text{OCH}_2\text{CH}_2\text{CF}_2-$  (e) and  $-\text{OCH}_2\text{CH}_2\text{CF}_2-$  (f) in PTFOA blocked chain respectively. Another newly appeared small peak at 1.26 ppm is assigned to  $-\text{CH}$  (g) protons of structural unit in PTFOA. Taking into consideration all the above results, the  $^1\text{H}$  NMR data further confirms that PCL-PTFOA was prepared successfully after a series of reactions. Furthermore, the compositions of PTFOA segment are calculated by comparing the relative intensities of the signal for  $-\text{OCH}_2-$  protons of the fluorinated blocked chain, at 4.30 ppm (e) for PTFOA, and the PCL chain (4.05 ppm (a)). The results are 1:9.17, 1:4.73 for PCL-PTFOA(2h), PCL-PTFOA(6h) respectively. This indicates that the length of PTFOA polymer chain can be controlled by extending the reaction time during the ATRP.  $^{19}\text{F}$  NMR data of modified PCL is used to further confirm that PTFOA was successfully introduced into modified PCL copolymer (as shown in S.5).

The results are as follows:  $^{19}\text{F}$ NMR (376 MHz,  $\text{CDCl}_3$ ): -79.84 (3F,  $\text{CF}_3$ ), -111.99 (2F,  $\text{CF}_3\text{CF}_2$ ), -120.20 (2F,  $\text{CF}_3\text{CF}_2\text{CF}_2$ ), -121.29 (2F,  $\text{CF}_3(\text{CF}_2)_2\text{CF}_2$ ), -121.91 (2F,  $\text{CF}_3(\text{CF}_2)_3\text{CF}_2$ ), -124.80 (2F,  $\text{CF}_3(\text{CF}_2)_4\text{CF}_2$ ).



S. 4.  $^1\text{H}$  NMR spectra of PCL(1), PCL-PTFOA(2h) (2) and PCL-PTFOA (6h)(3) polymers, in  $\text{CDCl}_3$ .



S. 5.  $^{19}\text{F}$  NMR spectra of PCL-PTFOA(2h) (a) and PCL-PTFOA (6h)(b) polymers, in  $\text{CDCl}_3$ .